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STUDIES OF THE MECHANISM OF POLYOLEFIN PHOTODEGRADATION

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Abstract — Through studies of the photodegradation of commercial polymers and their model compounds, the roles of ketone carbonyl and hydroperoxide functional groups in the overall photodegradation mechanism have been elucidated. Besides undergoing photochemical reaction themselves, polymeric ketones are capable of sensitizing the decomposition of the more reactive hydroperoxide functionality by energy transfer involving an exciplex intermediate.

It is now well established that the primary mechanism of photodegradation of hydrocarbon polymers when exposed to terrestrial UV involves the process of photooxidation. Although there has been much controversy in recent years about the relative roles of different absorbing groups in polyolefins, it seems clear that in most cases initiation of the photooxidation process is caused primarily by absorption of light by only two groups, namely the hydroperoxide group and the ketone carbonyl. The relative importance of these two groups in the photooxidation process may vary significantly depending on the structure of the particular polyolefin. In polyethylene, for example, it is well known that the steady state concentration of hydroperoxides during a photooxidation in the solid phase remains very low, while in polypropylene, substantial concentrations of hydroperoxide are produced and maintained in the photostationary state primarily because they exist in a sequential hydrogen bonded form. These hydrogen-bonded peroxides may be significantly more stable to UV photodecomposition than an isolated hydroperoxide group.

In polyethylene, careful studies of photooxidation rates under constant UV irradiation in the solid phase indicate that the process follows an exponential relationship, as shown in Fig. 1. Since under
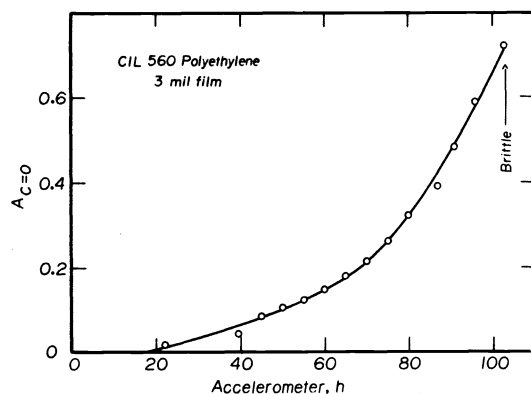

Fig. 1. Build-up in carbonyl absorbance during continuous irradiation of low density polyethylene in air.

weathering conditions the concentration of polymer and oxygen would be expected to remain relatively constant through the process, it is tempting to ascribe the increase in rate of photooxidation observed experimentally to an increase in the number of initiating sites. The exponential relationship of this

particular curve is shown more clearly when the logarithm of the absorbance due to the carbonyl group in the polymer is plotted versus time of irradiation, as shown in Fig . 2.
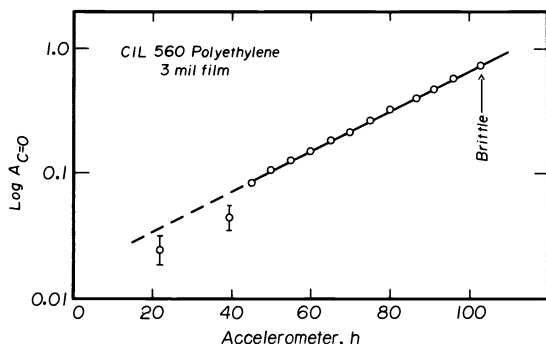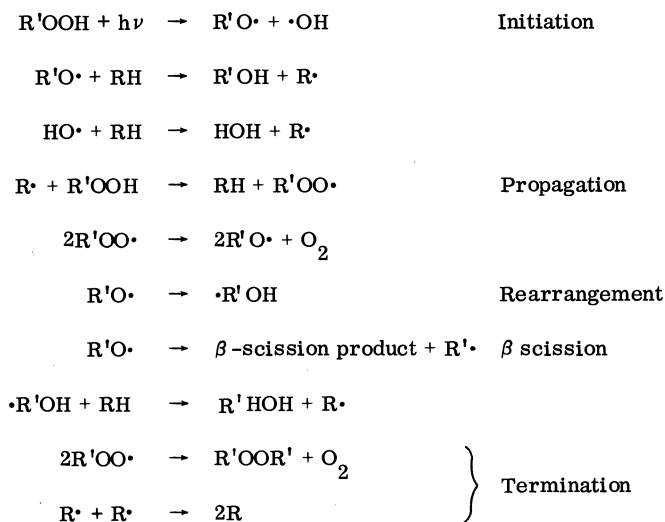

Fig. 2. Logarithm of carbonyl absorbance vs. irradiation time.

In our experience, most photooxidations of polyethylene, regardless of whether the polyethylenes contain additives to increase their photosensitivity or not, follow linear logarithmic curves of this nature. The generality of this relationship is of considerable importance in extrapolating early degradation data to predict ultimate failure of the polymer. In this case, the logarithmic relationship is followed up to at least the point where the polymer becomes completely brittle and fails as a structural or integral plastic material.

Regardless of whether the hydroperoxide or the carbonyl group is the primary initiating site, it is clear that the photooxidation itself takes place via the primary intermediacy of the hydroperoxide group. A complete kinetic scheme for this photooxidation process is shown below:

$$R'OOH + h\nu \rightarrow R'O\cdot + \cdot OH \qquad \text{Initiation}$$

$$R'O\cdot + RH \rightarrow R'OH + R\cdot$$

$$HO\cdot + RH \rightarrow HOH + R\cdot$$

$$R\cdot + R'OOH \rightarrow RH + R'OO\cdot \qquad \text{Propagation}$$

$$2R'OO\cdot \rightarrow 2R'O\cdot + O_2$$

$$R'O\cdot \rightarrow \cdot R'OH \qquad \text{Rearrangement}$$

$$R'O\cdot \rightarrow \beta\text{-scission product} + R'\cdot \quad \beta \text{ scission}$$

$$\cdot R'OH + RH \rightarrow R'HOH + R\cdot$$

$$2R'OO\cdot \rightarrow R'OOR' + O_2$$

$$R\cdot + R\cdot \rightarrow 2R \qquad \bigg\} \; \text{Termination}$$

There are two reasons for ascribing to the ketone carbonyl a primary role in this photooxidation process. The first of these is that the carbonyl group is the only group which actually builds up in the polymer as a function of time and would therefore give rise to the exponential behavior referred to previously. Hydroperoxides, on the other hand, because of their photolability rapidly reach a photostationary state at a relatively low concentration and in general do not seem to increase at a rate necessary to create the exponential behavior observed. The second reason is that the ketone group has a stronger absorbance in the terrestrial UV region, as shown in Fig. 3.
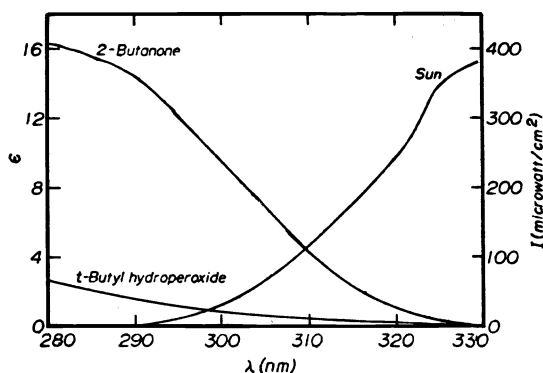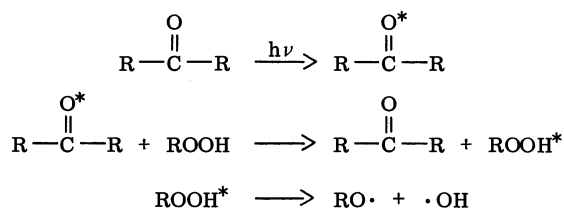
Fig. 3. Molar extinction coefficients of 2-butanone and t-butyl hydroperoxide
compared with solar emission at earth's surface (air mass = 1).

As a result of these considerations, we proposed a number of years ago (Ref. 1) that an important
mechanism for initiation of photooxidation was the sensitized decomposition of hydroperoxides by
interaction with excited state carbonyl groups.

$$R\!-\!\overset{\overset{\displaystyle O}{\|}}{C}\!-\!R \xrightarrow{\ h\nu\ } R\!-\!\overset{\overset{\displaystyle O^*}{\|}}{C}\!-\!R$$

$$R\!-\!\overset{\overset{\displaystyle O^*}{\|}}{C}\!-\!R + ROOH \longrightarrow R\!-\!\overset{\overset{\displaystyle O}{\|}}{C}\!-\!R + ROOH^*$$

$$ROOH^* \longrightarrow RO\cdot + \cdot OH$$

Later studies (Ref. 2) suggested that this interaction could take place by means of an exciplex, that is,
a complex between the excited state of the ketone carbonyl and the ground state of the hydroperoxide.
Further evidence for this suggestion has been maintained both by recent studies in our own labora-
tories (Ref. 3) and in those of Professor Geuskens in Brussels (Ref. 4).

The importance of the interactions between ketones and hydroperoxides in the photooxidation process
prompted us to look at other systems in which we could study hydroperoxide photochemistry both
in the presence and in the absence of other absorbing groups. Unfortunately, it is difficult to find
clean methods of synthesis to introduce hydroperoxide groups into olefin polymers without contamina-
tion with small amounts of other groups which might interfere with their photochemistry.

One of the cleanest reactions which will introduce a hydroperoxy group into a polymer is the reaction
of singlet oxygen with substituted olefins. We have used this so-called "ene" reaction to introduce
hydroperoxy groups into cis-polyisoprene. Subsequent photolysis of these groups gives an insight into
the photochemistry of hydroperoxides in polymeric systems. In recent studies by Ng and Guillet (Ref
5 and 6), it was shown that the photolysis of cis-polyisoprene hydroperoxide had many features simi-
lar to the photolysis of small model compounds such as t-butyl hydroperoxide. In the first place, the
hydroperoxide showed a very high quantum yield for decomposition ranging from two to seven, de-
pending on the temperature and intensity of the absorbed light. Secondly, the magnitude of the quan-
tum yield for hydroperoxide loss decreased with intensity. Furthermore, the quantum yields were
all consistently greater than one, which is indicative of a chain-induced decomposition. More im-
portant, it was shown that the number of bond scissions per hydroperoxide decomposed was very
small, usually of the order of 2%, thus indicating that the breaking of the polymer chain was not a
direct result of the decomposition of the hydroperoxide but of some secondary reaction which we later
associated with the β-scission of the alkoxy radical produced by direct photolysis rather than by the
induced photolysis of the hydroperoxy group. In cis-polyisoprene, the β-scission of the alkoxy radical
must compete with the abstraction of a proton from the allylic position in the cis-polyisoprene, shown
schematically in Scheme I. It was also shown that both the decomposition of hydroperoxide groups and the
number of bond scissions in cis-polyisoprene could be photosensitized by the addition of small mole-
cule ketone groups.

Additional studies were then made using polystyrene-MIPK copolymers which showed that the singlet
and triplet excited states of the ketone carbonyl can be quenched by collisional deactivation with
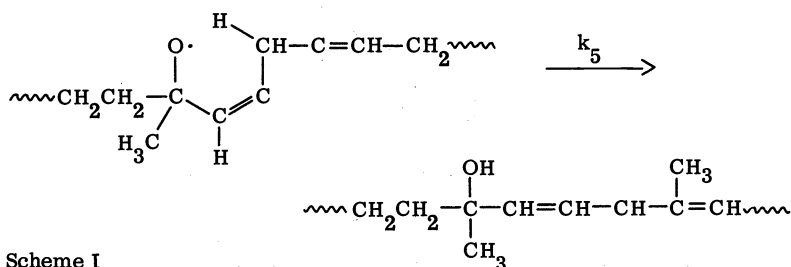
Scheme I

t-butyl hydroperoxide and that the process followed typical Stern-Volmer kinetics, consistent with a mechanism involving an exciplex intermediate, as shown in Fig. 4.
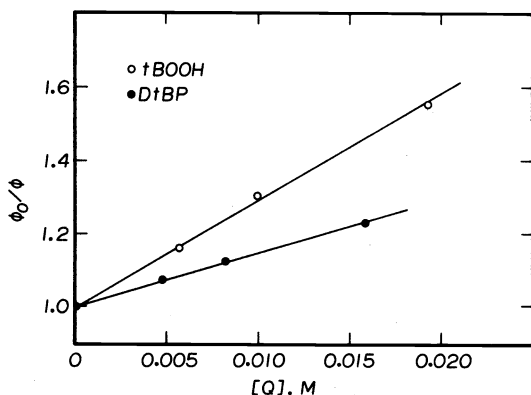

Fig. 4. Stern-Volmer plot for PS-MIPK quenched by t-butyl hydroperoxide and di-tert-butyl peroxide.

In contrast to the hydroperoxy groups, ketone carbonyl groups can be introduced into polyethylene rather cleanly by copolymerization with vinyl ketones. However, the structure of the ketone groups introduced depends on the type of vinyl ketone used and the conditions of polymerization because it has now been well demonstrated by studies by Guillet and Li (Ref. 7) that a variety of ketone structures results when the copolymerization takes place under high pressures, as a result of the so-called "back-biting" mechanism in polyethylene. These studies indicated that side chain ketone carbonyls were sub-stantially more photoactive than those contained in the backbone of the polymer chain. This is par-ticularly true when the carbonyl is used as a sensitizer for the photooxidation process, since backbone carbonyls such as those introduced by the copolymerization of ethylene with carbon monoxide have very low quantum yields for the formation of radicals by the Norrish type I process. In contrast, the side chain carbonyls such as those introduced by copolymerization with a vinyl ketone give high quantum yields of both type I and type II processes in the solid phase. These two processes are im-portant in imparting accelerated photodegradability of Ecolyte® photodegradable polyethylene. An additional advantage of these types of carbonyl groups is that they can be used in masterbatch form in order to induce photodecomposition, via a photooxidation mechanism, of pure polyethylene which does not contain carbonyl groups. This is the basis of the commercial Ecolyte process and provides a substantial flexibility in controlling degradation rates (Ref. 8).

When such copolymers are photolyzed in the absence of oxygen, it is observed that the ketone carbonyl is lost from the polymer relatively rapidly. However, in the presence of oxygen, new ketone carbonyl groups build up which absorb at different wavelengths in the infrared and are of presumably different structure and have lower sensitivity to ultraviolet light. This is shown in Fig. 5. The relative quantum yields for the different photochemical processes in solid films of ethylene copolymers are shown in Table 1, and it is clear that radical generating processes such as the Norrish type I are substantially higher in quantum efficiency in all vinyl ketone copolymers than type II photolysis and nearly ten-fold greater than for the backbone carbonyls of the ethylene carbon monoxide system. In these films, polyethylene is well above its glass transition temperature and hence relatively large-scale motions of the polymer chains are available. However, in the case of styrene-vinyl ketone
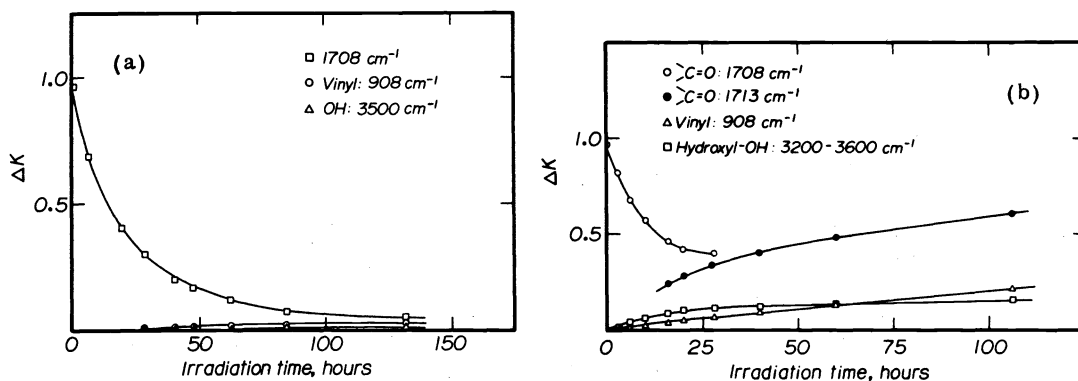
Fig. 5. Loss of carbonyl and increase of vinyl and hydroxyl groups for poly-(ethylene-co-2% methyl isopropenyl ketone) in solid film irradiated (a) in vacuo and (b) in air.

TABLE 1. UV irradiation of polyethylene copolymer films at different temperatures[a]

Temp., °C	1% CO		2% Methyl vinyl ketone			2% Methyl isopropenyl ketone		
	Φ_{-CO}	Φ_{II}	Φ_{1708}[b]	Φ_{1719}[b]	Φ_{II}	Φ_{-CO}	Φ_{908}[c]	Φ_{885}[c]
23	0.073	0.074	0.22	0.19	0.044	0.25	0.012	0.036
35	0.065	0.099	0.23	0.19	0.034	0.23	0.009	0.030
54.4	0.074	0.065	0.15	0.13	0.016	0.15	0.004	0.015
69.5	0.054	0.057	0.12	0.11	0.014	0.11	~0.001	~0.003

[a] Irradiation at 285 nm in N_2, film thickness ~0.01 mm. $I_0^i = 2.23 \times 10^{15}$ quanta $sec^{-1} cm^{-2}$.

[b] Φ_{1708} and Φ_{1718} represent the disappearance of carbonyl absorption at 1708 and 1718 cm^{-1}, respectively.

[c] Φ_{908} and Φ_{885} represent the development of vinyl and vinylidene absorption, respectively.

copolymers, it recently was shown (Ref. 9) that the effect is even more pronounced, since the radical forming processes do not seem to be greatly affected by the presence of a glassy polystyrene matrix, whereas the type II process is substantially reduced under these conditions. This is shown in Table 2. This is a very interesting example of the photoselectivity of a matrix in controlling the ratio of different types of photochemical reactions based on the amount of molecular mobility or free volume required for the reaction to occur.

STUDY OF MODEL COMPOUNDS

The difficulty in interpreting results from ethylene-vinyl ketone copolymers due to the multiplicity of ketone structures introduced by the backbiting mechanism in high pressure polymerization, prompted us to look again at the studies of model compounds which would have structures similar to those introduced by copolymerization of the vinyl ketone. Accordingly, a series of model compounds (Ref. 10) of the general structure shown in Table 3 was synthesized. The photochemical reactions of ketones of this general structure are summarized in the Scheme II. The quantum yields for the fundamental reactions of the various ketones are summarized in Table 4. In this case, the quantum yields can

TABLE 2. Various quantum yields upon irradiation of poly(styrene-_co_-vinyl aliphatic ketone)s at 313 nm at 23 °C in N_2

Comon-omer	Mol-%[a]	Φ_{-CO} film	Φ_{OH} [b] film	Φ_S [c] film	Φ_S' [c,d] solution
MVK	2.9	0.093	0.018	0.030	0.20
MIPK	6.1	0.26	~0.01	0.082	0.22
tBVK	6.7	0.45(0.45)[e]	0.015	0.088	--

[a] Determined by UV spectrophotometry with either the homopolymer or small molecule model compounds as standards.

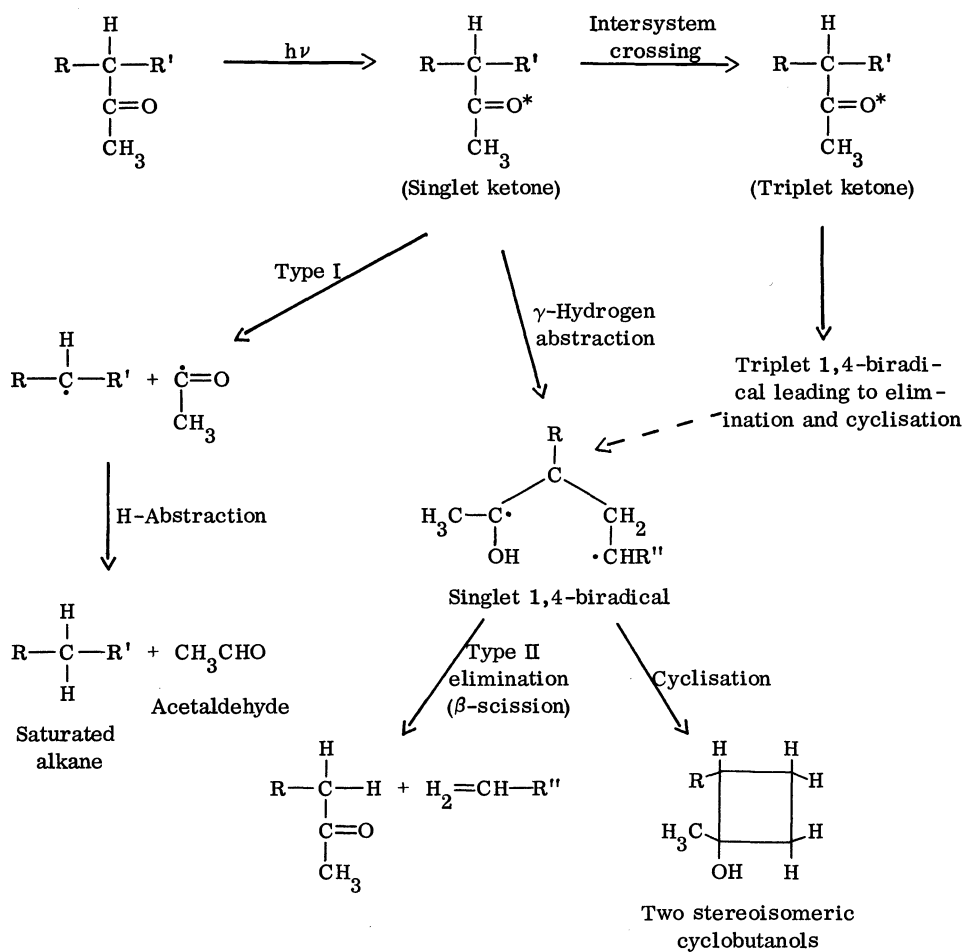[b] From IR measurements.   [c] From viscometry.

[d] In benzene solution.   [e] At 55 °C.

TABLE 3. Characterization of the α-alkyl substituted 2-alkanones

Ketone $H-\underset{\underset{R=0}{\overset{\overset{C_{18}H_{37}}{\mid}}{\underset{\mid}{R}}}{C}-COCH_3$	Melting point, °C	λ_{max},[a] nm	ϵ_{max},[a] ℓ mol^{-1} cm^{-1}
H	61.3	279	21.9
CH_3	34.5	287	23.6
C_2H_5	32.0	287	28.1
n-C_3H_7	34.5	286	32.8
n-$C_{18}H_{37}$	52.5	284	43.6

[a] UV spectra taken in heptane.

Scheme II. Photochemical processes in substituted alkanones.

TABLE 4. Quantum yields for the irradiation of the series of α-alkyl-substituted 2-alkanones in heptane at 23 °C under deoxygenated conditions[a]

$\begin{array}{c}\underline{n}\text{-}C_{18}H_{37} \\ \mid \\ H\text{-}C\text{-}COCH_3 \\ \mid \\ R\end{array}$	Φ_I	Φ_{II}'	Φ_{II}''	$\Phi_{II} = \Phi_{II}' + \Phi_{II}''$	Φ_{OH}[b]	$\dfrac{\Phi_{OH}}{\Phi_{II}}$	Φ_{-CO}[b]	$\Phi_{-CO}' = \dfrac{\Phi_{-CO}}{\Phi_{-CO} + \Phi_{II}''}$	Φ_{total}
H	0.0021	0.121	--	0.121	0.040	0.33	--	--	0.16
	0.0026	0.127	--	0.127	0.043	0.34	0.18	0.18	0.17
CH_3	0.028	0.066	--	0.066	0.034	0.53	0.15	0.15	0.13
C_2H_5	0.046	0.051	0.0063	0.057	0.038	0.66	0.15	0.16	0.14
	0.044	0.061	0.0074	0.0069	0.045	0.65	0.20	--	0.16
$\underline{n}\text{-}C_3H_7$	0.029	0.031	0.031	0.062	0.039	0.062	0.13	0.16	0.13
	0.030	0.031	0.032	0.063	0.040	0.63	0.12	0.14	0.13
$\underline{n}\text{-}C_{18}H_{37}$	0.056[c]	$\dfrac{0.049}{2}$	$\dfrac{0.049}{2}$	0.049	0.031	0.62	0.087	0.14[d]	0.14[d]

[a]Conversion about 10%. [b]From IR analysis.

[c]Φ_I from $(\Phi_{-CO} - \Phi_{OH})$, a limiting Φ_I value. [d]From $\Phi_{-CO} + \Phi_{II}''$.

all be determined quantitatively by gas chromatography and it was apparent that not only were the quantum yields comparable to those observed in ketone copolymers but that there was no "end effect" which has been postulated by other authors. That is to say that the reactivity of a ketone in a side chain attached to a polymer can be expected to be essentially identical with that of a ketone group on the end of a polymer chain.

Furthermore, when these polymers were dissolved in polyethylene and ethylene-propylene copolymer matrices, it was shown that the quantum yields were actually greater than in liquid solution. The higher quantum yields are presumably due to the internal scattering which increases the amount of light absorbed from that which would be calculated from the concentration of the ketone alone, but the lack of a viscosity effect is clear evidence that polymer matrices provide adequate mobility above their glass transition temperatures for all of the photochemical reactions undertaken by these types of ketones.

In order to confirm some of these ideas with actual oxidized polyolefins, a series of experiments (Ref. 11) was made on ethylene-propylene rubber which can be considered to be a useful model for the amorphous phase in most polyolefins. In this case, the rubber was thermally oxidized under controlled conditions at 125 °C for various times and the carbonyl content and hydroperoxide concentration determined. Additional samples were prepared in which the hydroperoxy groups were d composed thermally leaving only the ketones and other oxidation products in the polymer and then photolytic studies were made in the solid film and solution. The results confirm that the polymers without hydroperoxy groups were much slower to decompose than those with both hydroperoxy and ketone carbonyl groups. This suggests that the ketones present are probably not in the middle of the chain but closer to the ends as one might expect from the photooxidation mechanism. The results are tabulated in Table 5. However, even at the lowest amount of oxidation where the photooxidation appears to be most efficient, it can be calculated that only 13% of the light is abosorbed by the hydroperoxide, 87% by the ketone carbonyl groups.

The question arises as to the nature of the actual bond breaking step in a saturated hydrocarbon polymer. We suggest, based on evidence produced from other experiments, that the major bond-breaking process is the β-scission of alkoxy radicals produced by either the direct thermolysis or photolysis of hydroperoxide groups on the polymer chain, as shown below. Only the first step in the chain decomposition of hydroperoxy groups leads to an alkoxy radical and therefore the quantum yield for

TABLE 5. Photolysis of oxidized PEPP samples in toluene at
          313 nm in nitrogen

OOH conc. x 10^5 mol ℓ^{-1}	Ketone conc. x 10^5 mol ℓ^{-1}	Initial scission rate x 10^{10} mol min^{-1}		Φ_S
1.1	0.19	1.7		1.3
2.3	0.83	3.9		0.74
2.7	1.8	1.4		0.12
3.5	2.9	2.5		0.17
4.4	4.7	5.3		0.23
0	0.52	0.10		0.034
0	2.4	0.56		0.039
0	4.9	0.82	Av. = 0.036	0.028
0	9.7	2.4		0.044
0	17.8	3.0		0.035

chain breaking will always be significantly lower than the quantum yield for decomposition of hydroperoxide. Furthermore, this process must also compete with facile inter- and intramolecular hydrogen abstraction.
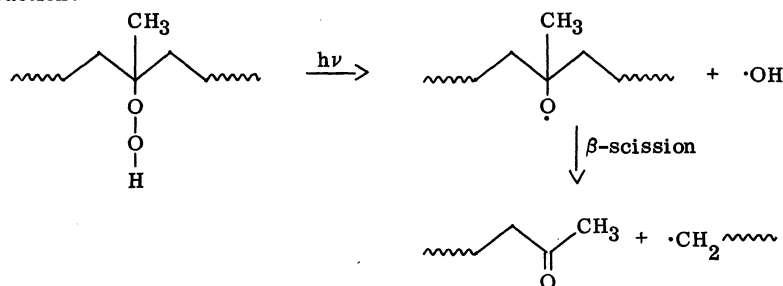
In the course of these studies, an additional chain breaking mechanism was identified. It was found that after photolysis of the hydroperoxide–containing polymer there was a significant dark reaction involving bond breaking as measured by viscometry. This process is second order with respect to the amount of hydroperoxide and the length of the preirradiation, but is independent of the presence or absence of oxygen. We ascribe this to the reaction of two polymeric peroxy radicals:
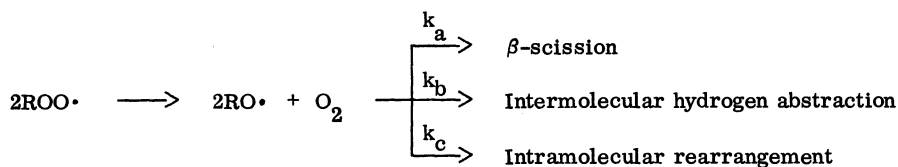
The active alkoxy radicals formed by this bimolecular process can then undergo scission by the β-scission process or they may competitively deactivate by internal or external hydrogen abstraction The relative rates of these competitive processes will also determine the efficiency of the bond breaking step.

From these studies, we con luce that the photooxidative degradation of polyolefins generally can be described in terms of a conventional photooxidative chain mechanism involving hydroperoxides as the reactive intermediates and ketone carbonyl groups as sensitizers. These carbonyls are formed in the decomposition of the hydroperoxide and accumulate in the polymer matrix as a result of the oxidation process. After the earliest stages of the initiation step, which may be due primarily to photolysis of

hydroperoxide groups, the photooxidative chain is maintained by light absorbed by ketone structures induced in the polymer by the preceding photooxidation process. Depending on the structure of the polyolefin, a substantial part of the photooxidation is maintained by an initiation mechanism involving the absorption of photons via a ketone carbonyl group and (a) subsequent energy transfer to hydroperoxide groups in the vicinity causing these to photodegrade and give alkoxy radicals in the primary step, or (b) photolysis to give primary radicals capable of initiating the photooxidative chain. The major chain breaking process leading to destruction of the physical properties is the β-scission of the alkoxy radicals. These are produced either by direct photolysis of hydroperoxide, by energy transfer from ketones to hydroperoxide groups, or by a dark reaction involving the bimolecular process of collision of two peroxy radicals. The relative inefficiency of the alkoxy radical in producing chain breaks in the polymer is due to the competitive reactions of inter- and intramolecular hydrogen abstraction which gives rise to the formation of OH groups. It seems likely that the quantification of the rate constants for these fundamental reactions will lead both to a better understanding of the photooxidation of polyolefins and a greater ability to predict both the lifetime and performance of the polymeric materials in outdoor environments.

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