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Photooxidative Degradation of Polyether-based Polymers

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SUMMARY : The mechanisms of photooxidation of several polyether based polymers were compared in order to give general rules of orientation of the oxidative reactions. These polymers were a poly(ether-ester) and two poly(ether-urethane)s. The behavior of the polyether component as homopolymer was also studied. This study was extended to copolymers of fluorinated olefins and allyl or vinyl ethers, and the non fluorinated homologues. The elucidation of the photooxidation mechanisms was based on the identification of the photoproducts by analysis of both the solid polymeric matrix and the gaz phase formed on irradiation. It was shown that the photochemical sensitivity of the polyether component was responsible for the rapid oxidation of the copolymers. However, in the case of the fluorinated compounds, different behaviors were observed. It was shown that the presence of the fluorine atoms strongly influenced the orientation of the reaction and modified the oxidation kinetics. The reactivity of the methylene groups in α-position of the oxygen atom of the ether groups were not found to be equivalent regarding oxidation and the secondary was more oxidizable than the tertiary one.

Introduction

The behavior of polyethers on exposure to UV irradiation has been studied in detail and the mechanism accounting for the photooxidation of these polymers can be considered as fairly well understood[1-5]. Polyethers have been shown to have significant sensitivity toward photooxidation. The first step of the oxidative reactions is an hydrogen abstraction on the polymeric backbone by a free radical formed by photonic excitation of chromophoric species. The macroradical produced reacts with oxygen, leading to a peroxy radical that gives a hydroperoxyde by abstraction of a labile hydrogen atom. Hydroperoxydes decompose thermally or photochemically to give alkoxy and hydroxyl radicals which can restart the chain oxidation reaction.

The reaction of hydrogen abstraction can be determinant for the modifications of the properties of a polymer in conditions of irradiation. Several potential sites of abstraction usually exist on a

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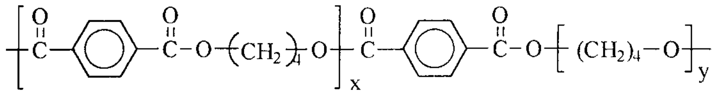
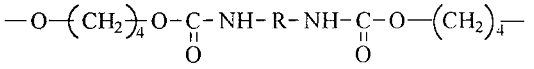
polymer chain. As an example, in the case of a tertiary carbon atom and a secondary one, the oxidation at the tertiary site leads preferentially to chain breaking, while the oxidation at the secondary carbon gives chain products without the scission of the backbone6).

It appears then that, when there are several sites of oxidation, determining the relative weight of each reaction pathway is of first importance, since the modifications of the polymer properties resulting from the oxidative photoageing are directly linked to these reactions.

This paper reports on the photooxidation of polyether-based polymers. These polymers are copoly(ether-ester)s and copoly(ether-urethane)s elaborated with poly(tetramethylene)glycol. They present the following units in their structures :



copoly(ester)s

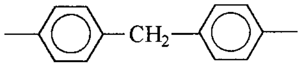


$$-O-(CH_2)_4-O-\underset{\underset{O}{\|}}{C}-NH-R-NH-\underset{\underset{O}{\|}}{C}-O-(CH_2)_4-$$

copoly(urethane)s

with R being $-(CH_2)_6-$ (HDI based polyurethane)

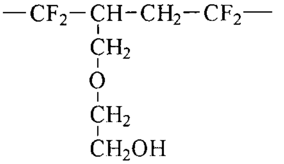
or



(MDI base polyurethane)

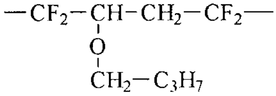
A peculiar attention is given to the photooxidation mechanism of the polyether component.

The present paper describes also how the influence of the environment of the potentialy reactive sites can be experimentally evidenced. Two copolymers of a fluorinated olefin with an allyl or a vinyl ether were chosen as a basis for this study. These copolymers are partly based on the following units :



$$\begin{array}{l} -CF_2-CH-CH_2-CF_2- \\ \qquad\quad | \\ \qquad\ CH_2 \\ \qquad\quad | \\ \qquad\quad O \\ \qquad\quad | \\ \qquad\ CH_2 \\ \qquad\quad | \\ \qquad\ CH_2OH \end{array}$$

Polymer C1

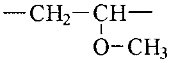


$$\begin{array}{l} -CF_2-CH-CH_2-CF_2- \\ \qquad\quad | \\ \qquad\quad O \\ \qquad\quad | \\ \qquad\ CH_2-C_3H_7 \end{array}$$

Polymer C2

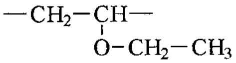
The structure of polymer C1 has two methylene groups in α-position from the oxygen atom of the ether group, and that of polymer C2 a secondary and a tertiary carbon α to the oxygen atom.

A comparison has been made with three polyethers, poly(vinyl methyl ether) (PVME), poly(vinyl ethyl ether) (PVE) and poly(vinyl isobutyl ether) (PVI) :



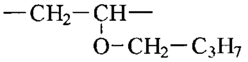
$$-CH_2-\underset{\underset{\displaystyle O-CH_3}{|}}{CH}-$$

PVME



$$-CH_2-\underset{\underset{\displaystyle O-CH_2-CH_3}{|}}{CH}-$$

PVE



$$-CH_2-\underset{\underset{\displaystyle O-CH_2-C_3H_7}{|}}{CH}-$$

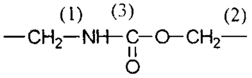
PVI

On a practical point of view, polymer C_1 constitutes a basis for crosslinkable materials used in thin coatings.

Results and discussion

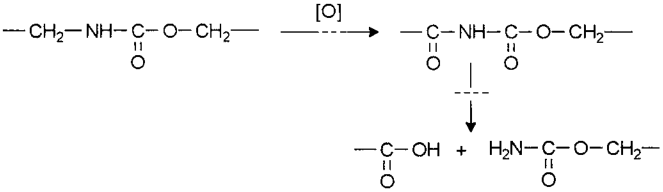
• *Aliphatic poly(ether-urethane)s*

Two different phases have to be considered. The first one corresponds to the oxidation of the polyether component by far the most oxidisable, which leads to the total disappearance of the ether functions. In the second phase, the oxidation of the urethane component is observed. This reaction involves the oxidation of the methylene groups α to the NH[7].



$$\overset{(1)}{-CH_2}-NH-\underset{\underset{\displaystyle O}{\|}}{\overset{(3)}{C}}-O-\overset{(2)}{CH_2}-$$

Oxidation leads to the formation of acetyl urethane functions that can decompose to give carboxylic acids and primary urethane.



$$-CH_2-NH-\underset{\underset{\displaystyle O}{\|}}{C}-O-CH_2- \xrightarrow{[O]} -\underset{\underset{\displaystyle O}{\|}}{C}-NH-\underset{\underset{\displaystyle O}{\|}}{C}-O-CH_2-$$

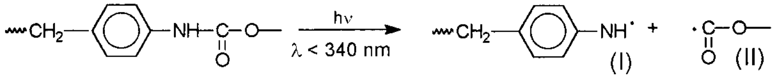
$$\downarrow$$

$$-\underset{\underset{\displaystyle O}{\|}}{C}-OH + H_2N-\underset{\underset{\displaystyle O}{\|}}{C}-O-CH_2-$$

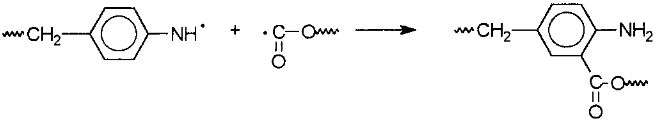
Short wavelength irradiation can provoke a direct homolysis of the C-N bond[7], C-C bond[8] and N-C bond[9]. The decarboxylation of the urethane groups occurs, and primary amines are formed.

- ***Aromatic poly(ether-urethane)s***

Direct absorption by the aromatic chromophores leads to the homolysis of the C-N bond. This reaction has been shown to occur for irradiation at wavelengths below 340 nm[4]. In this reaction two macroradicals are formed :



The major route of evolution of radicals (I) and (II) is a reaction on the ortho position by a photo-Fries type mechanism :



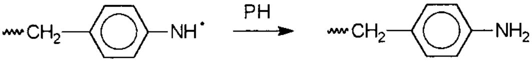
This reaction is responsible for the discoloration of the polymer under non-oxidative conditions. Direct evidences that this reaction occurs are obtained from the modifications of the IR spectra of samples irradiated in vacuum :

- decrease of the absorption band at 818 cm^{-1} (para-substituted aromatic ring) and formation of a band at 840 cm^{-1} (1,2,4-trisubstituted ring) ;

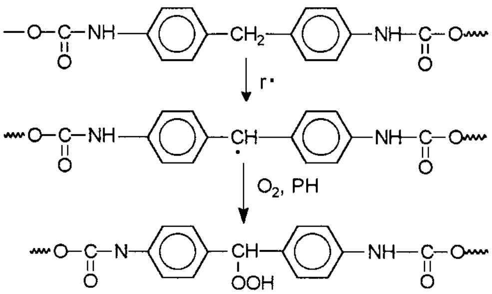
- decrease of the intensities of the urethane absorption bands.

Photoscission of N-C bonds has been shown to occur in the case of aliphatic polyamides through direct excitation of the -NH-CO- chromophore up to 340 nm[10].

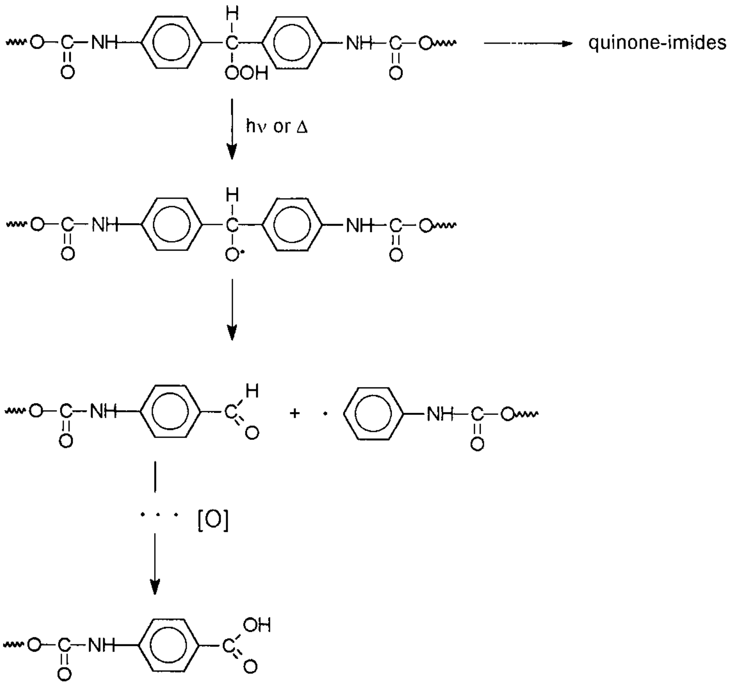
By hydrogen-abstraction to the polymeric backbone, radicals (I) lead to an aromatic amine :



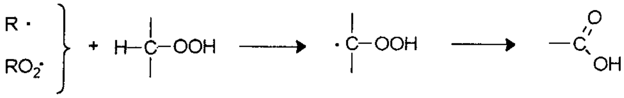
Oxidation of urethane segments is also experimentally observed. This reaction involves a radicalar attack on the central methylene carbon of the aromatic structures. Subsequent oxygen addition followed by hydrogen abstraction results in the formation of hydroperoxides according to :



The hydroperoxides are photo- and thermo-unstable and reach only low stationary concentrations. The homolysis of the O-O bond gives an alkoxy radical. The evolution of this alkoxy radical, which is responsible for the formation of several products, involves a β-scission that produces an aldehyde which is in turn oxidized in peracid and leads to benzoic acid type end-groups.

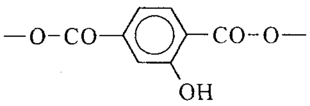


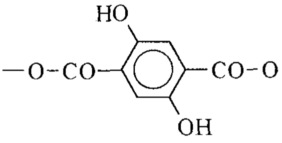
Another mechanism that could explain the formation of aromatic carboxylic acids involves a direct decomposition of the secondary hydroperoxydes, as recently proposed in the case of polyethylene oxidation[11] :



• *Poly(ether-ester)s*

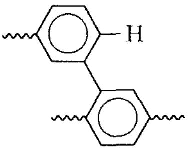
The exposure of copoly(ether-ester)s to UV light provokes the yellowing of the sample. The origin of this yellowing was investigated on poly(butyleneterephthalate) PBT, which is a good model for the rigid sequences of the poly(ether-ester)s studied. It was shown that the yellowing of photo-oxidized PBT can be attributed mainly to the formation of mono- and di-hydroxy-substituted compounds :





These photo-products result from the photolysis of hydroperoxidic groups formed on the aromatic ring, followed by hydrogen abstraction. A second possible route involves the formation of another hydroperoxidic group and the reaction of the HO$^\bullet$ radical with a phenyl radical. This hydroperoxidic group may be the hydroperoxide formed in the α-position of the ester.

A second source of the yellowing may be related to the recombination of the radical formed through direct photo-scission of the aromatic ester-chromophore



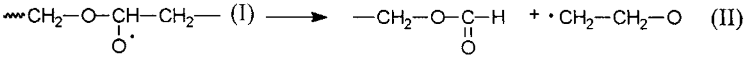
The contribution of *m*-biphenyl structures to the yellowing of PBT is however anticipated to be fairly low[12]. A mixture of conjugated photoproducts resulting from recombination processes may also account for the yellowing of PBT. The photo-yellowing of poly(ether-ester)s can be accounted for, at least in qualitative terms, as arising from polybutyleneterephthalate sequences.

The photooxidation of poly(ether-ester)s generates high concentrations of hydroperoxides mainly due to the ether component. These hydroperoxides can be photolyzed with the formation of a $HO^{\bullet}$ radical : in fact, this radical does not react with a phenyl radical to give the hydroxylated compound responsible for the yellowing. If such a reaction was possible, a higher rate of yellowing would be observed in the poly(ether-ester) than in PBT which is not the case ; therefore, it can be postulated that the only hydroperoxides involved in the formation of the hydroxylated aromatic compounds absorbing at 340-350 nm and 370 nm are the hydroperoxides formed in the ester phase.

• *Poly(tetramethyleneglycol) (PTMG)*

All the results given above for poly(ether-urethane) and poly(ether-ester) show that the oxidation of the polyether component is the main cause of the degradation of these polymers. Despite the fact that it does not absorb radiations of wavelengths longer than 200 nm, PTMG is very sensitive to photooxidation. The initiation of the photooxidation can be caused by internal or external impurities resulting from the thermal history of the polymer, which absorb UV light and produce radicals which react further with the polymer[13].

As recalled above, the photoinduced oxidation of PTMG leads to the formation of secondary hydroperoxides. The decomposition of these hydroperoxides leads to the formation of an alkoxy radical (I). The main route of decomposition of radical (I) is a β-scission which leads to formation of formates (1725/1175 cm^{-1}) :

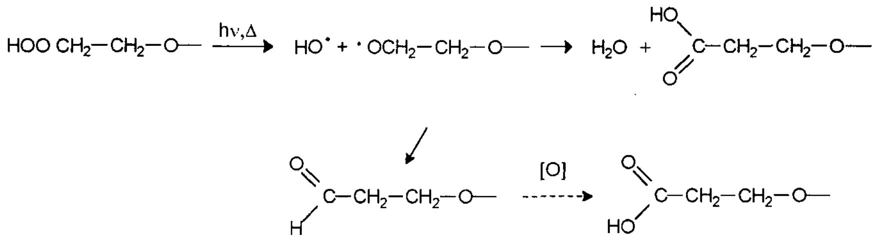


$$\sim CH_2-O-\underset{\underset{O^{\bullet}}{|}}{CH}-CH_2- \text{ (I) } \longrightarrow -CH_2-O-\underset{\underset{O}{||}}{C}-H + {}^{\bullet}CH_2-CH_2-O \text{ (II)}$$

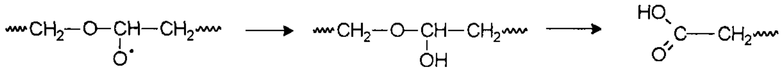
The primary radical (II) ${}^{\bullet}CH_2$-CH_2-O- obtained in this reaction may decompose by an oxidation leading to primary hydroperoxides.

$$^{\bullet}CH_2-CH_2-O- \text{ (II) } \xrightarrow{O_2,\ PH} HOOCH_2-CH_2-O-$$

The hydroperoxides are photochemically and thermally unstable, and can be decomposed to give carboxylic acids by a direct oxidation[11] or an oxidation involving the formation of aldehydes.



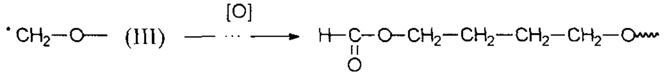
From the shape of the carbonyl band of photooxidised PTMG, it is observed that only very weak concentration of carboxylic acids are formed. The oxidation pathway of radical (II) to give carboxylic acid has then to be considered as minor, especially if one consider that carboxylic acids can be also formed by oxidation of hemiacetals obtained from the alcoxy radicals.



A second route of decomposition route for radical (II) is a β-scission reaction, involving the homolysis of C-C bonds :

$$\cdot CH_2-CH_2-CH_2-O- \text{(II)} \longrightarrow CH_2{=}CH_2 + \cdot CH_2-O- \text{(III)}$$

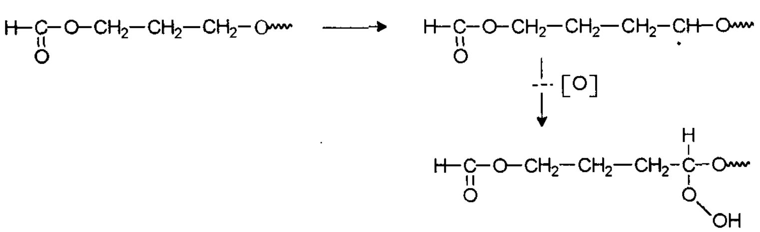
This reaction leads to the formation of ethylene, whose the formation has been observed by IR analysis of the gas phase (949 cm^{-1}). The primary radical (III) that is obtained by this reaction may be oxidised to give a formate.



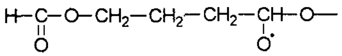
$$\cdot CH_2-O- \text{(III)} \xrightarrow{[O]} H-\underset{\underset{O}{\|}}{C}-O-CH_2-CH_2-CH_2-CH_2-O\sim$$

This constitutes a supplementary route of formation of formates.

Once formed these formates can be oxidised by reactions involving an initial hydrogen abstraction on a methylene group α to oxygen, and leading to the formation of a secondary hydroperoxide

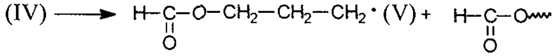


By decomposition of the hydroperoxide, an alkoxy radical (IV)



$H-C(=O)-O-CH_2-CH_2-CH_2-CH(O^{\bullet})-O-$ is obtained.

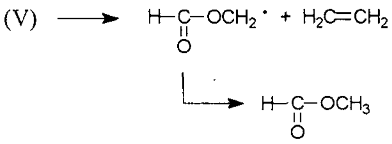
The identification of the low molecular weight photoproducts by analysis of the gaz phase indicates the formation of methyl formate (1750/1183 cm^{-1}) and ethylene. The formation of these products involves the decomposition of radical (IV) by homolysis of the C-C bond in a β -scission process which leads to a primary alkyl radical (V) and regenerates a formate.



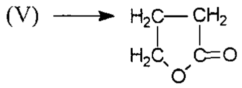
$(IV) \longrightarrow H-C(=O)-O-CH_2-CH_2-CH_2^{\bullet}\ (V) + H-C(=O)-O\sim$

This evolution is in accordance with the kinetic aspects of the oxidation, since it is experimentally determined that formates reach a stationnary state. By the repetition of this reaction, the chain can be considerably shortened.

The radical (V) can decompose by a β-scission reaction, which produces in turn ethylene and methyl formate.



The radical (V) can also decompose by an internal cyclisation that gives a γ-lactone responsible for the absorption band observed at 1780 cm^{-1} .



The infrared analysis of the polymeric matrix show that this product is trapped, at least partially, in the polymer. It appears after a short induction period whereas formates are detected from the early stages of the oxidative degradation of the polymer.

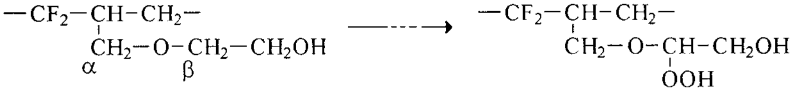
• *Fluorinated copolymers*

The influence of the factors that determine the reactivity of free radicals in aliphatic compounds have been reviewed in details. Several authors have discussed the different parameters controlling the orientation of free radical substitutions[14-16]. The orientation of the reactions has been discussed in terms of polarity of the transition state and strenght of the bonds being broken and being formed. Several qualitative rules which allow the prediction of the reactivity and regioselectivity of free radical substitution have been given.

More recently a detailed approach of the factors controlling the free radical reactions based on the role of orbital interactions has been published[17]. The results show that, depending on their electronegativity, radicals present different reactivities and can attack different sites of the same substrate. Electron withdrawing substituents enhance transfert reactions by electropositive radicals and retard reactions with electronegative radicals.

The experimental results obtained in the case of the fluorinated copolymers C1 and C2 [18] permit the proposal of mechanisms that can be rationalized on the basis of the general rules given in the literature.

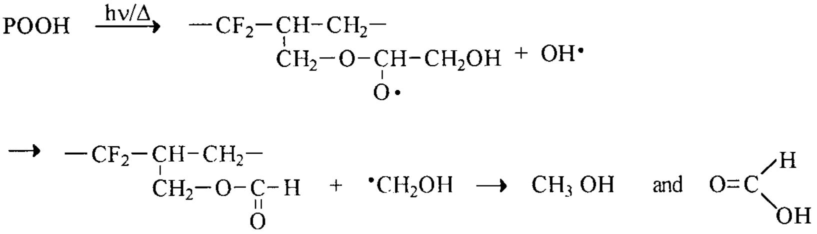
In a first phase, the induced oxidation of copolymer C1 leads to the formation of secondary hydroperoxides by oxidation of the carbon atom in α-position to the ether group.



$$\begin{array}{l} -CF_2-\underset{|}{C}H-CH_2- \\ CH_2-O-CH_2-CH_2OH \\ \alpha \qquad\quad \beta \end{array} \xrightarrow{\quad} \begin{array}{l} -CF_2-\underset{|}{C}H-CH_2- \\ CH_2-O-\underset{|}{C}H-CH_2OH \\ OOH \end{array}$$

The secondary carbons noted (α) and (β) are influenced by the donating effect of ether group and hydrogen abstraction by electrophilic reaction is then enhanced in comparison to that occuring at the tertiary center. Now, considering the relative reactivities of the secondary carbon atoms, the carbon (α) is influenced by the withdrawing effect of the CF_2 substituents. The C-H bonds near the electronegative CF_2 group are strenghened and present a weak reactivity towards hydrogen transfer. At opposite the β position is not deactivited and reacts more easily with an incoming radical.

The hydroperoxides can decompose thermally or photochemically. An alkoxy radical is obtained, and produces by β-scission a formate and radical $^{\bullet}CH_2OH$, which leads to methanol and formic acid.



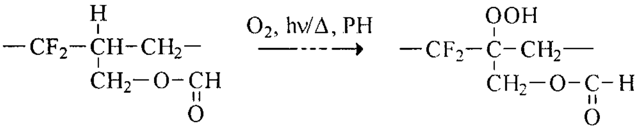
$$POOH \xrightarrow{h\nu/\Delta} -CF_2-\underset{\displaystyle CH_2-O-\underset{\displaystyle O^{\bullet}}{CH}-CH_2OH}{CH}-CH_2- \; + \; OH^{\bullet}$$

$$\longrightarrow -CF_2-\underset{\displaystyle CH_2-O-\underset{\displaystyle \overset{\|}{O}}{C}-H}{CH}-CH_2- \; + \; ^{\bullet}CH_2OH \longrightarrow CH_3OH \quad \text{and} \quad O{=}C\begin{smallmatrix}\diagup H\\ \diagdown OH\end{smallmatrix}$$

Methanol and formic acid can migrate from the polymeric matrix and are detected by analysis of the gas phase.

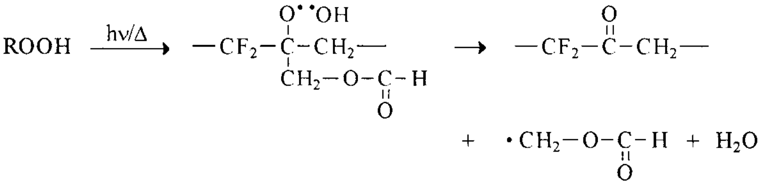
These reactions are consistent with the important decrease of the absorption bands of the methylene groups that are observed and explain also the decrease of the ether band and the decrease of the hydroxyl groups absorptions since the products like methanol and formic acid are loss by migration.

The evolution of the polymer in a second phase is consistent with the formation of tert-hydroperoxides initiated by the oxidation of the formates at the tertiary carbon atom.



$$-CF_2-\overset{\displaystyle H}{\underset{\displaystyle CH_2-O-\underset{\displaystyle \overset{\|}{O}}{CH}}{C}}-CH_2- \xrightarrow{O_2,\ h\nu/\Delta,\ PH} -CF_2-\overset{\displaystyle OOH}{\underset{\displaystyle CH_2-O-\underset{\displaystyle \overset{\|}{O}}{C}-H}{C}}-CH_2-$$

Scission of the O-O bond of the hydroperoxidse gives an alkoxy radical that generates by β-scission a chain-ketone and a radical $^{\bullet}CH_2\text{-}O-\underset{\displaystyle \overset{\|}{O}}{C}-H$ which leads to the formation of methyl formate.

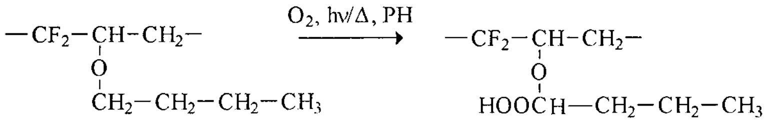


$$ROOH \xrightarrow{h\nu/\Delta} -CF_2-\overset{\displaystyle O^{\bullet}\ {}^{\bullet}OH}{\underset{\displaystyle CH_2-O-\underset{\displaystyle \overset{\|}{O}}{C}-H}{C}}-CH_2- \longrightarrow -CF_2-\overset{\displaystyle O}{\overset{\|}{C}}-CH_2- \; + \; {}^{\bullet}CH_2-O-\underset{\displaystyle \overset{\|}{O}}{C}-H \; + \; H_2O$$

The quantitative determination of the various photoproducts formed shows that the total concentration of formates is equal to the total concentration of methanol and formic acid. This result is in accordance with the proposed photooxidation mechanism.

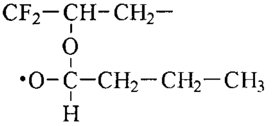
The behaviour of polymer C2 may be analysed similary. The tertiary and the secondary carbon atoms are on both sides of the oxygen atom, like in PVE or PVI, but the tertiary carbon atom is substituted by CF_2, which produces a strong polar effect. The result is that the rate of hydrogen abstraction is considerably reduced from the tertiary site. As a consequence the reaction takes place essentially at the secondary carbon atom.

The induced oxidation of polymer C2 leads to the formation of secondary hydroperoxides :

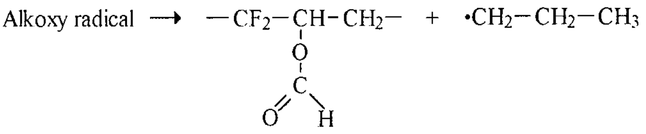


$$-CF_2-CH(O-CH_2-CH_2-CH_2-CH_3)-CH_2- \xrightarrow{O_2,\ h\nu/\Delta,\ PH} -CF_2-CH(O-CH(OOH)-CH_2-CH_2-CH_3)-CH_2-$$

Homolysis of the O-O bond of hydroperoxides gives an alkoxy radical and an hydroxyl radical $HO^\bullet$. A β-scission of the alkoxy radical by homolysis of the C-C bond leads to the formation of a formate and generates a new radical.



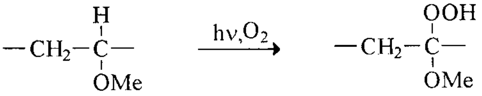
$$-CF_2-CH(O-CH(O^\bullet)-CH_2-CH_2-CH_3)-CH_2-$$



The homolysis of hydroperoxides and the β-scission of the alkoxy radical occur almost in one single step. The hydroxy radical $HO^\bullet$ and the radical $^\bullet CH_2-CH_2-CH_3$ are then formed in immediate proximity. Consequently there is an important probability that both these radicals recombine and form 1-propanol. Two supplementary routes of evolution can be tentatively proposed to explain the behavior of the alkyl radical : oxidation to give propionic acid, and isomerisation to form a more stable secondary radical $CH_3-\underset{\bullet}{C}H-CH_3$, which is oxidized in acetone and acetic acid.

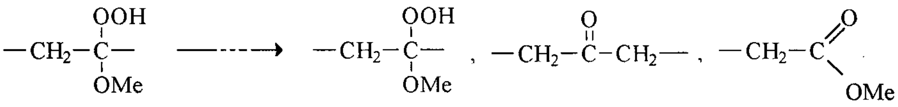
- ***Non fluorinated homologues***

Our experimental results show that PVME photooxidation occurs in two phases$^{4)}$. Hydroperoxidation comes about the first hours of irradiation. The oxidation takes place on the tertiary carbon atom.



$$-CH_2-\underset{OMe}{\overset{H}{C}}- \xrightarrow{h\nu,O_2} -CH_2-\underset{OMe}{\overset{OOH}{C}}-$$

The hydroperoxides formed react thermally of photochemically to yield several products that have been identified. The chain is rapidly damaged and molecules of low molecular weight are produced :

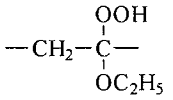


$$-CH_2-\underset{OMe}{\overset{OOH}{C}}- \dashrightarrow -CH_2-\underset{OMe}{\overset{OOH}{C}}-\ ,\ -CH_2-\overset{O}{\overset{\|}{C}}-CH_2-\ ,\ -CH_2-C\begin{matrix}{}^{/\!/ O}\\{}_{\setminus OMe}\end{matrix}$$

When the whole matrix is oxidised, the oxidation reaches a limit (second phase). The major carbonylated products are keto-diesters with a variable number of ketonic groups in the structure. Their formation produces methanol that has been detected in large amount in the gas phase.

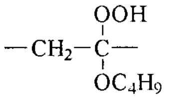
Carboxylic acids are minor products. The formation of the carboxylic acids results from the oxidation of the radical formed by Norrish I scission of the ketones.

The main routes of oxidation of PVE and PVI correspond respectively to the formation of the following tert-hydroperoxides :



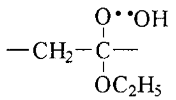
$$-CH_2-\underset{OC_2H_5}{\overset{OOH}{C}}-$$

and

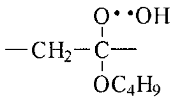


$$-CH_2-\underset{OC_4H_9}{\overset{OOH}{C}}-$$

By homolysis of the O-O band these products lead to the formation of the following alkoxy radicals.

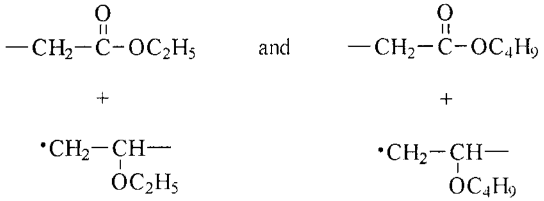


$$-CH_2-\overset{\overset{\displaystyle O^{\bullet}\,{}^{\bullet}OH}{|}}{\underset{\underset{\displaystyle OC_2H_5}{|}}{C}}-$$



$$-CH_2-\overset{\overset{\displaystyle O^{\bullet}\,{}^{\bullet}OH}{|}}{\underset{\underset{\displaystyle OC_4H_9}{|}}{C}}-$$

A plausible route of evolution for both these radicals is a β-scission reaction involving the homolysis of the C-C bonds. Ester groups and new radicals are obtained :



$$-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OC_2H_5 \quad \text{and} \quad -CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OC_4H_9$$

$$+ \qquad\qquad +$$

$${}^{\bullet}CH_2-\underset{\underset{\displaystyle OC_2H_5}{|}}{CH}- \qquad {}^{\bullet}CH_2-\underset{\underset{\displaystyle OC_4H_9}{|}}{CH}-$$

The formation of carboxylic acids indicates the oxidation of these radicals.

The β-scission of these radicals could also involve the homolysis of the C-O bands. However in this case ketones would be formed. Since no experimental evidence of the formation of such compounds has been obtained, this route may be neglected.

Conclusion

The results given in this article show that the expected reactivities deduced from the knowledge on "classical " polymers (polypropylene, ...) are not found in the case of fluorinated polyethers.

This can be related to the withdrawing effect of the fluorine atoms which modifies the reactivities of the various sites of hydrogen abstraction.

The fluorine atoms have a direct influence on the activation energy of the reaction of hydrogen abstraction. The presence of these atoms in α-position of the site of hydrogen abstraction by an electrophilic radical disfavours the formation of limit charged forms in the transition state(19).

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