THE PHOTO-OXIDATION OF POLYMERS. A COMPARISON WITH LOW MOLECULAR WEIGHT COMPOUNDS

G. Geuskens and C. David

Université Libre de Bruxelles, Faculté des Sciences 206/1, B-1050 Brussels, Belgium

Abstract - The photo-oxidation of polymers involves different steps in which their reactivity is different from that of low molecular weight compounds. This is mainly due to the close vicinity of reactive groups in polymers and to the rigidity of the matrix. As a consequence, transfer of energy has a major role in the initiation of the photo-oxidation of most polymers on exposure to sunlight. It results in the sensitized decomposition of neighbouring hydroperoxide groups which, however, produce free radicals and thus initiate the oxidation less efficiently than model compounds in fluid solution. Scission of the polymer backbone, responsible for the alteration of the physical and mechanical properties, involves the decomposition of isolated hydroperoxide groups by two different mechanisms the relative importance of which changes with temperature.

INTRODUCTION

All industrial polymers deteriorate more or less rapidly on continued exposure to sunlight in the presence of oxygen. This is the consequence of photo-oxidation that results in a progressive loss of the useful physical and mechanical properties of polymers. Despite of the enormous practical importance of that problem relatively few papers have been concerned with quantitative aspects of the photo-oxidation of polymers. The main reason for this is probably that the photo-oxidation is a superficial phenomenon and that oxidation products are distributed inhomogeneously in the sample. Moreover these are usually linked to the polymer chain and difficult to analyse and to characterize . Therefore the interpretation of the experimental results is often based on a comparison with low molecular weight compounds. However polymers often behave in a very specific way, specially when the close vicinity of reactive groups and their reduced mobility in a rigid matrix have an influence on the mechanism of the reaction. Recent results concerned with the photo-oxidation of polymers show that some data can not be interpreted without taking those specific effects into account. The aim of this paper is not to make a critical review of the photo-oxidation of polymers since that topic has been well documented in recent years (1-5) but to discuss some results recently published in the literature or obtained in our own laboratory and to present some new ideas that might be of interest not only to polymer chemists but also to photochemists.
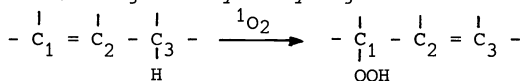

THE SINGLET OXYGEN MECHANISM OF OXIDATION

Two mechanisms have been proposed to explain the photo-oxidation of polymers in conformity with similar observations made on low molecular weight compounds.   One proceeds through direct reaction of singlet oxygen with the substrate while the other involves the production of free radicals and subsequent reaction with oxygen.

It has been clearly demonstrated that many photo-sensitized oxidation reactions proceed with participation of oxygen in an electronically excited singlet state (6)(7). The photochemical production of singlet oxygen is mainly due to quenching of the excited triplet state of suitable sensitizers :

$$^3S + {}^3O_2 \longrightarrow {}^1S_O + {}^1O_2$$
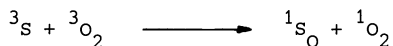
Singlet oxygen exhibits several specific reactions and the one that has been most often invoked in the photo-oxidation of polymers is the formation of a hydroperoxide by oxidation of an olefin containing an allylic hydrogen :

$$-\overset{|}{C_1} = \overset{|}{C_2} - \underset{H}{\overset{|}{C_3}} - \xrightarrow{\ ^1O_2\ } -\underset{OOH}{\overset{|}{C_1}} - \overset{|}{C_2} = \overset{|}{C_3} -$$

The possible participation of singlet oxygen in the photo-oxidation of polymers was mentioned for the first time by Trozzolo and Winslow ten years ago (8). These authors have suggested that carbonyl groups present as impurities in polyethylene might transfer energy to oxygen, thereby forming excited molecular oxygen in its $^1\Delta_g$ state. Singlet oxygen could then react with vinyl groups produced as a consequence of the Norrish type II reaction. The final result would be the formation of a hydroperoxide which could further decompose and lead to additional carbonyl groups :
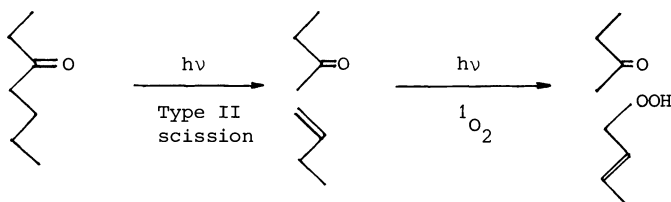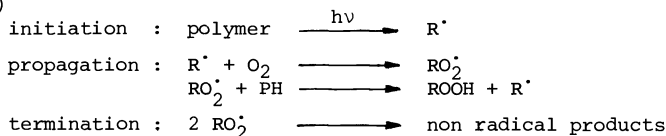

Since that time, several authors have proposed that the photo-oxidation of various polymers involves reaction with singlet oxygen (for a review, see (4)). In many cases, however, such a mechanism has never been proved. The arguments are based usually on the fact that a given polymer reacts in the solid state with singlet oxygen produced by microwave discharge or in solution with the same reactive species generated by energy transfer from suitable sensitizers. It has been shown quite conclusively that singlet oxygen produced by microwave discharge do not react with polyethylene or other saturated chain polymers (9)(10) while in the same conditions polybutadiene and polyisoprene react readily to produce hydroperoxide groups (8)(11). In solution, dyes such as methylene blue or rose bengal, that are well known to generate singlet oxygen on photolysis, sensitize the oxidation of polyisoprene (12) and polybutadiene (11) but have no influence on atactic polypropylene (13). It seems that previous contradictory results are due to the presence in the gaseous stream passed through the microwave discharge of other reactive oxygen species such as atomic oxygen or ozone. It can be safely concluded now that singlet oxygen is susceptible to react with unsaturated polymers but that saturated ones are completely inert even though they contain some double bonds as chain ends or impurities. However, this does not demonstrate that singlet oxygen really makes any considerable contribution to the photo-oxidation even of unsaturated polymers in the absence of an artificial source of excited molecular oxygen.

We propose that this should be checked by a method which is closer to the possible "natural", in situ, method of production of singlet oxygen during outdoor weathering of polymers. This has been tested in the case of polystyrene which is an interesting system to investigate since it is not saturated though the benzene ring is relatively inert to oxidation and it has been suggested by Rabek and Ranby (14) that singlet oxygen might be involved in the initial stage of the photo-oxidation of that polymer. We have incorporated in polystyrene a few percent benzophenone, the excited triplet level of which is suitable to sensitize the formation of single oxygen but can also initiate the photo-oxidation by abstraction of hydrogen atoms from the polymer matrix. The system is then irradiated at 365 nm in the presence of oxygen in conditions where polystyrene and most usual polymers are inert in the absence of the aromatic ketone. It can be measured that oxygen absorption occurs and that oxidation products are formed at a rate proportional to the benzophenone concentration but that the whole process can be completely inhibited by the presence of naphthalene (15). This, of course results from the quenching of the excited triplet state of the ketone by the aromatic hydrocarbon which, by the way, is promoted to its own excited triplet state also susceptible to sensitize the formation of singlet oxygen. On that basis it can be safely concluded that the participation of singlet oxygen in the mechanism of photo-oxidation of polystyrene is negligible. The competition between benzophenone and naphthalene as initiators of the photo-oxidation of polymers can be considered as a convenient method, much less questionable that the others, to determine the relative importance of the singlet oxygen and the free radical mechanism of oxidation of polymers

THE FREE RADICAL MECHANISM OF OXIDATION

The free radical mechanism of photo-oxidation of polymers proceeds through a chain reaction similar to that reviewed recently by Howard in the case of homogeneous liquid-phase oxidations (16)

$$\text{initiation :} \quad \text{polymer} \xrightarrow{h\nu} R^\bullet$$

$$\text{propagation :} \quad R^\bullet + O_2 \longrightarrow RO_2^\bullet$$
$$RO_2^\bullet + PH \longrightarrow ROOH + R^\bullet$$

$$\text{termination :} \quad 2\ RO_2^\bullet \longrightarrow \text{non radical products}$$

However, at each step some features specific to polymers are worth being discussed because they have an influence on the evolution of the reaction.

Initiation. Most usual polymers (polyethylene, polyolefins, polystyrene, polyvinylchloride) should be perfectly stable on exposure to solar radiation ($\lambda \geqslant 290$ nm) since corresponding model compounds do not absorb in that spectral range. Actually, this is not observed and it is generally admitted that structural defects or impurities are responsible for the initiation of the photo-oxidation. These are most likely oxidation products formed during the processing of the polymer at high temperature in the presence of atmospheric oxygen. Ketones and hydroperoxydes are usually mentioned as potential sources of free radicals since they are both detected in small amounts in industrial polymers.

Ketones undergo two dominant photochemical reactions : the Norrish type I and the Norrish type II processes. The type II reaction although it results in backbone cleavage of macro-ketones does not produce free radicals and thus cannot initiate the oxidation. The type I scission produces free radicals but the quantum yield of that reaction has been estimated to be as low as 2.10^{-3} in solution at room temperature for an ethylene-carbon monoxide copolymer (17). In the solid state it should be even lower because of the increased probability of radical recombination in a cage. Recently, it has been confirmed that polymers with backbone carbonyl groups have very low efficiency in initiating photo-oxidation while side chain ketone groups initiate rapidly the reaction (18). The efficiency of aliphatic ketones as photo-initiators is thus seriously questioned now. Moreover, several authors have shown that addition of long chain aliphatic ketones in polypropylene (19) or in high impact polystyrene (20) fails to accelerate the photo-oxidation. In contrast to aliphatic ketones, aromatic ketones susceptible to abstract hydrogen atoms such as benzophenone or acetophenone are efficient initiators of the photo-oxidation of polystyrene (15) and acetophenone groups have been detected as impurity in that polymer (21)(22)(23).

Whatever the initial mechanism of radical formation, hydroperoxides are produced after reaction with oxygen. These are thus key intermediates in the oxidation of polymers. They are formed in the presence of air even during mild processing at 165°C. Hot mixing of polyethylene in those conditions for 10 min. results in concentration of the order of 10^{-2} M in hydroperoxide groups while carbonyl groups are present in concentration about ten times less (24). Moreover, hydroperoxides are extremely photolabile; they usually decompose with quantum yields close to unity to produce free radicals that can abstract hydrogen atoms from the polymer and thus initiate the photo-oxidation :

$$ROOH \longrightarrow RO^{\cdot} + {}^{\cdot}OH$$

From a critical examination of the potential efficiency of different types of impurities as initiators of the photo-oxidation of polypropylene, Carlsson and al. conclude that hydroperoxides should play the major role (25). This conclusion is reached on taking into account the absorption coefficients of various chromophores and their ability to generate free radicals on decomposition. Scott and al. also come to the idea that the photo-oxidation of polypropylene depends primarily on the amount of hydroperoxides formed during the processing because removal of these by heat treatment in an inert atmosphere, although increasing ketonic carbonyl concentration, markedly decreases the rate of oxidation (26).

Hydroperoxide groups, however, have a very low absorption coefficient in the solar ultra-violet range : about $0,3$ l m^{-1} cm^{-1} for t-butylhydroperoxide (27) and for cumylhydroperoxide at 310 nm. This should be compared with absorption coefficients close to 30 l m^{-1} cm^{-1} for aliphatic macroketones (17) and to 50 l m^{-1} cm^{-1} for acetophenone (28) around 300 nm. Even at a concentration ten times lower than that of hydroperoxides in weakly oxidized polymers carbonyl groups are thus the main absorbing groups. Provided they can transfer their excitation energy to the more photolabile hydroperoxides as shown by Walling for model compounds (29) the rate of production of free radicals will be much higher than expected from hydroperoxides alone. This has been demonstrated in our work on the photo-oxidation of polystyrene. When that polymer is irradiated with U.V. light in the presence of oxygen the intensity of the phosphorescence emission of acetophenone groups, detectable in trace amount initially, first increases and then decreases although the concentration of those groups, monitored by I.R. or U.V. absorption spectroscopy, continuously increases. This is due to energy transfer to hydroperoxide groups the concentration of which increases with time making the transfer of energy progressively more efficient (23). Energy transfer from benzophenone or valerophenone to cumylhydroperoxide can also be demonstrated by phosphorescence measurements at 77°K in a methyltetrahydrofuran glass or in a polystyrene film (30)(31). Moreover, it has been shown that cumylhydroperoxide in a polystyrene film is decomposed on irradiation at 365 nm in the presence of benzophenone whereas no reaction occurs in those conditions in the absence of the ketone. During that period benzophenone remains practically unchanged and act thus mainly as a sensitizer (31). It can be measured on irradiation at 365 nm that the quantum yield of oxygen absorption in polystyrene containing benzophenone and cumylhydroperoxide at a concentration that makes the transfer of energy 40 % efficient is 6.7 10^{-2} whereas it is 2.7 10^{-2} when it contains benzophenone only and no oxygen absorption occurs in the same conditions with cumylhydroperoxide only (30).

Those results indicate that absorption of energy by carbonyl groups followed by transfer to hydroperoxides is probably the main process of production of free radicals during the photo-oxidation of industrial polymers. This idea is not incompatible with the conclusions of au-

thors who point to the role of hydroperoxides as initiators of the photo-oxidation since keto-
nes as sensitizers only absorb a higher fraction of the incident energy without producing any
appreciable direct effect. It can be easily understood that destruction of hydroperoxide
groups even if this results in an increased concentration of carbonyl groups results in a
reduction of the rate of oxidation. On the other hand, addition of aliphatic ketones to po-
lymers cannot be expected to have an effect on the rate of oxidation since at a hydroperoxi-
de concentration of about 10^{-2} M the efficiency of the transfer is almost negligible (30)(31).
It should be kept in mind, indeed, that in oxidized solid polymers hydroperoxides are very
close together, as discussed below, because they are formed in a chain reaction and cannot
diffuse away. As ketones are produced by decomposition of some of those hydroperoxides (27)
they are never more distant than 1 nm from a neighbouring hydroperoxide. This corresponds to
a local concentration of 0,4 M which makes the transfer about 60 % efficient. So the role of
carbonyl groups produced by decomposition of hydroperoxides but also acting as sensitizers of
that decomposition is specific to the photo-oxidation of polymers and is not observed with
low molecular weight compounds.

Finally, it should be mentioned that not only ketones can transfer energy to hydroperoxides.
Also aromatic hydrocarbons such as naphthalene or anthracene sensitize the photo-decomposi-
tion of hydroperoxides. In polystyrene the phenyl chromophore itself can transfer energy to
hydroperoxides : this explains why the excimer fluorescence of the polymer decreases during
the photo-oxidation (23).

Propagation. Macroradicals produced in polymers react readily with oxygen to produce peroxy
radicals easily identified by their characteristic asymetric E.S.R. spectrum. These abstract
hydrogen atoms from the polymer chain and so new macroradicals and hence new hydroperoxides
are produced. Hydroperoxides are formed in close vicinity by successive propagation steps;
they are linked to the polymer chain and thus remain very close together in a rigid matrix.
Indeed, I.R. spectroscopy indicates that in photo-oxidized polymers most hydroperoxide groups
are hydrogen bonded. In the solution oxidation of polypropylene, the intramolecular propaga-
tion step, via a six membered ring transition state, is highly favoured :
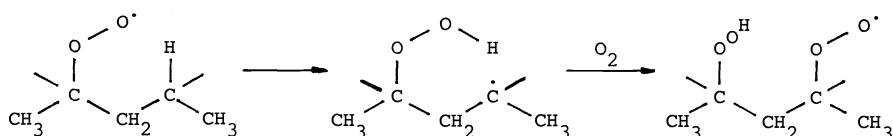
More than 90 % of the hydroperoxide groups are hydrogen bonded in sequences of two or more
(32). The intramolecular abstraction is also preponderant in the liquid-phase oxidation of
low molecular weight compounds such as 2,4-dimethylpentane (33) or 2,4,6-trimethylheptane
(34) but not in normal alkanes (35). It thus appears that a suitable conformation, probably
favoured by restricted chain rotation in branched alkanes, is required. If this is possible
in the solution oxidation of polypropylene, it is however not likely that the same situation
prevails in the photo-oxidation of solid polymers at room temperature. On the contrary, it
can be expected that in a rigid matrix the probability that a hydrogen atom is abstracted by
a macroradical is determined more by its accessibility than by the C-H bond energy. There-
fore the usual assumption that tertiary carbon atoms are the main sites of oxidation as in
low molecular weight compounds is probably not always valid. We have shown that in polysty-
rene secondary hydrogen atoms are also involved in the photo-oxidation process since alipha-
tic ketones of type A are produced together with aromatic ketones of type B (36).


These aliphatic ketones are produced either by photodecomposition of the corresponding hydro-
peroxide or in the termination step by a disproportionation reaction involving the corres-
ponding peroxy radical, as discussed below. As oxidation is not restricted to tertiary car-
bon atoms in solid polymers, some data of the literature should perhaps be reinterpreted.
For instance, the structure assigned to ketones produced in the photolysis of polypropylene
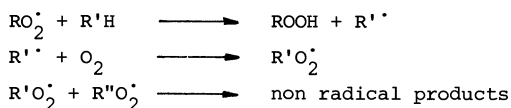hydroperoxides might not be correct (27) :
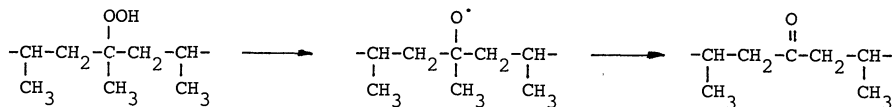
Indeed, the methane formed is only one fourth of the expected amount and the elimination of
a methyl radical has been shown to occur with a very low yield in a model compounds (13).

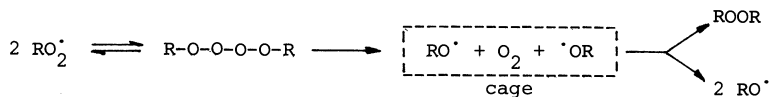Ketones derived from oxidation of secondary carbon atoms should be considered as an alternative structure :

$$- CH - \overset{\overset{\textstyle O}{\|}}{C} - CH -$$
$$\quad | \qquad\qquad |$$
$$\quad CH_3 \qquad\quad CH_3$$
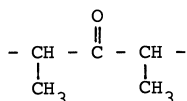
However, identification of different types of aliphatic ketones in polypropylene si difficult because the analysis of I.R. spectra is complicated by the small wavelength differences between species and the marked effect of the polarity of the environment causes important shifts (37).

Termination. At room temperature, peroxy radicals can not be detected by E.S.R. spectroscopy in irradiated polymers although they are quite stable at low temperature. Free radicals produced by gamma irradiation of polystyrene in vacuo at room temperature are transformed into peroxy radicals as soon as oxygen is admitted into the sample tube at 77°K. The concentration of peroxy radicals remains constant as long as temperature is maintained below 220°K but it decreases very quickly when the sample is allowed to warm up. This indicates that the termination step involving peroxy radicals is a very fast process even in a rigid matrix at room temperature. The same behaviour has been observed by other authors for macroradicals produced by mechanical degradation of polymers (38) and explained by a "chemical" mechanism for the diffusion of radicals in the presence of oxygen via the consecutive reactions :

$$RO_2^{\cdot} + R'H \longrightarrow ROOH + R'^{\cdot\cdot}$$
$$R'^{\cdot\cdot} + O_2 \longrightarrow R'O_2^{\cdot}$$
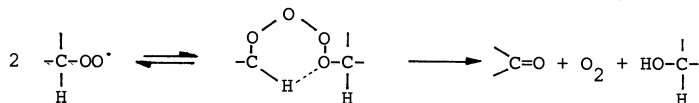$$R'O_2^{\cdot} + R''O_2^{\cdot} \longrightarrow \text{non radical products}$$

Even isolated macroradicals produced by irradiation of polystyrene in vacuo at 365 nm in the presence of benzophenone decay very quickly by a second order process when oxygen is admitted into the sample tube (39).

When tertiary peroxy radicals are involved, the only possible termination step proceeds through the formation of a tetroxide that decomposes to give two alkoxy radicals in a cage and an oxygen molecule :

$$2\ RO_2^{\cdot} \rightleftharpoons R\text{-}O\text{-}O\text{-}O\text{-}O\text{-}R \longrightarrow \boxed{RO^{\cdot} + O_2 + {}^{\cdot}OR} \begin{array}{l} \nearrow ROOR \\ \searrow 2\ RO^{\cdot} \end{array}$$
$$\text{cage}$$

In the autoxidation of cumene only 10 % of the caged alkoxy radicals recombine to give peroxides while 90 % escape and undergo reactions typical of alkoxy radicals (16). In polymers, however, the rigidity of the matrix prevents the diffusion of alkoxy macroradicals and cage recombination is expected to be the dominant process producing peroxy crosslinks between macromolecules. This can be invoked to justify to some extent the increased quantum yield of crosslinking when polystyrene is irradiated in the presence of oxygen. Quantum yields of crosslinking and chain scission have been measured to be respectively 3.9 10^{-4} and 2.4 10^{-3} when polystyrene containing cumylhydroperoxide is irradiated at 310 nm in vacuo whereas the corresponding values are respectively 9.4 10^{-4} and 5.6 10^{-3} in the presence of air (40). As mentioned above in this paper secondary peroxy radicals are also produced in the photo-oxidation of polymers. These can disproportionate in a self-reaction or by reaction with a tertiary peroxyradical to give a ketone and an alcohol (41) :

$$2\ \overset{|}{\underset{H}{\text{--C--OO}^{\cdot}}} \rightleftharpoons \overset{O}{\underset{H}{\text{--C}}}\overset{\diagup O \diagdown}{\underset{}{}}\overset{O}{\underset{H}{\text{O--C--}}} \longrightarrow \text{>C=O} + O_2 + \overset{|}{\underset{H}{\text{HO--C--}}}$$

Evidence for such a process in polymers is obtained by the formation of aliphatic ketones even in the dark when oxygen is allowed to react with free radicals produced by the mechanical degradation of polystyrene (31). In those conditions aliphatic ketones can not be formed by photodecomposition of secondary hydroperoxides.

## MOLECULAR WEIGHT CHANGES IN POLYMERS DURING PHOTO-OXIDATION

The detrimental effect of photo-oxidation on the properties of polymers is mainly the consequence of a reduction of the average molecular weight, though crosslinks are also formed but usually with a lower quantum yield. To make the experimental study easier this effect can be accelerated by incorporating in the polymer a suitable photo-initiator such as benzophenone. In those conditions, the ultimate tensile strength of polystyrene irradiated in air

at 365 nm has been shown to decrease linearly with time (15). The quantum yield of chain
scission 1.3 10^{-3} is constant in the whole dose range (40) and thus the number of scissions
per chain $\underline{n}$ also increases linearly with time

$$n = \frac{\overline{M}{}^o_n - \overline{M}_n}{\overline{M}_n}$$

where $\overline{M}{}^o_n$ is the initial number average molecular weight and $\overline{M}_n$ is the corresponding value
for a photo-oxidized sample. Therefore a linear relation is found between the ultimate ten-
sile strength and the reciprocal number average molecular weight (31) in agreement with the
empirical equation derived by Flory for a wide variety of samples with different molecular
weight distribution (42). None of the steps mentioned so far in the free radical mechanism of
photo-oxidation results in scission of the polymer chain. This is generally admitted to be
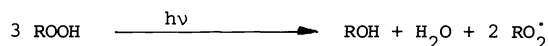the consequence of the photo-decomposition of hydroperoxide groups.

Photodecomposition of neighbouring hydroperoxide groups. In dilute solution hydroperoxides
decompose by a monomolecular mechanism and two radicals are produced by scission of the O-O
bond. In more concentrated solutions, however, the bimolecular mechanism becomes progressi-
vely more important (43) :

$$\overset{H}{\underset{\displaystyle |}{}}$$
$$R-O-O\text{---}H-O-O-R \xrightarrow{\;h\nu\;} RO^{\bullet} + H_2O + RO_2^{\bullet}$$
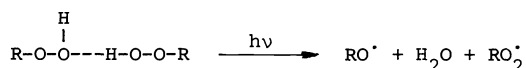
It is probably predominant in oxidized polymers at high local concentration (44). The alko-
xy radicals produced are very reactive and readily abstract hydrogen atoms from neighbouring
hydroperoxide groups if these are accessible. They are indeed not detected by ESR spectro-
scopy in the photodecomposition of hydroperoxides in concentrated solution (45) because of
the radical-induced decomposition

$$RO^{\bullet} + ROOH \longrightarrow ROH + RO_2^{\bullet}$$

The global reaction is then :

$$3\ ROOH \xrightarrow{\;h\nu\;} ROH + H_2O + 2\ RO_2^{\bullet}$$

and a quantum yield higher than one is expected for the photodecomposition of hydroperoxide
groups in polymers provided the local concentration is sufficiently high. Actually a value
of about 4 has been measured in polypropylene (27). In those conditions, the production of
free radicals susceptible to initiate the photo-oxidation is rather low : the quantum yield
of oxygen absorption is only 2.7 10^{-2} when polystyrene is irradiated at 253,7 nm (36).

The sequence of reactions involved in the decomposition of neighbouring hydroperoxide groups
if it produces only peroxy radicals does not result in any scission of the polymer backbone.
This is thus more likely the consequence of the photodecomposition of isolated hydroperoxi-
de group.

Photodecomposition of isolated hydroperoxide groups. In the photo-oxidation of polystyrene,
chain scissions proceed by the following mechanism, involving isolated hydroperoxide group
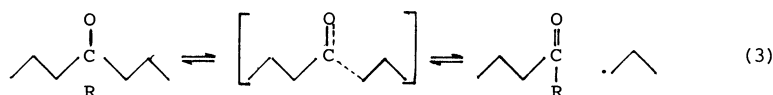(36) :

$$(1)$$
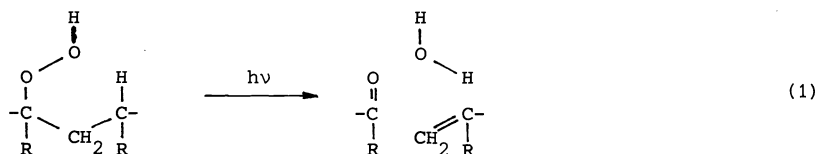
This is supported by the close agreement between quantum yields of chain scission and aceto-
phenone group formation in different experimental conditions (36)(40) and by the simulta-
neous formation of unsaturated chain ends.

An alternative mechanism sometimes proposed to justify chain scissions in the oxidation of
polymers proceeds through the fragmentation of alkoxy radicals :

$$(2)$$
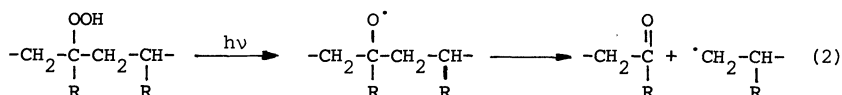
In a rigid matrix, however, the fragmentation of alkoxy macroradicals is expected to be very limited because the cage effect makes the dissociation of the activated complex postulated by Kochi (46) difficult :

$$\underset{R}{\overset{\overset{\displaystyle O}{|}}{\wedge\wedge^C\wedge\vee}} \rightleftharpoons \left[\wedge\vee^{\overset{\overset{\displaystyle O}{||}}{C}}\cdot\cdot\wedge\vee\right] \rightleftharpoons \wedge\vee^{\overset{\overset{\displaystyle O}{||}}{\underset{R}{C}}}\cdot\wedge \qquad (3)$$

Abstraction of hydrogen atoms by alkoxy radicals is thus probably predominant at room temperature. This reaction is indeed responsible for the initiation of the oxidation process after sensitized decomposition of hydroperoxides as discussed above. However, since the relative rates of fragmentation and hydrogen atom abstraction depend on the activation energy difference for the competing pathways, the temperature is an important variable to keep in mind. The photo-oxidation of polystyrene studied at different temperatures in air at 310 nm from 20°C to 100°C suggests that, indeed, the relative importance of reaction (2) increases with temperature. At that wavelength the absorption of light is due to acetophenone groups present as impurity (21)(23). These sensitize the decomposition of isolated hydroperoxide groups according to reaction (1) or (2). In both cases, new acetophenone end groups are produced and the fraction of incident energy absorbed thereby increases resulting in an auto-acceleration of the oxidation process. This effect is unnoticeable at 20°C but becomes clearly visible at higher temperature (31). The increase of the number of scissions per chain can be estimated from the increase of the concentration of acetophenone end groups monitored by I.R. spectroscopy. The influence of temperature on the quantum yield of chain scission can be attributed to the increasing importance of the fragmentation reaction of alkoxy macroradicals (reaction (3)).

CONCLUSION

Two mechanisms have been proposed for the photo-oxidation of polymers by comparison with low molecular weight compounds. The singlet oxygen mechanism is restricted to unsaturated polymers but, though the reaction of singlet oxygen with such polymers has been demonstrated, its contribution to their oxidation in natural weathering conditions has not yet been proved. The free radical mechanism of oxidation is undoubtedly more general. It is similar to the mechanism of oxidation of low molecular weight compounds but the relative importance of the various steps involved in the chain reaction is different. This is mainly due to the close vicinity of rective groups in polymers that results in a local concentration much higher than the average concentration in the sample and also to the restricted mobility of macroradicals in a rigid matrix. These features justify some specific effects observed in the photo-oxidation of polymers namely the importance of energy transfer process in the initiation of the photo-oxidation.

Another interesting deduction from the experimental results is that at high local concentration of hydroperoxide groups the efficiency of the transfer is high while the decomposition of neighbouring hydroperoxide groups produces few radicals susceptible to initiate the oxidation. Thus they tend to decay faster than they are produced. At low hydroperoxide concentration, however, the efficiency of the transfer is lower but the yield of free radicals is higher and hydroperoxides tend to accumulate. The mechanism of photo-oxidation of polymers is a compromise between these two extreme situations.

REFERENCES

1. Polymer Stabilization, edit. by W. L. Hawkins, Wiley-Interscience (1972).
2. Degradation of Polymers, vol. 14 of Comprehensive Chemical Kinetics, edit. by C. H. Bamford and C. F. H. Tipper, Elsevier (1975).
3. Degradation and Stabilization of Polymers, edit. by G. Geuskens, Applied Science (1975).
4. B. Ranby and J.F. Rabek, Photodegradation, photo-oxidation and photostabilization of polymers, J. Wiley (1975).
5. Aspects of Degradation and Stabilization of Polymers, edit. by H. H. G. Jellinek, Elsevier (1978).
6. K. Gollnick, Adv. in Photochemistry, 6, 1 (1968).
7. D. R.Kearns, Chem. Rev., 71, 395 (1971).
8. A.M. Trozzolo and F. H. Winslow, Macromolecules, 1, 98 (1968).
9. A. K. Breck, C. L. Taylor, K. Russel and J. S. S. Wan, J.Polymer Sci. Chem. Ed., 12, 1505 (1974).
10. D. J. Carlsson, T. Suprunchuk and D. M. Wiles, J.Polymer Sci. Polymer Letters, 14, 493 (1976).
11. J. F. Rabek and B. Ranby, J. Polymer Sci. Chem. Ed., 12, 295 (1974).
12. T. Mill, K. C. Ivin and F. R. Mayo, Rubber Chem. Technol., 41, 296 (1968).
13. T. Mill, H. Richardson and F. R. Mayo, J. Polymer Sci. Chem. Ed., 11, 2899 (1973).
14. J. F. Rabek and B. Ranby, J. Polymer Sci. Chem. Ed., 12, 273 (1974).

15. G. Geuskens and C. David, Pure Appl. Chem., 49, 479 (1977).
16. J. A. Howard in Free Radicals, Vol. II, p. 3, edit. by J. K. Kochi, J. Wiley (1973).
17. G. H. Hartley and J. E. Guillet, Macromolecules, 1, 165 (1968).
18. F. Sitek, J. E. Guillet and M. Heskins, J.Polymer Sci. Symposia, 57, 343 (1976).
19. D. J. Harper and J. F. Mc Kellar, Chem. Ind. (London), 842 (1972).
20. A. Ghaffar, A. Scott and G. Scott, Europ. Polym. J., 12, 615 (1976).
21. W. Klöppfer, Europ. Polym. J., 11, 203 (1975).
22. G. A. George and D. K. C. Hodgeman, Europ. Polym. J., 13, 63 (1976).
23. G. Geuskens, D. Baeyens-Volant, G. Delaunois, Q. Lu-Vinh, W. Piret and C. David, Europ. Polym. J., 14, 299 (1978).
24. M. U. Amin, G. Scott and L. M. K. Tillekeratne, Europ. Polym. J., 11, 85 (1975).
25. D. J. Carlsson, A. Garton and D. M. Wiles, Macromolecules, 9, 695 (1976).
26. K. B. Chakraborty and G. Scott, Europ. Polym. J., 13, 731 (1977).
27. D. J. Carlsson and D. M. Wiles, Macromolecules, 2, 597 (1969).
28. J. G. Calvert and J. N. Pitts, Photochemistry, J. Wiley (1966).
29. C. Walling and M. J. Gibian, J. Amer. Chem. Soc., 87, 3413 (1965).
30. W. Piret, Ph. D. Thesis, University of Brussels (1976).
31. Q. Lu-Vinh, Ph. D. Thesis, University of Brussels (1978).
32. J. C. W. Chien, E. J. Vandenberg and H. Jabloner, J. Polymer Sci. A-1, 6, 381 (1968).
33. T. Mill, G. Montorsi, Int. J. Chem. Kinet., 5, 119 (1973).
34. D. E. Van Sickle, J. Org. Chem., 37, 755 (1972).
35. D. E. Van Sickle, T. Mill, F. R. Mayo, H. Richardson and C. Gould, J. Org. Chem., 38, 4435 (1973).
36. G. Geuskens, D. Baeyens-Volant, G. Delaunois, Q. Lu-Vinh, W. Piret and C. David, Europ. Polym. J., 14, 291 (1978).
37. D. J. Carlsson and D. M. Wiles, J. Macromol. Sci. Rev., C 14, 65 (1976).
38. S. E. Bresler and E. N. Kazbekov, Adv. Polymer Sci., 3, 688 (1964).
39. C. David, W. Piret, M. Sakaguchi, G. Geuskens, Makromol. Chem., 179, 181 (1978).
40. C. David, D. Baeyens-Volant, G. Delaunois, Q. Lu-Vinh, W. Piret and G. Geuskens, Europ. Polym. J., 14 (1978) in press.
41. G. A. Russel, J. Amer. Chem. Soc., 79, 3871 (1957).
42. P. J. Flory, J. Amer. Chem. Soc., 67, 2049 (1945).
43. J. C. W. Chien, ref. (3), p. 95.
44. V. S. Pudov and A. L. Buchachenko, Russian Chem. Rev., 39, 70 (1970).
45. J. J. Zwolenik, J. Chem. Phys., 71, 2464 (1967).
46. J. K. Kochi, J. Amer. Chem. Soc., 84, 1193 (1962).