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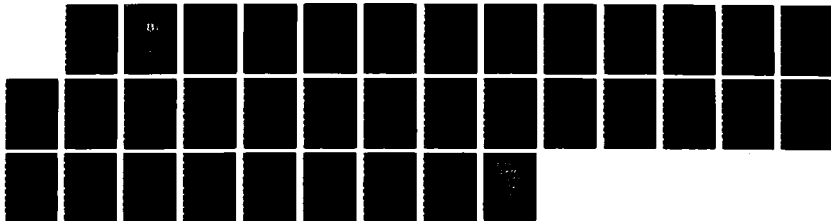
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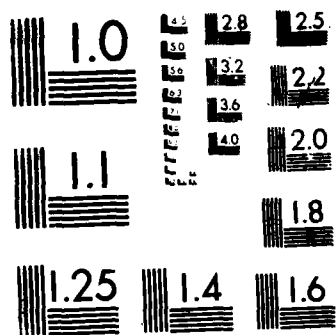
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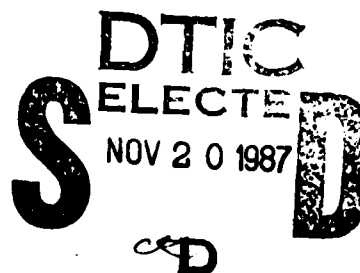


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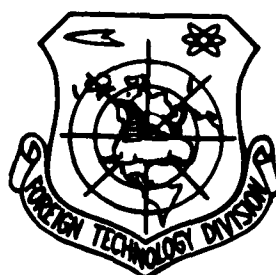
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THEORETICAL BASES OF POLYMER PHOTODEGRADATION AND PHOTOOXIDATION

by

J. Rabek



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FTD-ID(RS)T-0868-87

15 October 1987

MICROFICHE NR: FTD-87-C-000924

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PHOTOOXIDATION

By: J. Rabek

English pages: 30

Source: Polimery-Tworzywa Wieldczastechzkowe, Vol. 16,
Nr. 6, 1971, pp. 257-266

Country of origin: Poland

Translated by: FLS, Inc.

F33657-85-D-2079

Requester: FTD/TQTR

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THEORETICAL BASES OF POLYMER PHOTODEGRADATION AND PHOTOOXIDATION

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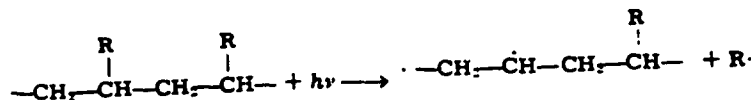
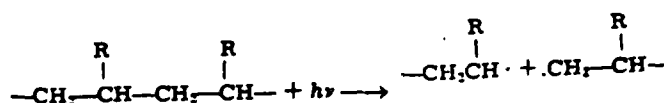
—The photodegradation and photooxidation of polymers are interrelated processes which occur simultaneously during the photoaging of polymers in the air. Only under laboratory conditions can one distinguish photodegradation from photo-oxidation by conducting reactions in an oxygen-free atmosphere.

Polymers synthesized on an industrial scale are contaminated with various low-molecular compounds derived from the technological process (initiators, inhibitors, moderators, solvents, etc.). In addition, when such processes are carried out in an atmosphere of air, numerous carbonyl, carboxyl, hydroxyl etc. groups form along the polymer chain. It is quite difficult and sometimes downright impossible to eliminate these impurities.

For this reason, an examination of the issue of polymer photoaging this should be multilateral, with consideration of the following basic processes [1-9]:

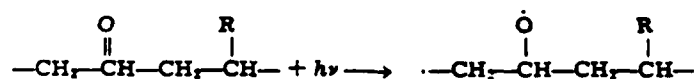
1. Photochemical reactions of the actual polymer related to absorption of a quantum of radiation and dissociation of the chemical bond in the primary chain or outside of it:

primary reactions

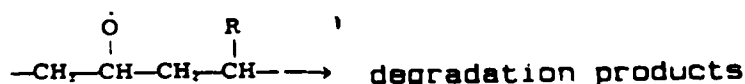


2. Photochemical reactions of an actual polymer which contains oxygen groups (for example a carbonyl group), which absorbs light, undergoing excitation and forming a free radical:

(2') primary reaction



(2'') Secondary reaction ,



In this case the primary reaction is the reaction which occurs directly as a result of absorption of a quantum of light. The secondary reaction is the reaction which takes place without the participation of light, but it is initiated by the primary reaction.

3. Reactions involving the degradation of the polymer initiated by free radicals produced by photolysis of small molecules in the polymer (impurities, sensitizers, etc.):

(3') primary reaction $RH + h\nu \rightarrow R\cdot + \cdot H$

(3'') secondary reaction $\text{polymer} + R\cdot \rightarrow \text{degradation products}$

4. Degradation reactions initiated by radicals formed through the participation of oxygen:

(4') primary reaction $RH + h\nu' \rightarrow R\cdot + \cdot H$

(4'') secondary reactions $R\cdot + O_2 \rightarrow RO_2\cdot$

(4''') $\text{polymer} + RO_2\cdot \rightarrow \text{degradation products}$

5. Oxidation and degradation reactions initiated by singlet oxygen formed in a primary, sensitized photochemical reaction:

(5') primary reactions $\left\{ \begin{array}{l} S + h\nu \rightarrow S^* \\ S^* + O_2 \rightarrow {}^1O_2 + S \end{array} \right.$

(5'') $S^* + O_2 \rightarrow {}^1O_2 + S$

(5''') secondary reactions $\text{polymer} + {}^1O_2 \rightarrow \text{degradation and oxidation products,}$

where S is a sensitizer

The mechanism of the primary photochemical reaction is identical for all the processes described above [10-12].

Absorption of a quantum of light radiation leads to transition of a molecule of a chemical compound from the ground state (S_0) to the excited singlet state (1S) (Fig. 1):

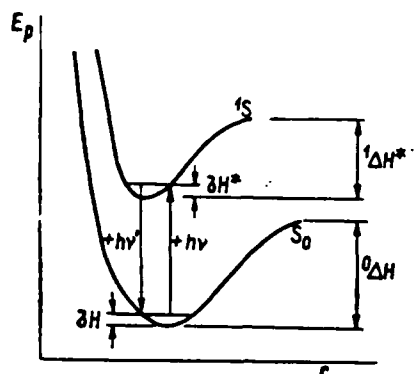
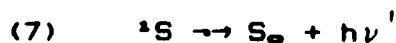


Fig. 1. Potential energy curves (E_p) for the ground state S_0 and excited singlet state 1S of a molecule as a function of distance (r). $h\nu$ - absorption, $h\nu'$ - fluorescence, $^0\Delta H$ - bond energy in the ground state S_0 , ΔH - bond energy in the excited singlet state 1S , σH and σH^* - destabilization energy based on the difference between the Franz-Condon configuration and equilibrium configuration in the ground state S_0 and excited singlet state 1S .



Light absorption is the consequence of the transition of an electron from one orbit to another according to selection rules. The lifetime of the excited singlet state is very short, from 10^{-7} to 10^{-9} sec, after which the particle undergoes deactivation or dissociation [13].

If such deactivation occurs with the emission of radiation $h\nu'$ then we observe fluorescence (Fig. 1) [14-15]:



Deactivation of the singlet state may also occur by so-called type II collisions with other molecules, atoms, electrons, etc. The excitation energy is emitted in the form of heat:



Another type of deactivation is the phenomenon of internal conversion of energy, based on the isoenergetic transition between states of the same multiplicity from the higher energy level to the higher oscillatory state of the lower electron level (Fig. 2). The high density of oscillatory and rotational levels in multiatomic molecules and the large number of and small distance between electron levels leads to resonance between certain levels in the excited and ground states. This allows for a nonradiant transition whose energy is used to raise the oscillatory and rotational energies of the ground state:

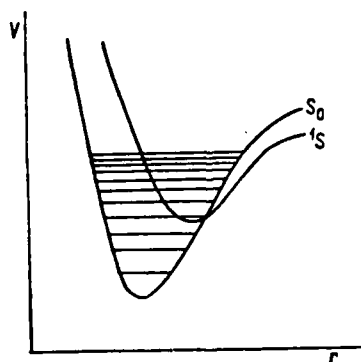


Fig. 2. System of potential energy curves which facilitate deactivation of an excited molecule by internal energy conversion

Table 1. Energy of Chemical Bonds Occurring in Some Thermoplastic Polymers [17]

Type of bond	Wavelength in Å	Energy, kcal/mole
C-N		209
C-C		200
C=O	2900	174
C=C		145
C-S		129
C=C		124
C-C-C	3000	121
C-F		119
O-H		110
C-C-C	3500	106
C-H		98
Si-O		95
C-O		89
S-H	4000	87
N-H		87
C-C		83
C-O		80
C-Cl	4500	78
C-S		76
Si-H		75
C-S		70
C-N		66
O-O		57

If the energy of the absorbed quanta of radiation is at least equal to the energy of the chemical bond [16, 17] (Table 1) then under certain conditions photodissociation (photolysis) of the molecule may occur with the formation of free radicals [18]:



In the case where the energy of the absorbed quanta is greater than the energy of the chemical bond, the free radicals formed possess an excess of unused energy. Such radicals are called thermally inequilibrated and designated by $R^\dagger$:



These radicals soon get rid of the excess energy by transferring it to rotation or by undergoing further decomposition. The chemical activity of free radicals depends among other things on their structure, excess energy, reaction medium, etc. [19-23].

Photolysis takes place only when:

- the radiation energy has been absorbed by one chemical bond and is not distributed to the entire molecule, and
- the potential energy curves of the excited singlet states of the molecule are such as to prevent dissociation (Fig. 3).

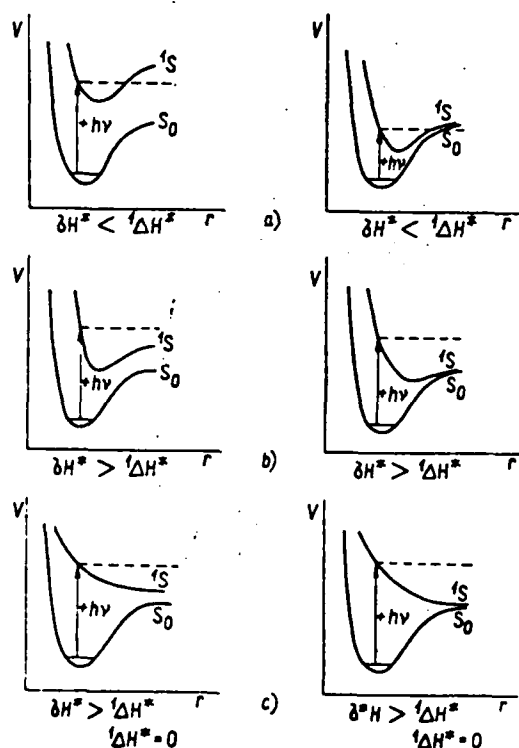


Fig. 3. System of potential energy curves. a - leading only to excitation of the molecule, b and c - leading to dissociation into free radicals in the excited singlet state 1S .

The two-dimensional potential curves for molecules of two atoms shown in Figs. 1-7 should not be used as a substitute for multidimensional planes corresponding to the diversity of chemical bonds in a molecule (Fig. 4). The more complex a molecule is, the greater the number of ways to slice the potential energy surfaces, and the greater the possibility of a predissociation reaction, which is far greater than in a two-atom system.

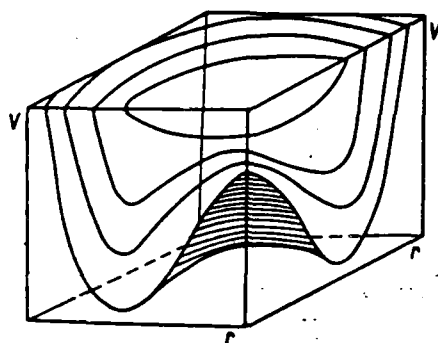


Fig. 4. Potential energy surface of a multiatomic molecule

Predissociation occurs as the result of transition of a molecule in the excited electron state to another transient excited state $^1S'$ in which spontaneous dissociation occurs. The maximal probability of such a transition is at the point of intersection of the surface if the selection rules permit this. Fig. 5 illustrates typical cases of intersection of potential curves of excited states (1S and $^1S'$) during predissociation.

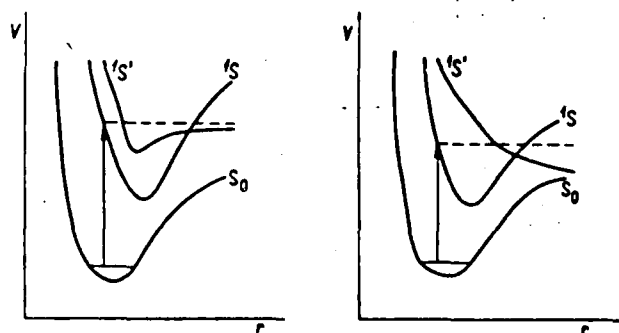


Fig. 5. System of potential energy curves which allow for predissociation

But the most important reaction which the excited singlet state can undergo is so-called intercombinational conversion (isoenergetic transition between states of different multiplicity), which results in transition of the molecule to a lower energy excited metastable triplet state (3S) [24-26]:



These reactions occur when the curves of potential energy of excited states, singlet and triplet, intersect (Fig. 6):

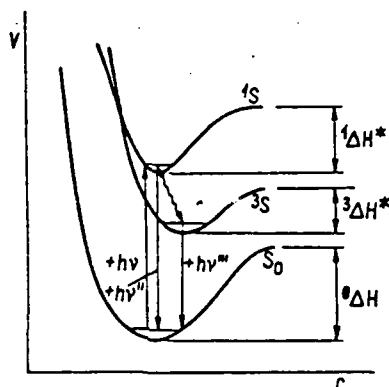


Fig. 6. Potential energy curves for the ground state S_0 , the excited singlet state 1S and the excited triplet state 3S . $h\nu$ - absorption, $h\nu''$ - delayed fluorescence, $h\nu'''$ - phosphorescence, ${}^0\Delta H$ - bond energy in the ground state S_0 , ${}^1\Delta H^*$ - bond energy in the excited singlet state 1S , ${}^3\Delta H^*$ - bond energy in the excited triplet state 3S .

In the ground state S_0 and in the excited singlet state 1S the electron spins of the molecule are antiparallel. In the triplet state the spins of the two electrons are parallel and thus they are in a form reminiscent of a biradical [27, 28]. But in the excited triplet state the unpaired electrons belong to a specific energy state of the molecule, while in a biradical they are assigned to specific atoms or fragments of the molecule. The EPR spectra of the triplet state may be thus designated as either triplet or biradical; in some cases, however, they differ from each other [29].

Of great importance in the study of excited triplet states is the method of flash spectroscopy [30-34]. The measuring apparatus for this method has been described in several papers [35-38].

The lifetime of the triplet state is longer than that of the singlet state, ranging from 10^{-3} sec to several minutes, thus increasing the probability that a reaction will occur with the participation of this state.

The molecule may again return from the triplet state to the excited singlet state and then to the ground state at the cost of rotation energy:



— At the same time a radiation called delayed fluorescence is emitted $h\nu''$ [39].

The direct transition of a molecule from the excited triplet state to the ground state (S_0) is rather rare and involves the emission of phosphorescence (Fig. 6).

A molecule in the excited triplet state may also undergo photodissociation with the formation of free radicals:



But in this case no thermally nonequilibrium radicals are formed. The course of such reactions depends on the shape of the potential curves for the excited triplet state (Fig. 7) and the energy of the excited triplet state.

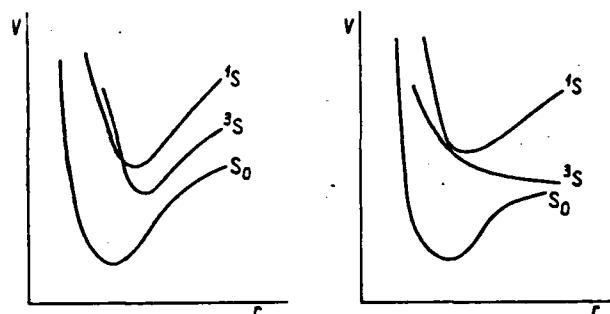
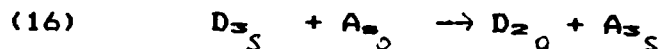


Fig. 7. System of potential energy curves: a -- leading only to an excited molecule, b - leading to dissociation into free radicals in the excited triplet state 3S .

Because of the long lifetime of the triplet state, there is a higher probability of transfer of the energy of excitation of a given molecule (called the donor, D) to another molecule (the acceptor, A), which is the basis of photosensitizing processes related to energy transfer [40, 41]:



Transfer of energy from the excited state of an electron donor to an acceptor may proceed according to the following mechanisms [42, 43]:

1. The donor emits radiation which is absorbed by the acceptor.

2. By intermolecular radiationless energy transfer;

- with the involvement of the resonance mechanism, which permits transfer of energy in the range of Coulomb forces and at greater distances of the [word missing] of radiation of donor and acceptor (50-100 Å); the rate constant for this reaction K^A is:

$$k_A = \frac{k}{\tau_D^c R^6} \int_0^\infty f_D(\nu) \epsilon_A(\nu) \frac{d\nu}{\nu^4}$$

where : k is constant,
 R is the distance between donor and acceptor,
 τ_D^0 is the lifetime of the excited state of the donor,
 $f_D(\nu)$ is the spectral decay of radiation emitted
 by the donor, and
 $\epsilon_A(\nu)$ is the molecular coefficient of absorption of the
 acceptor,

- in the case where the electron clouds of the donor and
 acceptor overlap (10-15Å), the reaction rate constant k^A is:

$$k_A = k' Z^2 \int_0^\infty f_D(\nu) \epsilon_A(\nu) d\nu$$

where: k' is constant and
 Z^2 is a value related to interaction of the electron
 clouds of the donor and acceptor and exchange of
 between them.

3. By intermolecular transfer of energy through the forma-
 tion of intermediate complexes of donor and acceptor. Such a
 complex absorbs light and the excitation of one of its fragments
 allows the energy to be transferred within the complex by internal
 conversion.

Electron-donor-acceptor complexes (charge transfer), com-
 plexes of ion pairs, and finally hydrogen bonds [42-48] play an
 important role in energy transfer. Hydrogen bonds, which upon
 transition of a molecule to the excited state may be either weak-
 ened or strengthened and thus take part in energy transfer (Fig.
 8), play a specific role.

The mechanism of transfer of the energy of excited electrons
 has been the subject of detailed studies [49-54]. In the area of
 polymer photochemistry several papers have been written on energy
 transfer from excited singlet states in a bond, with research on
 oscillators [55, 56]. Basile described energy transfer from

styrene to 1,1,4,4-tetraphenylbutadiene, which occurs in the range of Coulomb forces. David, Demarteau and Gueskens studied the transfer of excitation in the system polyvinylbenzophenone, a reaction which involves the excited triplet state [43]. Similar studies were carried out by Cozzens and Fox, who studied energy transfer from various sensitizers to poly-1-vinylnaphthalene and to a copolymer of styrene and 1-vinyl-naphthalene [58, 59].

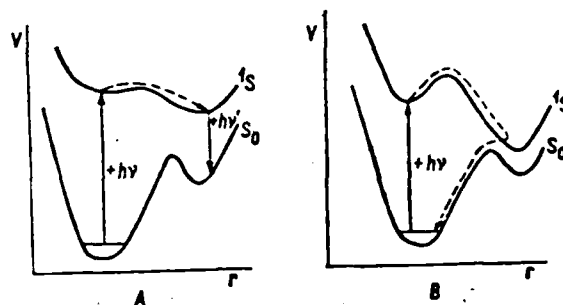


Fig. 8. Phenomena associated with electron excitation of a molecule which may form hydrogen bonds

A. Deactivation of the excited state occurs by exchange of fluorescent radiation,
 B. when the energy interval between the excited state and the ground state is not large, there may be radiationless deactivation.

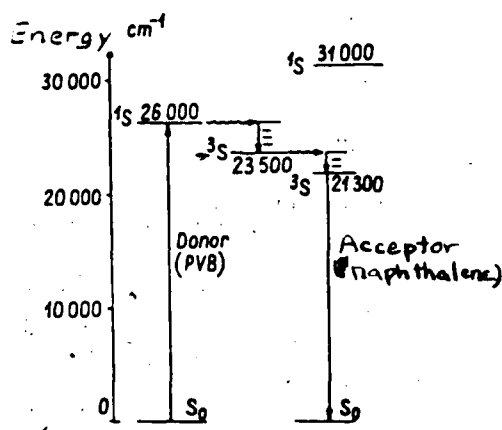


Fig. 9. Energy levels in polyvinylbenzophenone (PVB) and naphthalene [43]

Table 2. Quantum Yield of Photolysis of Some Polymers [74]

Polymer	quantum yield obtained at wavelength 2537 Å
Poly(ethylene terephthalate)	5×10^{-4}
Natural rubber	4×10^{-4}
Cellulose	10^{-3}
Cellulose acetate	$2.5 \times 10^{-3} - 10^{-4}$
Poly(methylvinyl ketone)	2.5×10^{-2}
Polyacrylonitril	2×10^{-4}
Polystyrene	2×10^{-5}

The photodegradation of a pure polymer has a very low quantum yield (Table 2), since the polymers, because of their chemical structure, absorb little radiation and that mainly in the shortwave range of the spectrum (Fig. 10). Under ultraviolet polymers exhibit fluorescence [60-63] and sometimes phosphorescence [61-64]. Charlseby and Patridge showed that thermoluminescence and phosphorescence of polyethylene depend on the number of carbonyl and carboxyl groups in a polymer [65, 66].

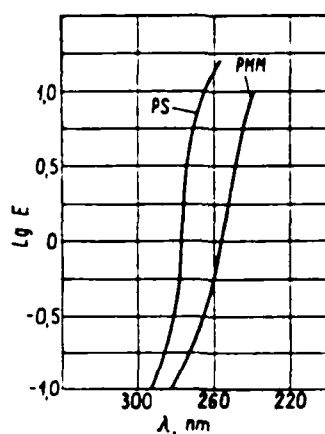
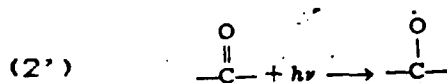


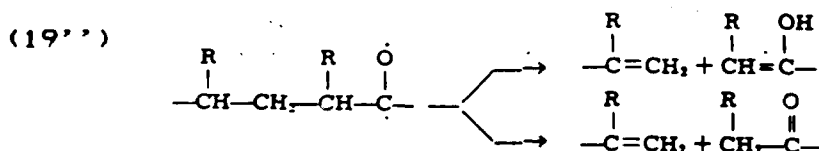
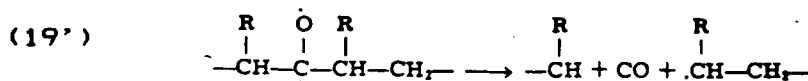
Fig. 10. Absorption spectrum of polystyrene (PS) and poly(methyl metacrylate) (PMM) [5].

When the polymers contain carbonyl groups, which usually form during synthesis and storage of a polymer, degradation proceeds by the following mechanism:

1. 2700-3300 Å UV radiation (region of absorption of ketone groups) causes excitation of the carbonyl group in the compound, with electron transitions of type $n \rightarrow \pi^*$ (from the nonbonding n orbital to the antibonding π orbital). In a subsequent reaction $^1(n, \pi^*) \rightarrow ^3(n, \pi^*)$ an excited triplet state of the carbonyl group is formed in which a biradical develops:



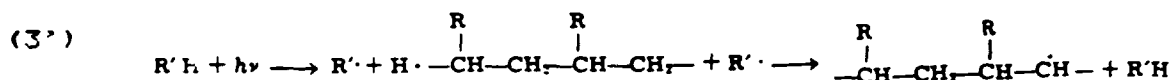
2. Typical reactions of excited electron states of the carbonyl group are type I and II Norrish reactions [67, 68]:



As can be seen from the above diagrams, Norrish reactions of both types lead to the degradation of macromolecules. Reactions of this type were found when studying the photodegradation of polyketones [1, 7, 69], polyethylene and polypropylene [70, 71], a copolymer of ethylene oxide and ethylene [72, 73] and other polymers [74-76].

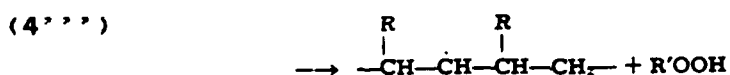
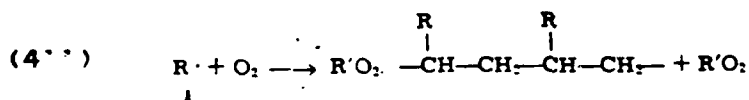
The readiness of polymers to undergo photoaging is among other things related to the presence of various type of trace impurities or other auxiliary materials added to the polymers.

These compounds absorb UV radiation and undergo photolysis with the formation of active radicals which then remove a hydrogen atom from the macromolecule, forming a macroradical:

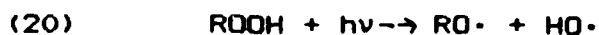


The latter then degrades by disproportionation. Typical compounds which cause this type of reactions are ketones, quinones, peroxides, etc. [77-80].

In the presence of oxygen, these radicals may react with it to form radicals of type $RO_2\cdot$ which subsequently react with the polymer [81]:



Radicals of type $RO_2\cdot$ and $\cdot\text{OH}$, which can form various types of peroxide compounds as a result of photolysis, also take part in these reactions:



This reaction proceeds readily since the bond energy of O-O is only 57 kcal/mole and radiation of wavelength 4000 Å is sufficient for its dissociation.

But the polymer photooxidation reaction considered most important is a reaction based on singlet oxidation.

Molecular oxygen occurs in nature in the triplet state 3O_2 , because of its particular electron structure [82]:

$$(21) \quad {}^3O_2({}^3\Sigma_g^-) KK(\sigma g 2s)^2(\sigma u 2s)^2(\sigma g 2p)^2(\pi u 2p)^4(\pi p^2 p)^2$$

In addition, there are excited states of oxygen of which the first two are known in the literature as singlet and designated by

$${}^1O_2({}^1\Delta_g) \text{ i } {}^1O_2({}^1\Sigma_g^+).$$

The lifetime and excitation energy of molecules of singlet oxygen are as follows:

${}^1O_2({}^1\Delta_g)$	45 min	22.5 kcal/mole (0.977 eV)
${}^1O_2({}^1\Sigma_g^+)$	10^{-3} sec	37.5 kcal/mole (1.63 eV)

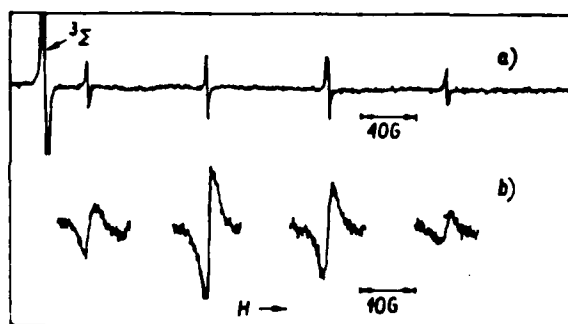
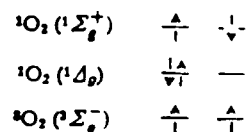


Fig. 11. EPR spectrum of singlet oxygen ${}^1O_2({}^1\Delta_g)$ [85].

a. Electron resonance observed in ${}^1O_2({}^1\Delta_g)$ obtained by electrical discharge at radio frequencies.

b. Electron resonance observed in ${}^1O_2({}^1\Delta_g)$ obtained by photosensitization reactions between an excited molecule of naphthalene and molecular oxygen ${}^3O_2({}^3\Sigma_g^-)$ in the gas phase.

The lifetime of both forms of singlet oxygen in solution is quite short, 10^{-7} sec, since it is readily deactivated by another type of collision. Singlet oxygen ${}^1O_2({}^1\Delta_g)$ exhibits a characteristic EPR spectrum in the gas phase (Fig. 11), while singlet oxygen ${}^1O_2({}^1\Sigma_g^+)$ does not have this spectrum [83-85]. The system of spins of electrons occupying the highest filled orbital in the different states is as follows [86]:



Singlet oxygen is formed in nature by UV radiation in the upper strata of the atmosphere [87]. Under laboratory conditions it may be obtained by electrical discharges at radio frequencies in an oxygen atmosphere [88] or chemically by a reaction between chlorine contained in hypochlorites and hydrogen peroxide [89-91]:



Other indisputably important reactions producing the singlet state are photosensitization by various types of organic compounds and dyes. These reactions have been described in many publications [92-97]. They may also involve the participation of excited singlet and triplet states as sensitizers:



It is now thought that energy transfer from an excited molecule of sensitizer to a molecule of molecular oxygen takes place by the following mechanism:

- in the first stage a transitional contact complex of the excited sensitizer molecule and the oxygen molecule is formed [85, 98];

- in the second stage a transient electron-donor-acceptor complex is formed in which there is transfer of energy of excitation together with electron exchange from the highest occupied electron orbital of the sensitizer molecule to the ground π -electrons of the oxygen molecule (Fig. 12); in this

process there is no change in electron spins so that it is permitted as far as regards spin [85].

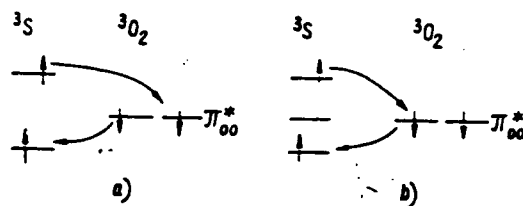


Fig. 12. Diagram of a system of electron spins representing transition of an electron from an excited sensitizer molecule to a molecule of molecular oxygen $^3O_2(^3\Sigma_g^-)$ [85]. a - leading to the formation of singlet oxygen $^1O_2(^1\Delta_g)$; b - leading to the formation of singlet oxygen $^1O_2(^1\Sigma_g)$.

Some excited sensitizer molecules are deactivated without the formation of singlet oxygen:



On the basis of experimental results [99] and arguments based on quantum mechanics [85] it has been shown that for sensitizers with a high-energy excited triplet state, or $E_{3S} > 40$ kcal, the basic reaction is the formation of singlet oxygen $^1O_2(^1\Sigma_g^+)$ while energy transfer and the formation of $^1O_2(^1\Delta_g^+)$ is 10 times slower and deactivation without the formation of singlet oxygen 100 times slower. E_3 less than 38 kcal but more than 22 kcal is shown only by singlet oxygen $^1O_2(^1\Delta_g^+)$. When E_{3S} is greater than 38 kcal then both singlet oxygen $^1O_2(^1\Delta_g)$ and $^1O_2(^1\Sigma_g)$ are formed simultaneously (Fig. 13). Table 3 lists the energies of excited triplet states of some organic compounds.

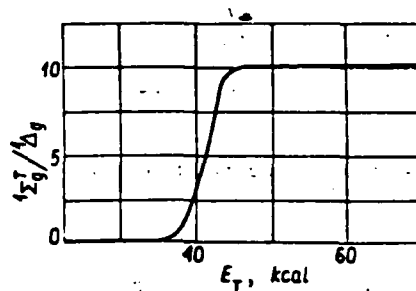


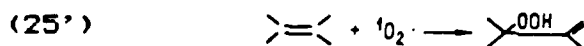
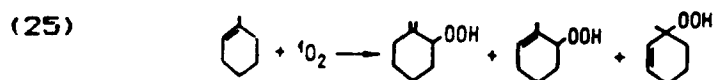
Fig. 13. Quantitative ratio of singlet oxygen formed $^1O_2(^1\Sigma_g^+):^1O_2(^1\Sigma_u^-)$ [sic] as a function of energy of excited triplet states of different sensitizers [99]

Table 3. Energy of excited triplet states of various organic compounds[11]

Compound	E _T , kcal/mole	Compound	E _T , kcal/mole
Benzene	85	Quinoline	62
Phenol	82	Phenanthrene	62
Benzoic acid	78	Flavone	62
Benzonitryl	77	Michler ketone	61
Aniline	77	Naphthalene	61
Xanthone	74	4-Acetyldiphenyl	61
Acetophenone	74	Nitrobenzene	60
Diisopropyl ketone	74	Acridine yellow	58
Phenyl sulfide	74	1-Naphthylphenylketone	57
Diphenylamine	72	Chrysene	57
Benzaldehyde	72	Diacetyl	55
Diphenylselenium	72	Coronene	55
Carbazol	70	Benzyl	54
Triphenylamine	70	Fluorenone	53
Hexachlorobenzene	70	Pyrene	49
Thiophene	69	Pentaphene	48
Benzophenone	69	1,2-Benzanthracene	47
Fluorophenone	68	Phenazine	44
Triphenylene	67	Eosine	43
4-Cyanobenzophenone	66	Anthracene	42
Diphenyl	65	3,4-Benzanthracene	42
Thioxanthone	65	Thiobenzophenone	40
Phenylglyoxal	63	Crystal violet	39
Anthraquinone	62	Naphthacene	29
		Oxygen	23

Several characteristic photooxidation reactions have been found in which singlet oxygen participates:

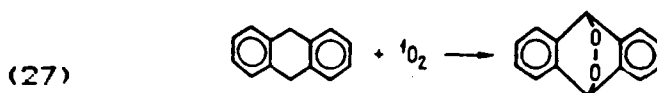
1. The formation of hydrogen peroxides with olefins, with the internal shift of a double bond [94, 95]:



2. The addition of singlet oxygen to a diene system [94, 95]:

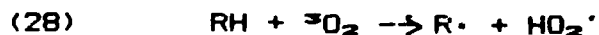


3. The formation of endoperoxides with aromatic hydrocarbons having a condensed ring system [100-103]:



The above reactions demonstrate a pronounced stereospecificity related to the structure of singlet oxygen and its reactivity. It has been shown for example that the quantitative decomposition of products of oxidation of the olefins shown differs depending whether the reactions are carried out using molecular oxygen or singlet oxygen [95, 96, 104].

No direct proof has yet been found that singlet oxygen may initiate the splitting of a hydrogen atom from a molecule of chemical compound, as happens in thermal autooxidation [8, 104]:



Nor do we know when singlet oxygen may add to a radical $R\cdot$ and form with it a radical of type $RO_2\cdot$.

Of particular interest is the fact that singlet oxygen is formed in chemoluminescence reactions [95, 105] and during the thermal decomposition of endoperoxides [106].

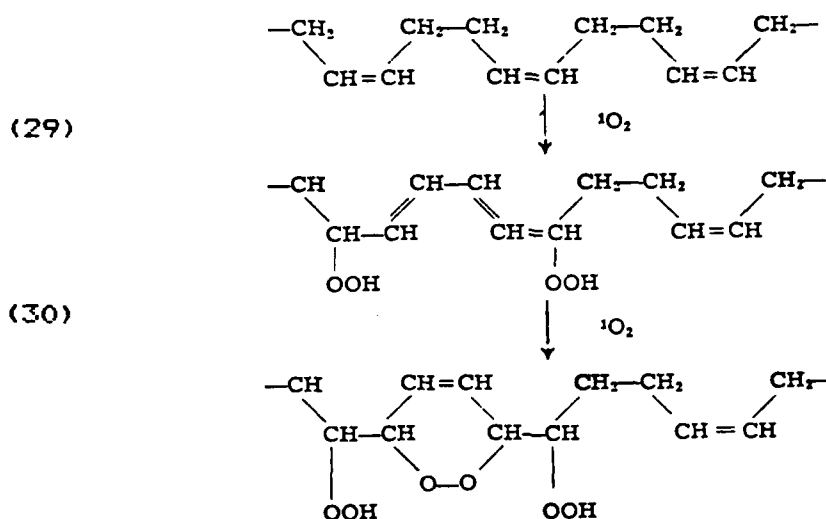
The formation of singlet oxygen is sensitized by a variety of different chemical compounds with a high enough energy of triplet excitation E_{T_3} (Table 3). Such compounds include anthracene, methylene blue, chlorophyll, etc. [86, 93, 94, 100-103, 107-¹¹⁰~~100~~].

Siewert [111], Mönig [112-114] and Fox [115] showed that adding anthracene, benzopyrene or 3,4-benzopyrene accelerates the decrease in viscosity of solutions of poly(methyl metacrylan) affected by UV or oxygen. Similar results were obtained by J. Rabek in a study of the effect of anthracene and anthracene peroxide on the photodegradation of polystyrene in benzene solution.

Mill et al. [116] and Rabek and Pajak showed that adding such dyes as methylene blue, Bengal rouge, rhodamine 6G or eosine accelerates the photooxidation and photodegradation of several polymers such as polyisoprene.

These reactions takes place exclusively when the system studied contains oxygen or is illuminated. In benzene solutions no effect of these dyes is observed on the decrease in viscosity of solutions of polymers. The course of these reactions may be explained only on the basis of the theory of the mechanism of photooxidation with the participation of singlet oxygen.

Recently Kaplan and Kelleher [117], studying the effect of singlet oxygen on the oxidation of polybutadiene and its copolymer ABS showed that hydrogen peroxides and cyclic peroxides could be formed along the polymer chain:



Degradation is a secondary reaction and occurs as a result of the decomposition of hydrogen peroxides. These authors also showed that the copolymer styrene-acrylonitrile (SAN) does not undergo oxidation in the presence of singlet oxygen.

Trozzolo and Winslow [118] also proposed a new theory of photodegradation and photooxidation of polyolefins with the participation of singlet oxygen. The mechanism of such reactions is as follows:

1. The carbonyl groups contained in the polymer absorb UV radiation, leading to excitation of these groups to the triplet state.

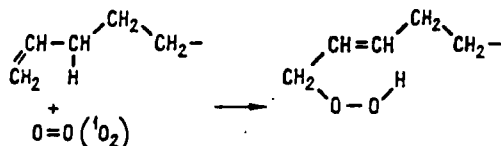
2. A carbonyl group in the excited triplet state may react as follows:

- [splitting] into a ketone and olefin by a type II Norrish reaction, which involves degradation of the macromolecule:



(32) ketone $^3(n, \pi^*) + {}^3O_2 \rightarrow \text{ketone} + {}^1O_2$

(33)



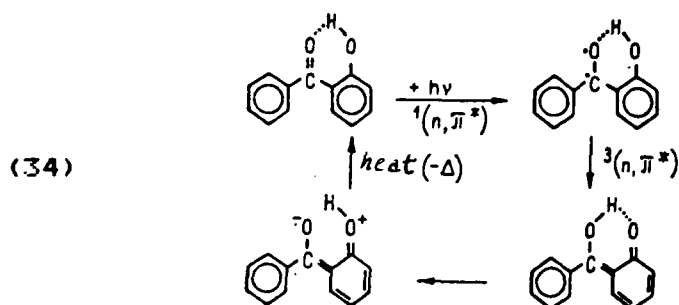
- adding photostabilizers to the polymer to inhibit photodegradation and photooxidation [121, 122],

- adding various compounds to the polymer to trap the free radicals formed in the above processes, including antioxidants [123, 124].

Photostabilizers may act by various mechanisms, the most important of which are:

1. Absorption of UV radiation and its conversion to luminescent radiation (such as salicylane [125]).

2. Absorption of UV radiation and its conversion to heat energy in an intramolecular regrouping with the participation of a hydrogen bond. Examples of such photostabilizers are o-hydroxy acids, their esters and amides [126-128], o-hydroxybenzophenone [129, 130], and phenylbenzotriazole derivatives with a hydroxyl or amine group in the ortho position [131-133]. In a reaction of this type, in the excited energy state there is transfer of a proton in intramolecular hydrogen bonds to give an ionic form. This is followed by deactivation with the liberation of energy as heat. The mechanism of this reaction was shown on the example of o-hydroxybenzophenone:



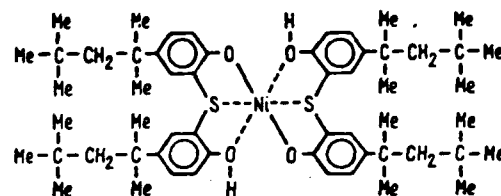
Some authors consider that screening plays a specific role in the photostabilization of o-hydroxybenzophenones [133, 134]. It was also shown that hydrogen bonds formed between the photostabilizer and polymer molecules must also be quite important [135]. o-Hydroxybenzophenones were shown to inhibit the thermal

oxidation of polypropylene, most probably through the formation of hydrogen bonds which decompose at high temperatures.

3. Deactivation of excited singlet and triplet state of a polymer or the impurities in it [133]. An example of such a reaction is the protective effect demonstrated by 1,3-cyclooctadiene (COD) when added to a polyolefin [73]. It has been shown that this compound readily deactivates the excited triplet state of the carbonyl group of acetone [136]. Similar properties are shown by piperylene [137-139]. From a practical point of view, it is most important to find a photostabilizer which would deactivate both the excited singlet and triplet states. Such types of compounds are for example chelated nickel compounds, which have already found industrial application for the photostabilization of polyolefins [133, 140-142]. These compounds have the following chemical structure:

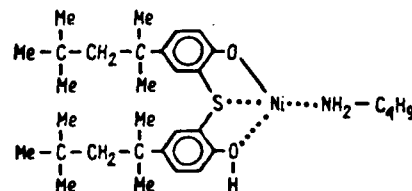
(I)

Ferro AM 101 (Ferro Corp.)



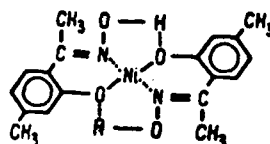
(II)

Cyasorb 1084 (Amer. Cyanamid)



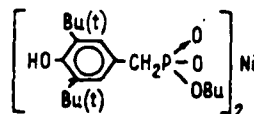
(III)

Negopex A (ICI)



(IV)

A 63'99 (Geigy)



The photostabilization of polymers has been treated in detail in several original and survey papers [71, 133, 143-153]. In recent years it has turned out that development of effective photostabilizers must be based on a thorough understanding of the mechanisms of photodegradation and photooxidation.

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