Primary Hydroperoxidation in Low-Density Polyethylene

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ABSTRACT: Low-temperature thermooxidation (85 or 95 °C) and photooxidation at λ >300 nm of eight different low-density polyethylene and high-density polyethylene samples have been examined. Throughout thermooxidation two oxidative pathways are observed. Hydroperoxidation in the α position with respect to the vinylidene groups gives rise to isolated (non-hydrogen-bonded) hydroperoxide groups that absorb at 3550 cm^{-1} and are stable at 85 °C. Carbon atoms α to the vinylidene group are quantitatively oxidized prior to saturation of the double bonds. A parallel hydroperoxidation occurs on the saturated chain, affording hydrogen-bonded hydroperoxides which are fairly unstable at 85 °C. In thermooxidation, carbon atoms α to vinyl groups do not give rise to isolated hydroperoxide groups. In photooxidations at long wavelengths, both hydroperoxides are produced and readily photolyzed. The vinylidene pathway is still an important route of photooxidation.

The role of hydroperoxides in the photooxidation of polymers is of major importance for an understanding of the mechanism of oxidation as well as for developing a better insight into the functions of photostabilizer systems. However, little information is available on the exact structure of the hydroperoxides and their photoinductive properties, except in polypropylene where the structure, association, and photoinductive properties of tertiary hydroperoxides have been clearly demonstrated.[1-7]

In polyethylene, a poor understanding of the structure and behavior of hydroperoxides is generally pointed out, and here, only the general lines of the overall oxidation mechanism are known. The stationary concentrations of hydroperoxides are much lower in polyethylene than in polypropylene, and difficulties obviously exist for the determination of the primary hydroperoxidation sites in low-density polyethylene (LDPE) as well as in high-density polyethylene (HDPE).

In a NMR study, Cheng et al.[8] reported on the structure of hydroperoxides formed in the thermooxidation at 140 °C of two LDPE with 17 and 22 branching points per 2000 secondary hydrogen atoms. These authors observed essentially secondary hydroperoxides and rationalized their results by estimating the ratio of the rate constants for abstraction of tertiary and secondary hydrogen atoms as being 9.8 ± 1.0, respectively. Tertiary hydroperoxidation was considered to be a minor route.

In 1975, Scott et al. compared the rate of formation of hydroperoxides (analyzed by chemical titration) to the change in concentration of vinylidene, vinyl, and carbonyl groups in samples of LDPE exposed to UV after various times of mild processing,[9] and the following two main conclusions were made. First, during processing at 165 °C, hydroperoxidation occurs in the α position to the vinylidene group, and second, the hydroperoxides formed in the processing operation are able to photoinduce the oxidation of LDPE.

In a recent paper,[10] we have shown that the hydroperoxides formed during thermooxidation of LDPE at 90 °C have no photoinductive effect. This is in contrast to the inductive behavior of the tertiary hydroperoxides formed in polypropylene oxidation.

In the present work, we are reporting complementary data on the behavior of hydroperoxides produced in the thermooxidation and photooxidation of LDPE.

Table I
Characteristics of LDPE

film no.	density	CH_3 branching ratio[a]	vinylidene concn, M	vinyl concn, M
1	0.921	23	1.7×10^{-2}	7.2×10^{-3}
2	0.922	21	1.7×10^{-2}	5.0×10^{-3}
3	0.923		1.6×10^{-2}	2.1×10^{-2}
4	0.918	30	1.9×10^{-2}	1.7×10^{-2}
5	0.916	42.5	3.3×10^{-2}	1.6×10^{-2}
6	0.912		3.4×10^{-2}	8.6×10^{-3}

[a] CH_3 branching ratio per 1000 carbons.

Experimental Section

Samples. Six low-density polyethylene samples have been used in the form of films (thickness, 150 μm): film number 1 from ATO Chimie, France; film number 2 from CdF Chimie, France; film number 3 from CdF Chimie, France; film number 4 from BASF, Germany; film number 5 from BASF, Germany; film number 6 from ICI, England.

The initial content of vinylidene, vinyl, and vinylene groups has been determined by IR spectroscopy, on the basis of average molar extinction coefficients of model compounds such as hexenes, heptenes, octenes, etc.: ϵ(888 cm^{-1}, vinylidene) = 158 ± 7 M^{-1} cm^{-1}; ϵ(909 cm^{-1}, vinyl) = 122 ± 7 M^{-1} cm^{-1}; ϵ(965 cm^{-1}, vinylene) = 100 ± 10 M^{-1} cm^{-1}. The values calculated for vinylidene and vinyl are reported in Table I. The content of vinylene in each film (—CH=CH—) is low (less than (1-2) × 10^{-3} M). The CH_3 branching ratio shown in Table I is the conventional "methyl index" measured from the IR absorbance at 1378 cm^{-1} (ASTM D 2238-64 T).

The polymer used for film 3 is a LDPE copolymerized with some propylene as a transfer agent. The usual methyl index cannot be measured since the branch points correspond essentially to pendent methyl groups and not to C_4 branches as assumed in ASTM D 2238-64 T.

For comparison, the thermooxidation at 95 °C of two high-density polyethylenes has been studied: film number 7 from CdF Chimie, France (d = 0.948; vinylidene, 6.5 × 10^{-3} M, vinyl, 6.3 × 10^{-2} M); film number 8 from Phillips Petroleum (d = 0.964; vinylidene, 1.2 × 10^{-3} M, vinyl, 7.6 × 10^{-2} M).

Irradiation Conditions. Samples were irradiated in a polychromatic apparatus, Sepap 40.07, obtained from our Service d'Etude du Photovieillissement Accéléré des Polyméres de l'Université de Clermont II. This equipment is briefly described below.

A 500-W "high-pressure" mercury lamp (Osram HBO 500 W) associated with a Schott-Jena filter supplied radiation of wavelengths longer than 300 nm. Seven samples were placed on a

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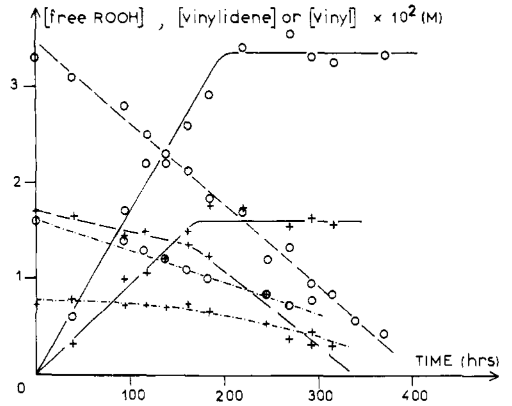


Figure 1. Variations in free hydroperoxide concentration (—), vinylidene concentration (- - -), and vinyl concentration (-·-) during thermooxidation at 85 °C: (+) sample 1; (O) sample 5.

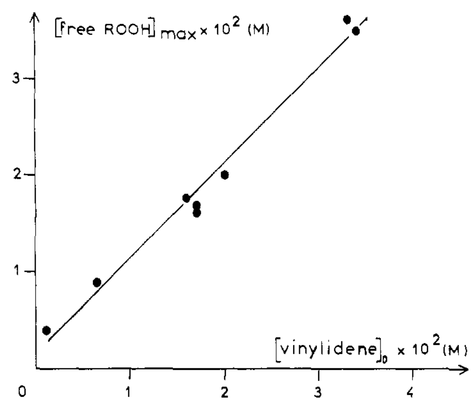


Figure 2. Variations in the maximal concentration of the free hydroperoxides vs. the initial concentration of vinylidenes.

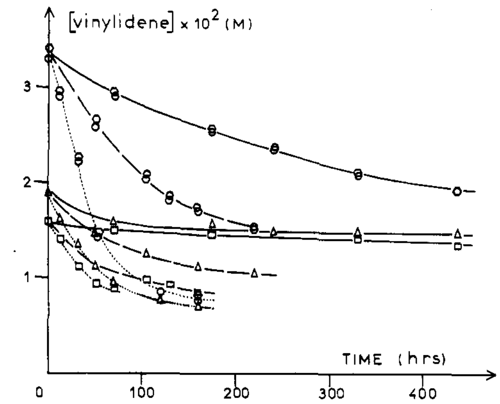


Figure 3. Variations in the vinylidene concentration vs. irradiation time (λ >300 nm) at 40 (—), 60 (- - -), and 80 °C (···): (□) sample 3, (△) sample 4, (O) sample 5, (O) sample 6.

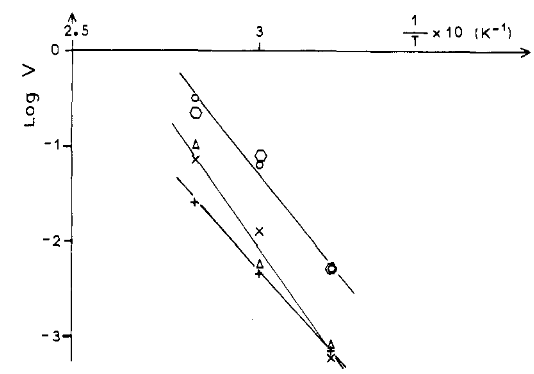


Figure 4. Determination of the activation energy of the vinylidene decomposition process: (+) sample 1, (×) sample 2, (△) sample 4, (O) sample 5, (O) sample 6.

support in a thermoregulated chamber. The support moved in a uniform movement perpendicular to the beam. The surface temperature of samples was controlled by a thermocouple at 40, 60, and 80 °C.

Analytical Technique. An IR spectrophotometer, Perkin-Elmer Model 682, equipped with an accurate expansion was used for measuring the concentration of unsaturation and of photooxidation products. An FTIR spectrometer, Bruker Model 113 V, was used for analysis of the thermooxidation products. Chemical titration of hydroperoxides was made, on the basis of oxidation of Fe(II) and complexation of Fe(III).[11]

Experimental Results

(1) Variations in Unsaturation and Hydroperoxide in LDPE Thermooxidation. The 3550-cm^{-1} (isolated hydroperoxides), 909-cm^{-1} (vinyl), and 888-cm^{-1} (vinylidene) absorption bands were measured at room temperature for the LDPE films formed by thermooxidation at 85 °C. Typical curves are represented in Figure 1 for films 1 and 5 as examples of LDPE containing low and high vinylidene concentrations.

The results in Figure 1 show two interesting features. First, the concentrations of vinyl- and vinylidene-type unsaturations decrease during the early stages of thermooxidation; second, the isolated hydroperoxide concentration, measured at 3550 cm^{-1} (ϵ = 80 M^{-1} cm^{-1}, determined on *tert*-butyl hydroperoxide), increases simultaneously and reaches a limiting value well before the unsaturation has completely disappeared. Therefore, hydroperoxide formation precedes the vinylidene disappearance.

In Figure 2, the maximum concentration of isolated hydroperoxides [ROOH]$_{max}$ has been plotted as a function of the initial content of vinylidene [$\rangle C{=}CH_2]_0$ in the various LDPE films and for the two HDPE 7 and 8 films. From these results it is seen that [ROOH]$_{max}$ is proportional to [$\rangle C{=}CH_2]_0$ and in fact the slope of the experimental straight line is close to 1. In each type of polyethylene [ROOH]$_{max}$ is virtually equal to [$\rangle C{=}CH_2]_0$.

We must stress that there is no direct relation between [ROOH]$_{max}$ and the initial content of vinyl [$-CH{=}CH_2]_0$. The isolated hydroperoxides absorbing at 3550 cm^{-1} appeared only in polyethylene containing vinylidene double bonds. Vinylene type unsaturation (965 cm^{-1}) was found to be invariant during thermooxidation.

(2) Variations in Unsaturation in LDPE Photothermal Oxidation. The three unsaturated groups of LDPE, namely vinylidene, vinyl, and vinylene, behave differently throughout the course of a photothermal oxidation.

As shown in Figure 3, the vinylidene groups observed at 888 cm^{-1} in the IR spectra of the LDPE samples decrease very quickly in the early stages of the photooxidation. Later, their concentration decreases only slowly. The initial rate of disappearance is obviously a function of the initial vinylidene content. An approximative first-order law is observed at initial time. The initial rate of disappearance of the vinylidene groups is also temperature dependent (see Figure 3). The activation energy was calculated to be 10–11 kcal mol^{-1} (Figure 4). A similar value was reported by Verdu et al.[12]

In Figure 5a, the variations of the carbonyl absorbance at 1713 cm^{-1} are plotted as a function of the variation in absorbance at 888 cm^{-1} for LDPE with a high initial content of vinylidene (samples 5 and 6). In the early stages of the oxidation, the concentration of carbonyl compounds (essentially ketonic groups ($\epsilon_{1715} \simeq$ 250 M^{-1} cm^{-1})) exceeded the concentration of the destroyed vinylidene groups ($\epsilon_{888} \simeq$ 160 M^{-1} cm^{-1}). This result is also valid for LDPE with a low initial content of vinylidene (cf. Figure

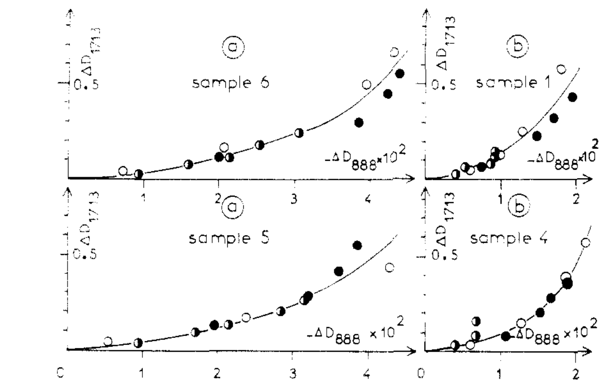


Figure 5. Variations in the absorbance at 1713 cm^{-1} vs. absorbance at 888 cm^{-1} (vinylidene) during the photothermal oxidation of LDPE at 80 (○), 60 (●), and 40 °C (◑).

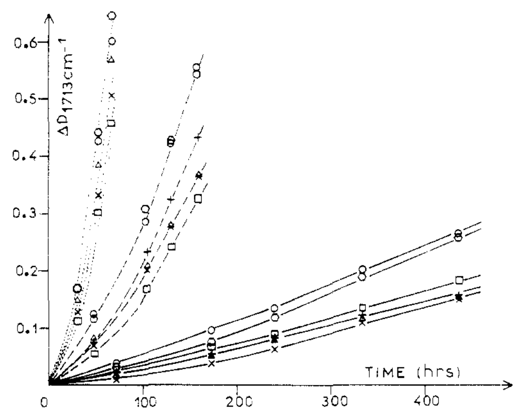


Figure 6. Variations in the absorbance at 1713 cm^{-1} vs. time of irradiation at 40 (—), 60 (- - -), and 80 °C (---): (+) sample 1, (×) sample 2, (□) sample 3, (△) sample 4, (○) sample 5, (○) sample 6.

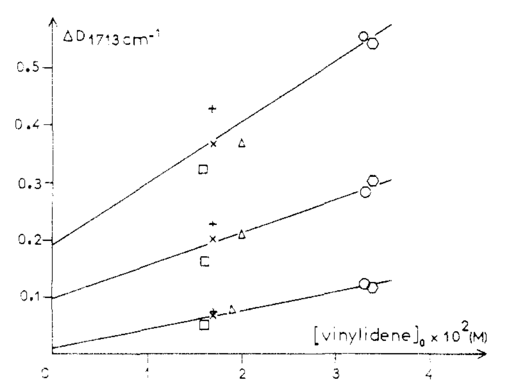


Figure 7. Absorbance at 1713 cm^{-1} vs. initial vinylidene content at different times of irradiation at 60 °C: (+) sample 1, (×) sample 2, (□) sample 3, (△) sample 4, (○) sample 5, (○) sample 6.

5b). Vinylidene groups are not therefore the only precursors of carbonyl compounds, since no chain reaction had been found in LDPE.

The rate of appearance of carbonyl compounds at 1713 cm^{-1} (ketonic, then acid groups) depends on the initial vinylidene content as shown by the data in Figure 6. The absorbance of carbonyl compounds at 1713 cm^{-1} may be plotted as a function of the initial content of vinylidene after various irradiation times, at 60 °C (cf. Figure 7). It is seen that there is a linear relationship, and the ordinate intercept increases with an increase in irradiation time. This suggests that an oxidation which does not involve vinylidene groups is proceeding simultaneously with the vinylidene-induced oxidation.

The concentration of vinyl groups observed at 909 cm^{-1} (or at 1645 cm^{-1}) in the IR spectra of the photooxidized

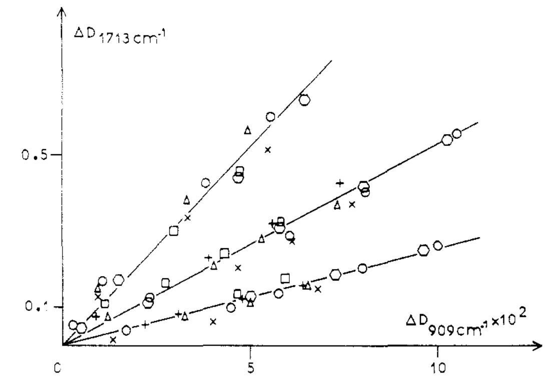


Figure 8. Variations in the absorbance at 1713 cm^{-1} vs. absorbance at 909 cm^{-1} (vinyl) during the photothermal oxidation of LDPE at different temperatures (40, 60, and 80 °C): (+) sample 1, (×) sample 2, (□) sample 3, (△) sample 4, (○) sample 5, (○) sample 6.

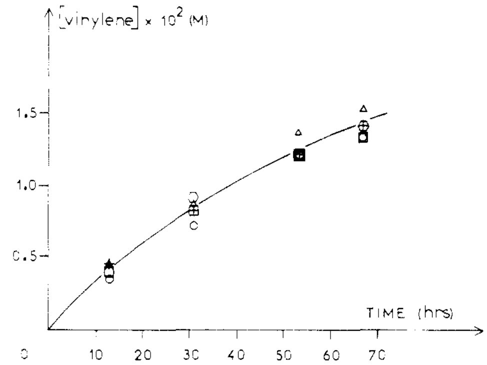


Figure 9. Variations in the vinylene concentration vs. irradiation time (λ >300 nm) at 80 °C: (+) sample 1, (□) sample 3, (△) sample 4, (○) sample 5, (○) sample 6.

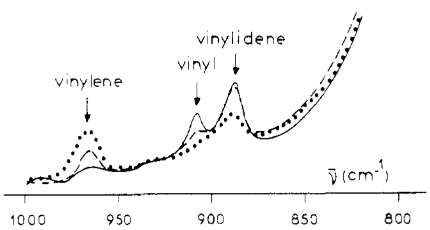
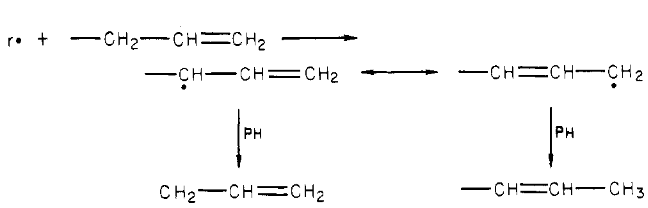


Figure 10. IR spectra of sample 4 in the unsaturation region for different peroxide cross-linking times at 180 °C: (—) t = 0, (---) t = 1 min, (···) t = 4 min.

sample increases even at low levels of oxidation. The decrease in vinylidene groups precedes the development of vinyl groups. The absorbance at 1713 cm^{-1} varies linearly with the absorbance at 909 cm^{-1} (as shown in Figure 8). Both absorptions developed simultaneously but independently of the initial vinylidene content. It was also found that at higher temperatures the absorbance at 1713 cm^{-1} increases at a faster rate than the variation in absorbance of the vinyl groups.

The concentration of vinylene groups also increases during the photothermal oxidation of LDPE, and the variation of absorbance at 965 cm^{-1} was nearly independent of the LDPE sample (Figure 9). This increase in vinylene concentration can be related to a similar observation in the peroxide cross-linking of LDPE. The thermal decomposition at 180 °C of 5% (by weight) of di-*tert*-butyl peroxide in LDPE (sample 4) induced a decrease in concentration of vinylidene and vinyl groups and the formation of vinylene groups (see Figure 10). The concentration of vinylene groups which formed (calculated with $\epsilon_{965} \simeq$ 100 M^{-1} cm^{-1}) was approximately equal to the concentration of the vinyl groups that were destroyed (assuming ϵ_{909}

$\simeq$ 120 M^{-1} cm^{-1}). The radical-induced conversion of vinyl into vinylene involves mesomerism in allylic radicals.



This common concept in radical chemistry has been used to rationalize, for example, the oxidation mechanism of alkenes.[13]

Discussion

LDPE is a typical example of a "nonabsorbing" polymer; i.e., absorption of the light is attributed to unidentified chromophores which can vary between samples. The absorbing impurities like hydroperoxides or ketones formed during processing cannot be completely controlled. The discussion of the photooxidation mechanism therefore must be based on the relative formation of the products rather than on the absolute rate of appearance of each photoproduct.

Usually a typical LDPE sample has about 20–40 tertiary hydrogen atoms (branch points) and about 0.5–1 unsaturated groups like vinylidene, vinyl, and vinylene sites per 1000 carbon atoms in the chain.

Any radical formed in LDPE during UV exposure would either abstract a hydrogen atom or add to an unsaturated group. It is expected that abstraction of a secondary hydrogen atom from a saturated chain would prevail over the abstraction of a tertiary carbon. Allara and Edelson reported on the ratio of the rate constants for abstraction of tertiary hydrogen atoms to the rate constant for abstraction of secondary atoms by $RO_2\cdot$ was close to 8 in model hydrocarbon systems.[14] According to Cheng et al.,[8] the reactivity ratio of branch points to linear chains is 9.8 ± 1 in LDPE. Hydroperoxidation on the 20–40 tertiary carbon atoms would represent at most only 10–20% of the total hydroperoxidation.

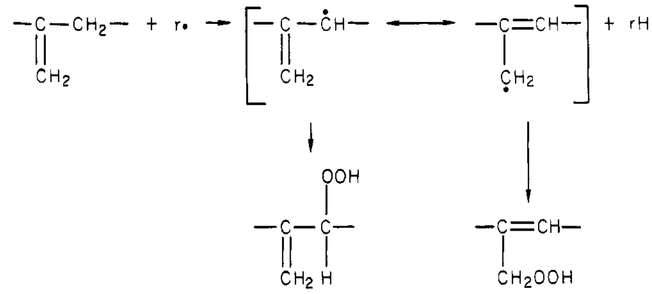
It has been shown in the oxidation of acyclic alkenes of low molecular weight that peroxy radicals can either abstract an allylic hydrogen or add to the double bond.[15] Except when the allylic hydrogen is of tertiary nature as in 3-methyl-1-butene, rate constants of abstraction and addition are of the same order of magnitude. In LDPE, radical reactions with vinylene, vinyl, or vinylidene groups can occur either by an abstraction or by an addition mechanism.

From the data obtained up to now on model compounds and from LDPE, it appears impossible to predict whether the rate of formation of hydroperoxidic groups is greater on the saturated chain or on unsaturated groups.

Considering the 3550-cm^{-1} band previously attributed to an isolated secondary hydroperoxide on the saturated chain,[10] the following deductions may be made on the basis of our observations here. Since no 3550-cm^{-1} band is observed in the thermooxidation at 95 °C of HDPE in which only vinyl groups are present initially, hydroperoxidation on the saturated chain in the α position to the vinyl cannot explain the observation of the 3550-cm^{-1} band. In thermooxidation of LDPE at 85 °C, the maximum intensity of the 3550-cm^{-1} band is not related to the initial content of the branch point. In film 3, containing many tertiary carbon atoms, the maximum intensity of the 3550-cm^{-1} band is about the same as in LDPE with a low branching ratio (samples 1, 2, and 4). The maximum intensity of the 3550-cm^{-1} band is clearly related to the initial vinylidene content. The ratio of the maximum concentration of ROOH formed at 85 °C to the initial concentration of vinylidene is close to unity in any LDPE sample. Vinylidene groups were found to be rapidly destroyed during the formation of hydroperoxides. Hydroperoxidation of the vinylidene sites must therefore precede the disappearance of these groups without modifying the wave number of their IR absorption band (at 888 cm^{-1}), and the disappearance of the vinylidene groups is not induced at 85 °C by the decomposition of hydroperoxides.

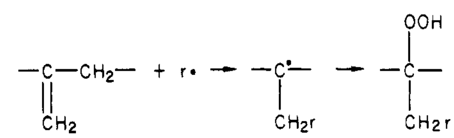
Hydroperoxidation of vinylidene groups does imply an abstraction or an addition mechanism and the structure of hydroperoxides formed would depend on the reaction pathway:

abstraction mechanism



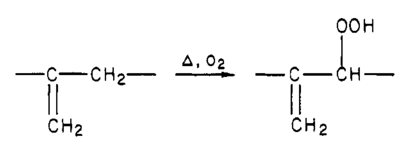
A B

addition mechanism



C

Formation of primary hydroperoxides (type B), which are probably unstable, implies a simultaneous transposition of vinylidene into ethylidene groups. An increase of absorption at 810–830 cm^{-1} for such a group was not observed however. Formation of tertiary hydroperoxides (type C) implies a parallel disappearance of the double bond and hydroperoxidation, which contradicts the observed facts. Formation of secondary hydroperoxides without any transposition of the double bond and without any shift of the IR absorption band at 888 cm^{-1} accounts for the experimental results.

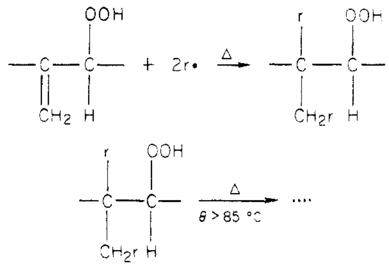


(absorbs at 888 and 3550 cm^{-1})

In oxidation of simple olefins competition between addition and abstraction mechanisms was observed.[15] According to our experimental results, hydroperoxidation of vinylidene sites in the matrix implies only an abstraction mechanism.

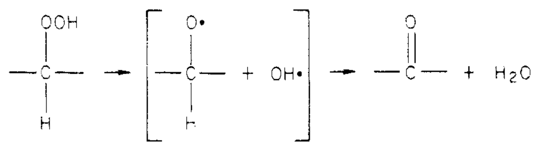
It is worthwhile to note that the isolated form of hydroperoxide appears only as a chemical defect in polyethylene. In polypropylene, no isolated hydroperoxide absorbing at 3550 cm^{-1} has ever been detected in thermooxidation, photooxidation, or photocatalytic oxidation.

It is proposed that saturation of the oxidized vinylidene sites occurs afterward by attack by radicals other than those derived from decomposition of the ROOH in the α position to the double bond.



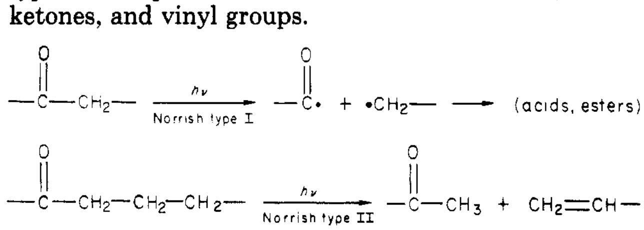
This mechanism differs from the hydroperoxidation process described by Scott during the processing of LDPE at 165 °C.[9] Under such oxidative conditions the sequence of reactions cannot be analyzed and all processes occur simultaneously.

In the early stages of thermooxidation of LDPE at 85 °C, the ketonic and carboxylic groups were readily found at a concentration which was found to be higher than the initial concentration of vinylidene groups. Meanwhile, no significant decomposition of the hydroperoxides formed on the vinylidene sites was observed. The same observation was made for HDPE, in which no significant 3550-cm^{-1} absorption was detected when the concentration of carbonyl compounds exceeded the initial concentration of unsaturated groups. Obviously, hydroperoxidation of the saturated chain proceeds simultaneously, leading only to hydrogen-bonded hydroperoxides (observed at 3400 cm^{-1} in IR spectroscopy). As suggested previously,[10] these hydroperoxides rapidly decompose directly into ketones at 85 °C.



In the photooxidation of LDPE, the stationary concentration of hydroperoxide absorbing at 3550 cm^{-1} is very low unless a photoactive pigment is present.[16] The vinylidene site disappears rapidly due to radical attack. Many sources of radicals could be considered, such as primary radicals, ROOH on a saturated chain, or ROOH α to the vinylidene. The carbonyl compounds appear in concentrations much higher than the initial degree of unsaturation. A double path of hydroperoxidation on the saturated chain and at a site α to the vinylidene groups must therefore be considered again.

The overall photooxidation of polyolefins is generally described as a primary-chain reaction forming hydroperoxides, the thermal or photochemical decomposition of the hydroperoxides into ketones or alcohols, and finally the photochemical conversion of ketones through the usual type I and II processes into acids (and then esters), shorter ketones, and vinyl groups.



On the basis of the results found here, two important deductions on the mechanistic pathway may be made. First, the formation of vinyl groups in the Norrish type II process is rapidly followed by the disappearance of these groups through reactions with radicals. No initial decrease of the vinyl absorption band (909 cm^{-1}) has been observed. The formation of the vinyl groups parallels the formation of the acid groups. According to our experimental data, the appearance of acid groups through a multistep mechanism is more favored by a temperature increase than by the direct photochemical formation of vinyl. Second, the decrease in the vinylidene group concentration is rapid only in the early stages of the photooxidation. It is expected that the vinyl groups formed in the samples compete for radicals with the vinylidene groups, thus inhibiting the decrease in vinylidene group concentration.

Briefly, it is proposed that both thermo- and photooxidation of polyethylenes proceed by two different mechanisms. These are (i) hydroperoxidation in the α position to the vinylidene groups which forms isolated hydroperoxides that absorb at 3550 cm^{-1} and are thermally stable at 85 °C and (ii) hydroperoxidation on the saturated chain affording hydrogen-bonded hydroperoxides which are fairly unstable at 85 °C.

Both hydroperoxides form a secondary cage structure that decomposes directly into ketones and water. It is expected that this hydroperoxide has a poor photoinductive ability as suggested previously.[10]

Registry No. Polyethylene, 9002-88-4.

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