

## THE ROLE OF HYDROPEROXIDES IN PHOTOOXIDATION OF POLYOLEFINS, POLYAMIDES AND POLYURETHANE ELASTOMERS

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**Abstract** A special attention is focussed on the various hydroperoxides which appear as primary products in the photooxidation of polypropylene, polyethylene and polyurethanes. Hydrogen-bonded tertiary hydroperoxides accumulate in atactic and isotactic polypropylene, pigmented or not (up to 100-200 mmol kg<sup>-1</sup>). Through photolysis, these hydroperoxides induce new oxidation chains and they are photocatalytically decomposed by photoactive pigments. In polyethylene, hydroperoxidation in  $\alpha$  position to the vinylidene group affords monomeric hydroperoxides (absorbing at 3550 cm<sup>-1</sup>), thermostable until 85°C and easily photolyzed. Hydroperoxidation on the saturated chain affords hydrogen-bonded hydroperoxides fairly unstable at 85°C under vacuum. The polyethylene hydroperoxides are not able to induce significantly new oxidation processes. In polyamides (PA 11, PA 12, PA 6), hydroperoxidation  $\alpha$  to the nitrogen atom is predominant. Hydroperoxides are revealed only by chemical titration at room temperature. Thermally unstable above 60°C, photounstable at  $\lambda < 300$  nm, they decompose into imides and hydroxylated groups  $\alpha$  to the nitrogen. Four different types of hydroperoxides are observed in four thermoplastic polyurethane elastomers processed from aromatic and aliphatic isocyanate and based on polyester- or polyether-amorphous zones. Hydrogen-bonded hydroperoxides are only observed and accumulated up to 800 mmol kg<sup>-1</sup> specially in poly(ether-urethane) elastomers. Large variations in thermal and photochemical stabilities are observed as a function of the structure of hydroperoxides and of the nature of the matrix.

### INTRODUCTION

Hydroperoxidic groups which appear in the oxidation of polymers are key compounds for an understanding of the primary mechanism of oxidation as well as for developing a better insight in the function of photostabilizer systems. Many studies have been devoted to hydroperoxidation in most materials. However, many basic questions can be still considered.

i) *Are there any specific sites for hydroperoxidation on a polymer chain?* After the initial formation of radicals (mostly unknown), hydrogen abstraction is generally observed in polyolefins, polyamides and polyurethanes (radical addition on double bond presents as defects in saturated polyolefins is not observed as a primary event). This reaction is essentially controlled by the lability of the corresponding bond. As shown later, many specific hydroperoxidation sites have been identified, due to large differences in bond dissociation energies.

ii) *What is the thermal stability of hydroperoxides in the matrix in the time scale of the experiment?* It is generally pointed out that the thermal stability of any oxidation products formed on a polymer chain is dependent on the matrix. Thermal stability cannot be considered as an intrinsic property of the product but as a property of the products in interaction with their close neighbourhood. Large differences in the thermal stability of tertiary hydroperoxides for example are observed.

iii) *What are the photochemical properties of hydroperoxides i.e. absorption and photolysis quantum yield?* Hydroperoxides present a  $\sigma^* \rightarrow \sigma$  transition band, localized on the O-O bond, almost completely forbidden but which extends until very long wavelengths (up to 360 nm for example); the extinction molar coefficients are generally low, sometimes below  $1 \text{ M}^{-1}\text{cm}^{-1}$ . The quantum yield of photolysis is generally very high, but most measurements have been carried out in solutions and not in the solid state (1,2,3).

iv) *What is the reactivity of hydroperoxides with radicals?* The question is specially important in photocatalyzed oxidation. The reactive species formed on a photoactive pigment are able to induce the decomposition of hydroperoxide. In many solution works, the reactivity of hydroperoxide with radicals has been recognized, due to the lability of the O-O-H bond. Such a process accounts for the chain mechanism observed in the photolysis of R-OOH (1).

v) *What is the photoinductive ability of hydroperoxide in the polymer matrix?* The hydroperoxides formed are potential sources for radicals, specially reactive radicals like OH $\cdot$ . However, the radical pairs formed in thermal or photothermal dissociation can react together in the solid state (in "cage reaction") or migrate apart. The ability to initiate new oxidation chain depends on this competition as far as the hydroperoxide can dissociate.

If the first question is specially related to the structure of hydroperoxides, answers to the four other questions are needed to account for the behaviour of these intermediates in the overall mechanism of the oxidation.

Up to now, these basic questions have not been satisfactorily solved although many useful pieces of information have been brought up by many research groups. Such a situation is not really surprising since hydroperoxides appear usually at low stationary concentration (except in polypropylene) and, before the FTIR development, analytical techniques were limited to chemical titrations in solutions and conventional ir spectrophotometry. Chemical titrations present high sensitivity (even after dissolution) but are unspecific. Ir spectrometry was poorly sensitive but more informative on the structure of hydroperoxides and on their interactions (e.g. hydrogen-bonding).

In the past recent years, we have developed in our group the use of photoactive pigments as tools for the understanding of the chemical evolution of "non-absorbing" polymers (cf. 4 for example). The fundamental advantages of TiO<sub>2</sub>, ZnO, CdS pigments are the following:

- they afford an efficient control of the absorption of the light and of the initiation rate when added to a polymer in which the absorbing species are not identified;
- they act as inner screens to protect the photoproducts and prevent their disappearance in further photochemical steps (except when the products are photocatalytically oxidized);
- in the presence of pigment, oxidative phenomena are limited to the surface of sample; oxygen diffusion is never a controlling factor.

The use of pigments is interesting for the study of hydroperoxides since they insure a controlled formation and sometimes a controlled disparition of these intermediates. Moreover; it is often observed that in the presence of pigment, hydroperoxides accumulate until a stationary concentration much higher than in transparent matrix. For several years, we have been therefore currently comparing the formation and disappearance of hydroperoxides in thermal, photothermal and photocatalytic oxidation. Each initiation mechanism has its own advantages and disadvantages and comparison is often fruitful.

In the present paper, we are reporting the main observed properties of hydroperoxides in polyolefins, polyamides and polyurethanes.

#### PRIMARY HYDROPEROXIDATION IN POLYOLEFINS

*Atactic polypropylene* would be the most simple, but academic, system as far as hydroperoxidation is only concerned. In this completely amorphous matrix, hydroperoxides accumulate until very high concentration ( $0.14 \text{ mol kg}^{-1}$  (4,5)) in photothermal oxidation ( $60^\circ\text{C}$ ,  $\lambda > 300 \text{ nm}$ ). Only hydrogen-bonded hydroperoxides were observed in the ir spectra ( $\nu_{\text{max}} \approx 3400 \text{ cm}^{-1}$ ) together with alcoholic groups, and their contribution to the total absorption was kept fairly small. It is important to stress that no monomer form of hydroperoxides absorbing at  $3550 \text{ cm}^{-1}$  could be observed.

In the presence of ZnO (of various types), the initial rate of hydroperoxidation was far higher than in unpigmented samples; this observation was easily explained by the increase in the rate of the light absorption in the pigmented sample. However, as shown in Table 1, the mean photostationary concentration in pigmented samples was only 60% higher than in unpigmented samples.

The rate of disappearance of hydroperoxides was therefore largely increased by the photoactive pigment. The decomposition of ROOH induced by the reactive species formed onto the pigment is leading to higher concentrations of peroxy radicals and favours therefore rupture processes. The scheme I summarized the processes implied in the ZnO photocatalyzed oxidation of isotactic polypropylene.

The photocatalyzed decomposition of hydroperoxide has been directly observed on *tert*-butyl hydroperoxide in solution in *n*-heptane. Suspensions of various photoactive pigments in *n*-heptane containing  $1.6 \times 10^{-2} \text{ M}$  of *tert*-butyl-hydroperoxide have been exposed to

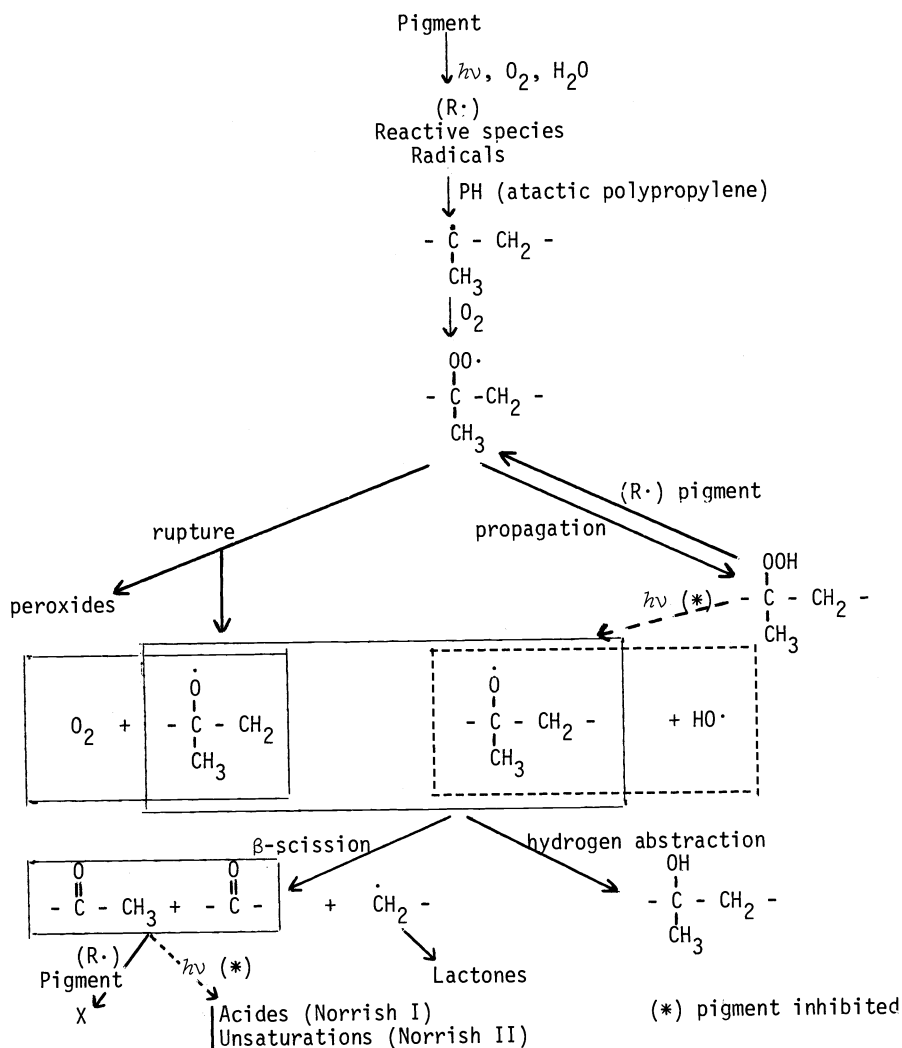
TABLE 1. Variations in hydroperoxide concentration ( $\text{mol kg}^{-1}$ ) with irradiation time  $t_i$  (hours) in photothermal (PT) or ZnO-photocatalyzed (PC, 3% ZnO\* A) oxidation of atactic polypropylene

$t_i$ (h)	50	93	160	202	273	326	350
PT	0.010 $\pm 0.010$	0.010 $\pm 0.010$	0.052 $\pm 0.010$	0.075 $\pm 0.010$	0.096 $\pm 0.010$	0.120 $\pm 0.012$	0.140 $\pm 0.010$
PC	0.037 $\pm 0.010$	0.063 $\pm 0.010$	0.100 $\pm 0.010$	0.147 $\pm 0.014$	-	0.193 $\pm 0.019$	0.220 $\pm 0.022$

a polychromatic light carefully filtered. Wavelengths shorter than 320 nm are completely avoided. Total absorption of the light in the pigment is checked through variations of the concentrations of the pigment (up to 14% by weight). Direct excitation of the low-absorbing hydroperoxide is therefore unimportant. In Fig.1, disappearance of the hydroperoxide and appearance of *tert*-butyl alcohol are represented as functions of the irradiation time using the following pigments:

- $\text{TiO}_2$  in the rutile form, untreated (RL 11 A) or after surface treatment (RL 18 S) (from Produits Chimiques de Thann et Mulhouse, France);
- ZnO\* type A
- ZnO type A reheated at 600°C or at 900°C.

SCHEME 1



\* ZnO A from Société des Mines et Fonderies de Zinc de la Vieille Montagne, Belgique.

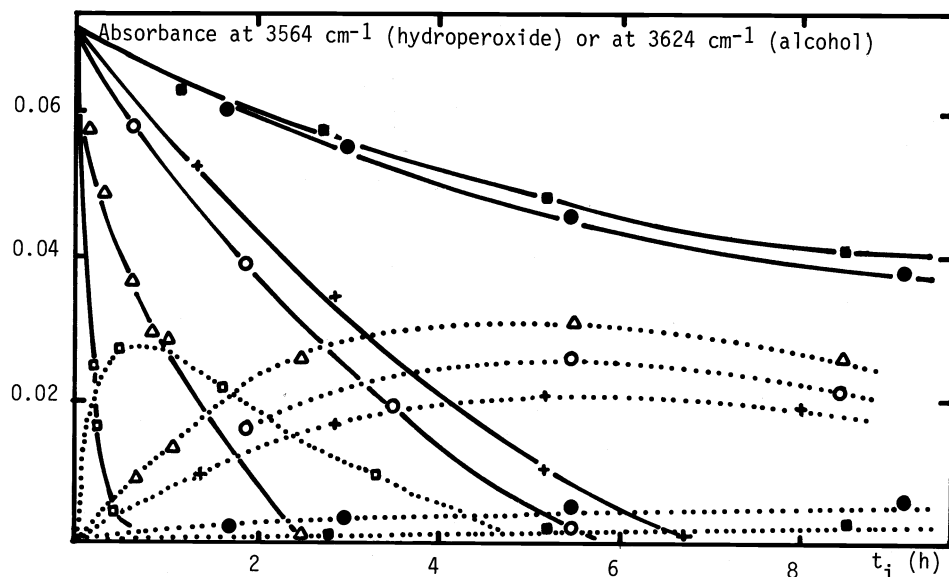


Fig.1.  $\text{TiO}_2$ - and  $\text{ZnO}$ -photocatalyzed decomposition of *tert*-butyl hydroperoxide in *n*-heptane solution ( $1.6 \times 10^{-2}$  M)

—: hydroperoxide disappearance .....: *tert*-butyl alcohol appearance  
 Polychromatic irradiation:  $\lambda > 300$  nm; time  $t_i$  (hours); temperature:  $30^\circ\text{C}$

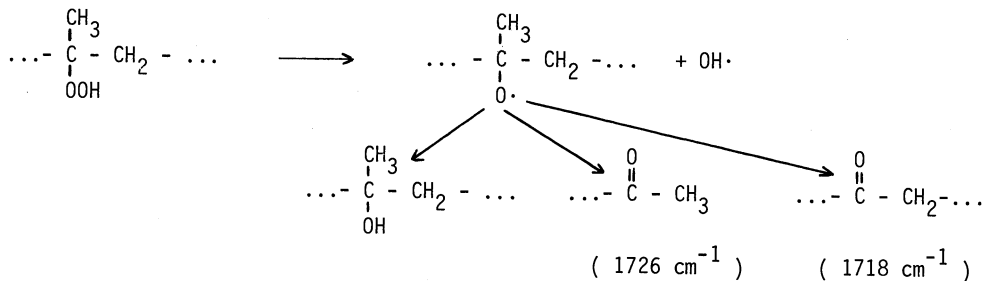
■ control      ●  $\text{TiO}_2$  RL 185 (5%)      □  $\text{TiO}_2$  RL 11 (5%)  
 + ZnO A (5%)      ○ ZnO A reheated at  $650^\circ\text{C}$  (5%)      △ ZnO reheated at  $900^\circ\text{C}$  (5% and 14%)

In this direct evidence of the pigment-induced decomposition of a model hydroperoxide, large variations in the photoreactivity of the pigment are observed. Passivation through a surface treatment on  $\text{TiO}_2$ -rutile is clearly observed. From the influence of reheating of type A-ZnO (i.e. decrease of the specific area and increase of the lattice defects), it is shown that the main parameter controlling the photoreactivity of this medium-area pigment ( $9.4 \text{ m}^2/\text{g}$ ), are the lattice defects.

*Isotactic polypropylene* appears to be more complex as a semi-crystalline matrix. Hydroperoxides accumulate too until high concentrations (for example,  $0.1 \text{ mol l}^{-1}$  in photochemical oxidation at  $\lambda > 300$  nm). Only hydrogen-bonded hydroperoxides are observed (at  $3400 \text{ cm}^{-1}$ ) but again large contribution of alcoholic and acid groups overlaps this absorption even in the early stages of the oxidation. No monomer form has ever been observed in ir-spectra (at  $3550 \text{ cm}^{-1}$ ); as opposite to polyethylene, no local defect plays an important role in the primary hydroperoxidation (see below). Properties of the tertiary hydroperoxides forms are fairly well known since the basic work of Wiles *et al.* (6,12) and of Mayo *et al.* (13,15). These hydroperoxides are generally appearing in close vicinity and sequences of groups have been observed (through reduction and dehydration of the corresponding tertiary alcohols (16)). A consequence of such associations has been recently observed in polypropylene stabilized with HALS. The effectiveness of HALS has been at least partially explained by interactions of HALS with several hydroperoxidic groups (17).

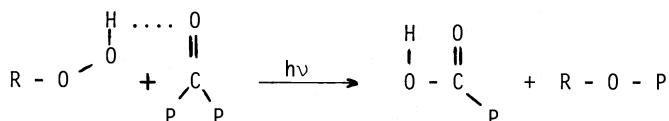
The thermal and photochemical decomposition of hydroperoxides leads, after the homolytic cleavage of the O-O bond, to alcohols, and various ketones (although the  $\beta$ -scission of alkoxy radicals at room temperature has been recently questioned by Geuskens (18).

#### SCHEME 2



Introduction of a photoactive pigment in such a semi-crystalline polymer is not so demonstrative as in atactic polypropylene. The ZnO- or TiO<sub>2</sub>-photocatalyzed oxidation of isotactic polypropylene appears as a superposition of the pigment-catalyzed oxidation of amorphous zones (similar to atactic polypropylene photocatalyzed oxidation) and of the photo-thermal oxidation of unpigmented zones. Hydroperoxides and ketones are not only reacting with the species formed onto the pigment, direct excitation is occurring and final photo-products like acids or esters are formed as opposite to the atactic case.

An amorphous copolymer PP/PE has been very recently examined by Geuskens *et al.* (18). Hydrogen-bonded hydroperoxide were observed at 3400 cm<sup>-1</sup> and chemically titrated. An original photochemical property of the formed hydroperoxides (essentially secondary hydroperoxides) was observed. Excitation of the hydroperoxide chromophore in interaction with ketones was proposed to afford directly an acid group.



According to Geuskens, this explains why vacuum photolysis at 365 nm of a pre-photooxidized sample in presence of benzophenone (which is consumed in the prior irradiation) led to acid formation through the decomposition of hydroperoxide, although no ketone photolysis proceeded (as demonstrated by the absence of Norrish type II process).

The situation is specially controversial in *polyethylene* where only the general lines of the overall oxidation mechanism are sketched. The stationary concentrations of hydroperoxides are far lower in polyethylene than in polypropylene and difficulties obviously exist for the determination of the primary hydroperoxidation sites in LDPE as in HDPE. In 1976, Cheng *et al.* reported a NMR study of the hydroperoxides formed in the thermooxidation at 140°C of two LDPE (17 and 22 branching points per 2000 secondary hydrogen atoms) (19). These authors observed essentially secondary hydroperoxides and rationalized by estimating the ratio of rate constants for abstraction of respectively tertiary and secondary hydrogen atoms being  $9.8 \pm 1.0$ . Tertiary hydroperoxidation can only be a minor route.

In 1975, Scott *et al.* compared the evolution of hydroperoxides (chemically titrated) to the evolution of vinylidene, vinyl and carbonyl groups in samples of LDPE exposed to uv after different times of mild processing (20). Two main conclusions were derived. First, during the process at 165°C, hydroperoxidation occurs in the  $\alpha$  position of the vinylidene. Second, the hydroperoxides formed in the processing operation are able to photoinduce the oxidation of LDPE.

In a recent paper (23), we have shown that the hydroperoxides formed during the thermooxidation at 90°C of LDPE has no photoinductive effects as opposite to the tertiary hydroperoxides formed in polypropylene oxidation.

We have recently studied six low-density polyethylenes as described in Table 2. They have been used in the form of films (thickness 150  $\mu\text{m}$ ). The initial content of vinylidene ( $-\text{CH}=\text{CH}-$ ) is low (less than  $1.2 \times 10^{-3}$  M). CH<sub>2</sub> branching ratio indicated in Table 2 is the conventional "methyl index" measured from the ir absorbance at 1378 cm<sup>-1</sup> (ASTM D 2238-64 T). The polymer used for film 3 is a LDPE obtained with propylene as transfer agent. The usual methyl index cannot be measured since the branch points correspond essentially to pendant methyl groups (and not to C<sub>4</sub> branches as assumed in ASTM D 2238-64 T).

Table 2. Characteristics of LDPE

Film No.	Density	CH <sub>2</sub> branching ratio (per 1000 C)	vinylidene (M)	vinyl (M)
1	0.921	23	$1.7 \times 10^{-2}$	$7.2 \times 10^{-3}$
2	0.922	21	$1.7 \times 10^{-2}$	$5.0 \times 10^{-3}$
3	0.923	-	$1.6 \times 10^{-2}$	$2.1 \times 10^{-2}$
4	0.918	30	$1.0 \times 10^{-2}$	$1.7 \times 10^{-2}$
5	0.916	42.5	$3.3 \times 10^{-2}$	$1.6 \times 10^{-2}$
6	0.912	-	$3.4 \times 10^{-2}$	$8.6 \times 10^{-3}$

As shown in Table 2, a typical LDPE presents per 1000 carbon atoms in the chain, around 20-40 tertiary hydrogen atoms (branch points) and around 0.5-1 unsaturated groups like vinylidene, vinyl and vinylene sites. Any radical formed in LDPE, under uv exposure for example, would either abstract an hydrogen atom or add to an unsaturated group. Considering the hydrogen abstraction on the three different sites (saturated chain, branch point,  $\alpha$  position to an unsaturated group), it is expected that abstraction of a secondary hydrogen

atom from the chain would prevail on the abstraction of a tertiary atom. Allara and Edels reported the ratio of the rate constant of abstraction of tertiary hydrogen atom to the rate constant of abstraction of secondary atom was close to 8 in model hydrocarbon oxidation (21). According to Cheng *et al.* (19), the reactivity ratio of branch points to linear chain is indeed  $9.8 \pm 1$  in LDPE. Hydroperoxidation on the 20-40 tertiary carbon atoms would represent only 10 to 20% at most 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 (22). Except when the allylic hydrogen is of tertiary nature (like in 3-methyl 1-butene), rate constant 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. Summarizing the data obtained up to now on model compounds and in LDPE, it appears impossible to predict if the formation of hydroperoxidic groups on the saturated chain prevails or not the hydroperoxidation of unsaturated groups. Considering the  $3550\text{ cm}^{-1}$  band, the following remarks can be pointed out. No  $3550\text{ cm}^{-1}$  band was observed in the  $95^\circ\text{C}$  thermooxidation of HDPE in which only vinyl groups are present initially ( Film 7:  $d = 0.948$ ; vinylidene =  $6.5 \times 10^{-3}\text{ M}$ ; vinyl =  $7.6 \times 10^{-2}\text{ M}$ . Film 8:  $d = 0.964$ ; vinylidene =  $1.2 \times 10^{-3}\text{ M}$ ; vinyl =  $7.6 \times 10^{-2}\text{ M}$ ). In thermooxidation of LDPE at  $85^\circ\text{C}$ , the maximum intensity of the  $3550\text{ cm}^{-1}$  band was not related to the initial content of the branch point. In film 3 containing many tertiary carbon atoms, the maximum intensity of  $3550\text{ cm}^{-1}$  was about the same as in LDPE with low branching ratio (samples 1,2,4). The maximum intensity of the  $3550\text{ cm}^{-1}$  band was clearly related to the initial content of vinylidene.

On Fig.2, it appeared that the concentration of vinylidene-type unsaturations decreased as soon as thermooxidation began. Simultaneously, the monomer hydroperoxide concentration, measured at  $3550\text{ cm}^{-1}$  ( $\epsilon = 80\text{ M}^{-1}\text{cm}^{-1}$ ) increased and reached a limiting value well before the unsaturation has completely disappeared. Therefore, hydroperoxidation precedes the vinylidene disappearance. However, the wavenumber of the ir absorption of vinylidene groups was not modified by peroxidation.

$10^{-2}\text{ mol l}^{-1}$

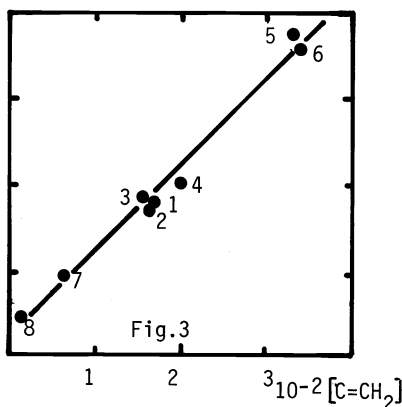
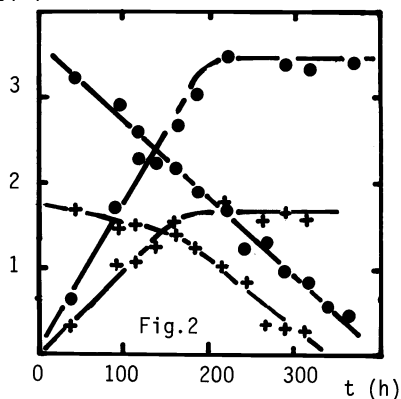


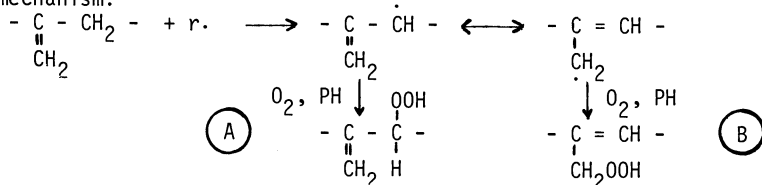
Fig.2. Variations of free hydroperoxides and vinylidene concentrations ( $10^{-2}\text{ mol l}^{-1}$ ) during the thermooxidation of LDPE at  $85^\circ\text{C}$ : ● sample 5, + sample 1

Fig.3. Variations of maximum concentration ( $10^{-2}\text{ mol l}^{-1}$ ) of hydroperoxide monomer as a function of initial concentration ( $10^{-2}\text{ mol l}^{-1}$ ) of vinylidene in the thermooxidation of LDPE and HDPE ( for definition of samples 1-8 see Table 2 and subsequent text)

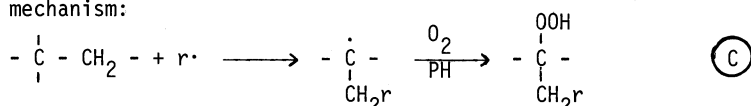
On the other hand, in Fig.3, the maximum concentration of free hydroperoxides  $[\text{ROOH}]_{\text{max}}$  has been plotted as a function of the initial content of vinylidene  $[\text{>C=CH}_2]_0$  in various LDPE and for the two HDPE 7 and 8. It can be pointed out that  $[\text{ROOH}]_{\text{max}}$  is proportional to  $[\text{>C=CH}_2]_0$ . In each type of polyethylene,  $[\text{ROOH}]_{\text{max}}$  is almost equal to  $[\text{>C=CH}_2]_0$ .

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

Abstraction mechanism:



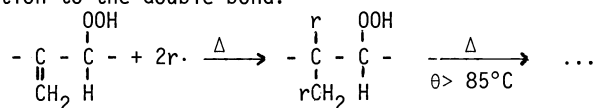
Addition mechanism:



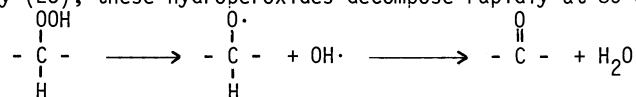
Formation of this hydroperoxide (type B), probably very unstable, implies simultaneously the transposition of vinylidene into ethylene groups. Increase of absorption at 810-830  $\text{cm}^{-1}$  of such a group was not observed. Formation of tertiary hydroperoxide (type C) implies a parallel disappearance 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  $\text{cm}^{-1}$  accounts for the experimental results.



Saturation of the oxidized vinylidene sites is provoked afterwards by radical attack, the radicals being formed in other oxidative steps than the decomposition of the ROOH in  $\alpha$  position to the double bond.



In the early stages of thermooxidation of LDPE at 85°C, the carbonyl compounds (ketonic, then acid) were readily formed at a concentration which was soon higher than the initial concentration of vinylidene groups. Meanwhile, no significant decomposition of the hydroperoxides formed on the vinylidene sites was observed. Same observation can be pointed out in HDPE, in which no significant 3550  $\text{cm}^{-1}$  absorption was detected when the concentration of carbonyl compounds exceeded largely the initial concentration of unsaturations. Obviously, hydroperoxidation of the saturated chain proceeded simultaneously leading only to hydrogen-bonded hydroperoxides (observed at 3400  $\text{cm}^{-1}$  in ir spectrophotometry). As suggested previously (23), these hydroperoxides decompose rapidly at 85°C, directly into ketones.



In photooxidation of LDPE, the stationary concentration of hydroperoxide absorbing at 3550  $\text{cm}^{-1}$  was kept low unless a photoactive pigment is affording a photochemical protection (4). The vinylidene site disappears rapidly on radical attacks. Many sources of radicals could be considered (primary radicals, ROOH on saturated chain or ROOH  $\alpha$  to the vinylidene). The carbonyl compounds appear in concentration much higher than the initial unsaturations. In Fig. 4, the variations of the absorbance at 1713  $\text{cm}^{-1}$  were plotted as a function of the variations of the absorbance at 888  $\text{cm}^{-1}$  for LDPE with high initial content of vinylidene (samples 5 and 6) at different temperatures. In the early stages of the oxidation, the concentration of carbonyl compounds (essentially ketonic groups with  $\epsilon_{1713} \approx 250 \text{ M}^{-1}\text{cm}^{-1}$ ). This remark was valid too for LDPE with low initial content of vinylidene (samples 1 and 4). Vinylidene groups are not, therefore, the only precursors of carbonyl compounds, since no chain reaction has been pointed out in LDPE.

Thermooxidation and photooxidation of LDPE proceed therefore through hydroperoxidation in  $\alpha$  position to the vinylidene group and on the saturated chain, affording respectively monomeric hydroperoxides absorbing at 3550  $\text{cm}^{-1}$  and thermostable at 85°C, and hydrogen-bonded hydroperoxides fairly unstable at 85°C. Both hydroperoxides formed present a secondary structure and, through a cage direct decomposition into ketones and water, it is expected that these hydroperoxides have a poor photoinductive ability as suggested previously (23).

#### PRIMARY HYDROPEROXIDATION IN ALIPHATIC POLYAMIDES

The behaviour of aliphatic polyamides, especially nylon-type polymers, on exposure to uv irradiation has attracted much attention. However, most of the research in this field concerns, either vacuum photolysis of the polymer, or photooxidation at wavelengths shorter than 290 nm. Photooxidation of model compounds like N alkyl amides  $\text{RCH}_2\text{CO NH CH}_2\text{R}'$  have also been considered (24,27). Since 1978, we are currently studying the photooxidation of polyamides in the solid state (films of 40  $\mu\text{m}$  thickness), either at wavelengths longer than 300 nm or at 254 nm. The first polymers studied were polyundecanamides (PA 11). In the polymer matrix it appeared possible to characterize four intermediate products, i.e. hydroperoxides, imides, hydroxyl groups  $\alpha$  to the nitrogen atom and aldehydes and two final groups (amines and acids) (28).

In the scope of the present paper, the following properties of the primary hydroperoxides have to be pointed out.

The hydroperoxide groups are revealed only by chemical titration in a very special

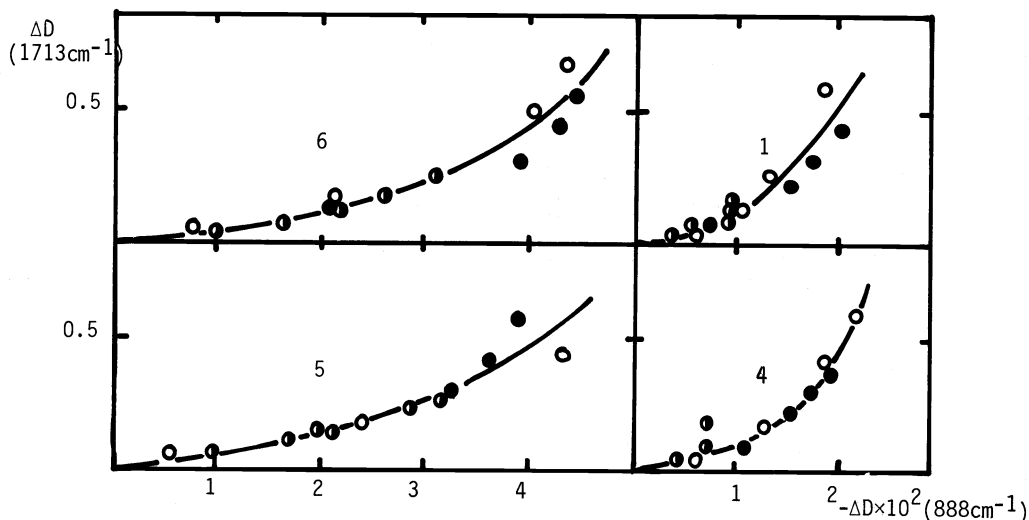


Fig.4 Variations in absorbance  $\Delta D$  at  $1713\text{ cm}^{-1}$  vs variations in absorbance at  $888\text{ cm}^{-1}$  in polychromatic photooxidation (SAIREM SEPAP 12.24;  $\lambda > 300\text{ nm}$ ; sample temperature:  $60^\circ\text{C}$ ) of LDPE films (thickness  $150\text{ }\mu\text{m}$ )

solvent (hexafluoro-2 propanol). The titration is based on the oxidation of  $\text{Fe}^{2+}$  and complexation of  $\text{Fe}^{3+}$  by  $\text{SCN}^-$  anions (20,29). Iodometric methods were unsuitable since they are carried out in a boiling  $\text{CH}_3\text{COOH}$ -2 propanol mixture.

The hydroperoxides formed in the sample exposed to long wavelength photooxidation at  $60^\circ\text{C}$  in a SEPAP 12.24 set-up (this set-up was described in many papers, for example (28,30)) accumulated until a stationary concentration close to  $1.5 \times 10^{-2}\text{ mol kg}^{-1}$ . As opposite, on exposure at short wavelength ( $254\text{ nm}$ ), the stationary concentration of hydroperoxides is far lower, around  $0.3 \times 10^{-2}\text{ mol kg}^{-1}$ . The photolysis of ROOH at  $254\text{ nm}$  was directly observed after a pre-irradiation at long wavelengths, through successive titrations.

Hydroperoxides appeared to be fairly stable in the matrix under  $60^\circ\text{C}$ , in the dark. Lifetime of ROOH was about 30 hours at  $60^\circ\text{C}$ ; at  $110^\circ\text{C}$ , the lifetime was found to be around 5 min. The thermal decomposition of hydroperoxide led to imides (revealed in the ir spectra at  $1735$  and  $1690\text{ cm}^{-1}$ ) and to hydroxylated groups  $\alpha$  to the nitrogen atom (to a lesser extent). The photothermal decomposition of hydroperoxides at  $254\text{ nm}$  led directly to acid groups without any accumulation of intermediates (like imides). The hydroperoxides were readily reduced in the matrix by reducers like phosphites.

In the presence of 3% by weight of photoactive pigment (like  $\text{TiO}_2^*$  RL 65 or  $\text{TiO}_2$  RL 90, rutile forms which have received a surface treatment with alumina and silica or type C-ZnO\*\*), PA 11 samples undergo on uv exposure a photocatalyzed oxidation (31). The hydroperoxide groups formed in the sample photocatalytically oxidized at  $60^\circ\text{C}$  in a SEPAP 12.24 set-up, accumulated until  $2.4 \times 10^{-2}\text{ mol kg}^{-1}$ . Although, this mean concentration was not corrected for light absorption profile (in the presence of 3%  $\text{TiO}_2$  more than 90% of the light (at  $\lambda < 380\text{ nm}$ ) are absorbed in the first  $10\text{ }\mu\text{m}$  of the  $40\text{ }\mu\text{m}$  film), it appeared clearly that the photostationary concentration was higher in the presence of pigment than in its absence. At room temperature ( $25^\circ\text{C}$ ), on the same uv exposure, the photostationary concentration of hydroperoxides was found to be the same ( $2.35 \times 10^{-2}\text{ mol kg}^{-1}$ ). Although, the hydroperoxides were fairly unstable at  $60^\circ\text{C}$ , it appeared that the stationary concentrations of hydroperoxides were essentially controlled by photocatalysis at  $60^\circ\text{C}$ .

In photocatalytic oxidation, the primary formation of reactive species is wavelength independent, as long as the energy of the radiation is higher than the width of the forbidden band of the photoactive pigment (3.5 eV in  $\text{TiO}_2$ , 3.2 eV in ZnO). Excitation in the range  $300\text{--}400\text{ nm}$  or at  $254\text{ nm}$  must therefore induce the same phenomena. Titration of hydroperoxide has been carried out in a sample containing 3%  $\text{TiO}_2$  RL 65 and exposed to  $254\text{ nm}$  irradiation. The mean photostationary concentration of hydroperoxides appeared to be somewhat lower at  $254\text{ nm}$  than under long wavelength irradiation ( $1.2 \times 10^{-2}$  vs  $2.5 \times 10^{-2}\text{ mol kg}^{-1}$  respectively). The photostationary concentration of hydroperoxide groups in an unpigmented polyundecanamide sample photooxidized under the same experimental conditions has been shown to be about  $0.2 \times 10^{-2}\text{ mol kg}^{-1}$ . The inner filter effect of the pigment at  $254\text{ nm}$  is therefore clearly observed, the photolysis of ROOH being inhibited by the absorbing pigment. A residual wavelength effect appeared since long wavelength and  $254\text{ nm}$  irradiation did not afford the same mean stationary concentration of ROOH. Differences in profile light absorption at  $254\text{ nm}$

\*  $\text{TiO}_2$  RL 65 and RL 90 from Produits Chimiques, Thann et Mulhouse, France

\*\* Type C-ZnO from Société des Mines et Fonderies de Zinc de la Vieille Montagne, Belgique



and the polychromatic radiation may account for the differences. Moreover, as isotactic polypropylene, PA 11 is a semi-crystalline polymer, the wavelength-dependent photochemistry (and especially the photolysis of ROOH) occurring in the unpigmented zones is expected to be superposed on the photocatalytic oxidation of amorphous and pigmented zones. In the pigmented zones, the formation and decomposition of hydroperoxides are induced by the reactive species appearing on the excited pigment, which form stationary concentrations of hydroperoxide. At short wavelengths, the direct photolysis of the primary hydroperoxides proceeds faster than at long wavelengths; the direct photolysis in the unpigmented zones is an additional route of disappearance of the hydroperoxides and lower stationary concentrations are observed.

In the photothermal oxidation at long wavelengths and at 254 nm of PA 12 (polydecanamide) and PA 6 (polyhexanamide) very similar intermediates (hydroperoxides, imides, hydroxylated groups  $\alpha$  to the nitrogen atom, aldehydes) have been observed throughout both photothermal oxidations. Therefore, the same oxidation mechanism implying a primary direct photolysis at short wavelengths ( $\lambda < 330$  nm) and a photoinduced oxidation at wavelengths longer than 254 nm is valid for every aliphatic polyamides studied. PA 11, PA 12 and PA 6 differ only on quantitative grounds. For example, the initial rates of the direct photolysis (measured as the rates of appearance of aldehyde groups) are in the ratio 1/3.2/4.5 respectively for PA 12, PA 11, PA 6. Dealing with hydroperoxides, chemical titrations in hexafluoroisopropanol supplied the results represented in Fig. 5 on long wavelength exposure ( $\lambda > 300$  nm). The photostationary concentrations of hydroperoxides are respectively 45, 20 and 12 mmol kg<sup>-1</sup> for PA 12, PA 11 and PA 6. At 254 nm, the photostationary concentrations are much lower (7, 2.5 and 3.8 respectively for PA 12, PA 11 and PA 6).

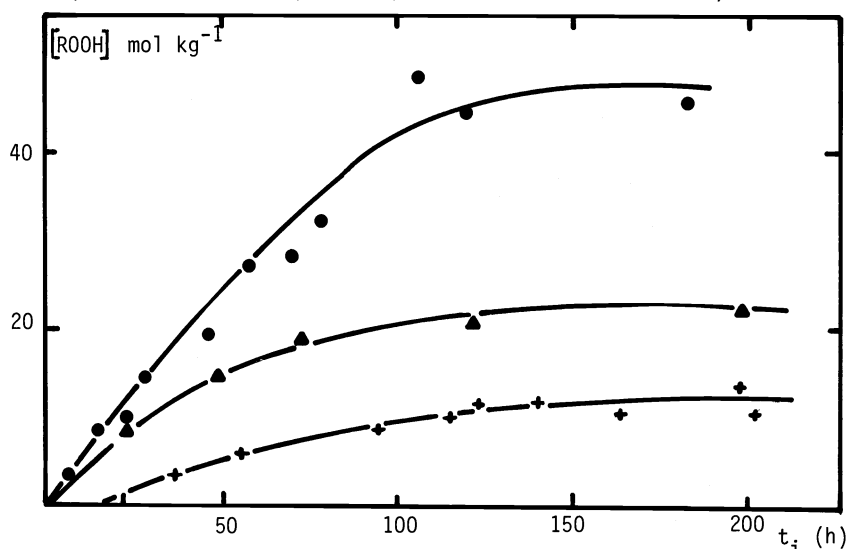


Fig.5. Variations in hydroperoxide concentration throughout photooxidation (at  $\lambda > 300$  nm) of aliphatic polyamides carried out in ● PA 12; ▲ PA 11 (new data); ◆ PA 6.

A sample of PA 12 pre-photooxidized at long wavelengths until the build-up of 45 mmol kg<sup>-1</sup> of hydroperoxide was photolyzed under vacuum at long wavelengths. Hydroperoxides were shown to decompose essentially into imides which meant that hydroperoxidation is occurring  $\alpha$  to the nitrogen atom.

#### PRIMARY HYDROPEROXIDATION IN THERMOPLASTIC POLYURETHANE ELASTOMERS

Polyurethanes and especially aromatic polyurethanes are complex polymers. Very few fundamental studies of their photooxidation have appeared (32,34). Since 1978, we are analyzing the photochemical behaviour of aromatic and aliphatic polyurethanes with a special emphasis to the properties of the hydroperoxides primarily formed in these materials. In the preceding sections, we described hydroperoxidation which reflects the lability of some C-H bonds under a radical attack. It appeared that each hydroperoxidized site behaved very differently. The photothermal oxidation of various types of polyurethanes have therefore been studied, focussing our attention to the various possible hydroperoxidation sites.

The four studied thermoplastic polyurethane elastomers have been processed in film polymerization using combinations of the following monomers: ES= polytetramethylene adipate glycol (molecular weight 1900); ET= polyoxytetramethylene glycol (molecular weight 2000); MDI= diphenylmethane p,p' diisocyanate; HDI= hexamethylene diisocyanate.

A polyester-urethane ESMDI was prepared by a pre-polymer method: in this two-step process, a long chain diisocyanate is first obtained by reaction of the polyester ES with the MDI diisocyanate. The obtained pre-polymer is then extended by reaction with the chain extender (1,4 butanediol-BD). Other polymers ESHDI, ETMDI and ETHDI were prepared by a one-shot method, the three components are mixed and melt reacted. The following ratios of monomers

have been used: ESMDI: (1 ES/ 3 MDI/ 2 BD); ESHDI: (1 ES/ 4 HDI /3 BD); ETMDI: (1 ET/ 4 MDI/ 3 BD); ETHDI: (1 ET/ 4 HDI/ 3 BD). The thickness of the films obtained was in the range 100-200  $\mu\text{m}$ .

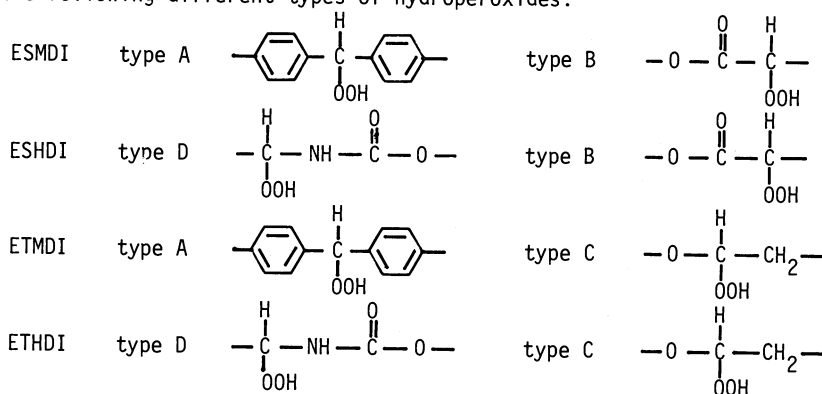
Chemical titrations of the total hydroperoxides formed in the polyurethanes samples on exposure to uv in a SEPAP 70.07 set-up (35) were carried out using the standard iodometric method (36). Results are reported in Table 3. In this table, the total concentration of the hydroperoxides is compared to the observed absorbance at 3425 or 3475  $\text{cm}^{-1}$  of 120  $\mu\text{m}$ -photo-oxidized samples (absorbance related to the total amount of hydroxylated products). It is apparent that hydroperoxides accumulate to high concentrations, specially in polyurethanes which contain ether groups (ETMDI and ETHDI).

TABLE 3. Comparison of the relative extent of photothermal oxidation (expressed in relative absorbance at 3475  $\text{cm}^{-1}$  - first line - to the total concentration of hydroperoxides (mol  $\text{l}^{-1}$  - second line).

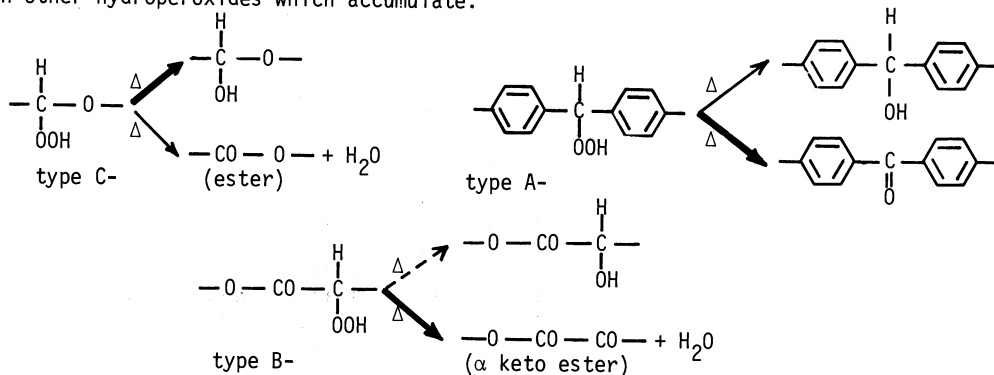
ESMDI*	0.07	0.09	0.13	0.18	0.29	0.30	0.32
	0.04	0.05	0.09	0.06	0.12	0.12	0.12
ESHDI	0.06	0.10	0.16	0.24			
	0.03	0.04	0.06	0.06			
ETMDI	0.05	0.14	0.27	0.80			
	0.05	0.14	0.21	0.43			
ETHDI	0.16	0.26	0.35	0.73	0.74	0.81	0.91
	0.19	0.26	0.42	0.45	0.54	0.60	0.80

\* Absorbance measured at 3425  $\text{cm}^{-1}$ .

Considering the structure of the various studied polyurethanes, it was expected to observe the following different types of hydroperoxides.



The relative importance and the behaviour of each type of hydroperoxide has been studied in the polyurethane elastomers. The following facts were observed. A specific absorption band in the hydroxyl stretching region can be attributed to each hydrogen-bonded type, i.e. 3425  $\text{cm}^{-1}$  to type A, 3450  $\text{cm}^{-1}$  to type D and 3475  $\text{cm}^{-1}$  to types B and C. All types of hydroperoxides were fairly stable up to 90°C. At 120°C, they decompose readily (in 15 h). If results of chemical titrations were considered, it appeared that type C-hydroperoxides decomposed thermally in groups absorbing in the hydroxyl stretching region. As opposite, type A- and B-hydroperoxides were completely converted into products which were not absorbing between 3600 and 3400  $\text{cm}^{-1}$ . No conclusion on the thermal decomposition of type D-hydroperoxides can be drawn since their concentration is kept low in any oxidative conditions. Conclusions are sounder on other hydroperoxides which accumulate.



Reduction of hydroperoxides with  $I_3^-$  or  $SO_2$  was carried out to check the vacuum thermolysis conclusions. The decrease of the absorbance between 3500 and 3400  $cm^{-1}$  after a  $SO_2$  treatment was equal indeed to the thermolytic decrease in polyester-urethane and exceeded the thermolytic decrease in polyether-urethane. Hydroperoxides which accumulated in the various photo-oxidized samples were exposed to long wavelength radiation ( $\lambda > 313$  nm) in vacuum. Decrease of the absorption in the hydroxyl stretching range was generally observed. The decrease rate of type A-hydroperoxide was much higher. Type C were rather photostable, even at 254 nm.

In each polyurethane sample, the variations at 3425  $cm^{-1}$  (ESMDI) or at 3475  $cm^{-1}$  (ESHDI, ETMDI, ETHDI) of the absorbance of hydroperoxides can be explained. In ESMDI polymers, type A-hydroperoxides were readily formed and reached a limiting concentration; type B- were formed slowly but accumulated. In ESHDI samples, type B- and type D-hydroperoxides were formed less rapidly but they accumulated too. In ETMDI and ETHDI elastomers, the major hydroperoxides formed were type C- and these hydroperoxides were rather photostable; high concentrations of type C-hydroperoxides were therefore observed in both polymers. In ETMDI, type A- were simultaneously formed and rapidly photolyzed as opposite to ETHDI in which type D-appeared fairly photostable. However, in any elastomers, type D- did not accumulate until high concentrations. These conclusions are represented in Fig. 6.

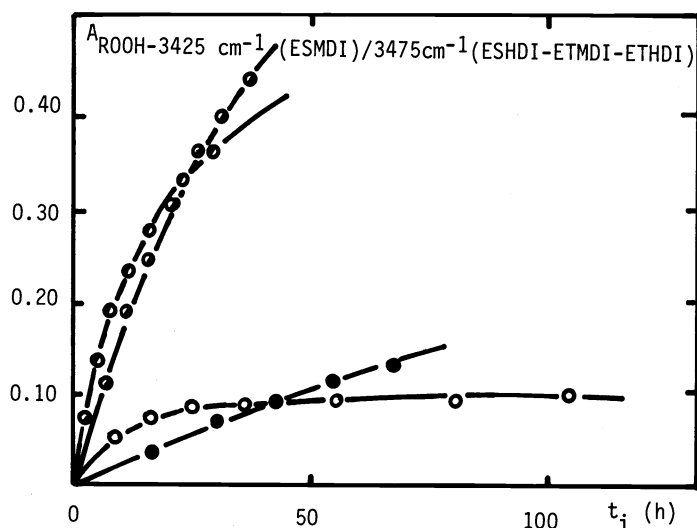
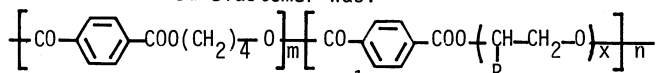


Fig.6 . Variations in the calculated absorbance of hydroperoxides vs irradiation time  $t_i$ : ○ ESMDI; ● ESHDI; ○ ETMDI; ● ETHDI.

Type C-hydroperoxides can be formed in films of polyester-polyether (HYTREL from DU PONT or ARNITEL from AKZO) exposed to uv radiations of long wavelengths ( $\lambda > 300$  nm). The structure of the studied elastomer was:



Absorbance at 3475  $cm^{-1}$  increased continuously throughout the photochemical oxidation and the contribution of type C-hydroperoxides can be estimated using  $SO_2$ -treatment or vacuum photolysis. These hydroperoxides presented a maximum of absorption at 3475  $cm^{-1}$  as type C- in polyurethane did. The thermal decomposition of type C-hydroperoxides led to products which did not absorb in the hydroxyl stretching range as opposite to the polyurethane situation. After  $SO_2$  treatment or vacuum thermolysis of a photooxidized sample, the same residual absorbance at 3475  $cm^{-1}$  was observed. Moreover, it has to be pointed out that these hydroperoxides decomposed thermally at 80°C, i.e. at a lower temperature than in polyurethanes. It is therefore apparent that two hydroperoxides of similar structures in two different matrix behave differently.

#### CONCLUSIONS

Although the various questions appearing in the introduction have not been completely answered in the polymers under investigation, special attention to the hydroperoxide behaviour has brought some useful pieces of information.

Most polymer materials exhibit specific hydroperoxidation sites. Though the corresponding hydroperoxides formed present qualitatively similar properties, large differences on quantitative grounds are observed. Mostly attributed to the molecular structure of the various hydroperoxidized groups, these differences must be accounted too by matrix effects. Studies

on model compounds would therefore hardly afford any relevant information on the properties of hydroperoxide in the matrix. Improvements in analytical technics are certainly positive factors for the understanding of the role of hydroperoxides (and may be for collecting better information on their molecular structure and their interactions with their neighbourhood). Such progress would be still more fruitful in systematic comparison of various oxidative conditions. As shown in the previous sections, it appeared interesting to compare the formation and the evolution of hydroperoxide groups in low-temperature thermooxidation, in short- and long-wavelengths photooxidation and in photocatalyzed oxidation.

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