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Infrared analysis of the photochemical behaviour of segmented polyurethanes: aliphatic poly(ether-urethane)s

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The photooxidative degradation of a polyether/aliphatic diisocyanate based polyurethane, ETHDI, was studied using *FT*i.r. spectroscopy. It was confirmed that the oxidation of this type of polyurethane results from the important sensitivity of the polyether soft segments to oxidative degradation. The photooxidation mechanism of the polyether segment was studied using the photodecomposition of polytetramethylene glycol, PTMG, as a model for that of the soft segments of ETHDI. The photooxidation of PTMG was studied until the ultimate degradation of the polymer and the different photoproducts were identified by analysis of both the solid polymeric matrix and the gas phase. Oxidation of the ether groups produced formates, which further decomposed to give ethylene and methyl formate, and regenerated the formates. For irradiation of the ETHDI polymer until the total disappearance of the ether groups, the decomposition of the urethane functions was observed and the corresponding photoproducts characterized. © 1998 Published by Elsevier Science Ltd. All rights reserved.

(Keywords: segmented polyurethanes; aliphatic; polyether)

INTRODUCTION

This series of articles reports on the photooxidation of thermoplastic polyurethane elastomers based either on aromatic or aliphatic diisocyanates with soft segments being formed from hydroxy terminated polyesters or polyethers.

In the first article we described the photooxidation of aliphatic hexamethylene-diisocyanate (HDI) based poly(ester-urethanes)[1]. The different photoproducts formed were identified and a mechanism accounting for the formation of the photoproducts was proposed. It was shown that on irradiation at ‘long’ wavelengths ($\lambda \geq 300$ nm), the photooxidation was initiated by an hydrogen abstraction from the methylene in the α position relative to the nitrogen atom. On irradiation at short wavelengths, two types of reaction were observed: an induced oxidation, and a direct oxidation involving the photochemical homolysis of the C–N and C–O bonds of the urethane groups. In both cases, the polyester segments were shown to be relatively photostable.

The present article reports on the photochemical evolution of polyether-based aliphatic polyurethanes. We have chosen polyoxytetramethylene glycol (PTMG) as macroglycol, HDI as diisocyanate and 1,4-butanediol (BDO) as chain extender.

Former results obtained in our laboratory[2] have shown that the extreme photochemical sensitivity of the soft segments was the reason for the rapid degradation of the polyether-based polyurethanes upon exposure to solar radiation. The first step of the photooxidation has been shown to involve the formation of primary hydroperoxides by oxidation of the methylene groups in the α position to the oxygen atom. The stationary concentrations of the hydroperoxides reached significant levels (0.8 mol kg^{-1}) upon irradiation at wavelengths above 300 nm.

The photochemical reactivity of polytetramethyleneglycol (PTMG) as homopolymer has been studied formerly[3]. It has been shown that the hydroperoxides formed by photooxidation of PTMG decomposed photochemically or thermally to give formates, esters and hemiacetals. The last products are thermally unstable and give alcohols and carboxylic acids. The route leading to the formates has been shown to represent 70% of the total decomposition pathway.

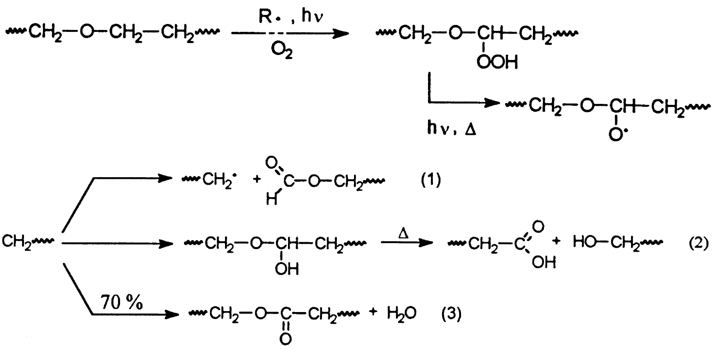

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Table 1 Attribution of infrared absorption bands of the polyether segment (PTMG) in a ETHDI matrix (identification based on analysis of the literature data[6,7] and comparison with low molecular weight models)

*fx*14 ν (cm^{-1})	Attribution
2941	antisym. str. $(CH_2)\beta$
2918	antisym. str. $(CH_2)\alpha$
2857	sym. str. $(CH_2)\beta$
2796	sym. str. $(CH_2)\alpha$
1476	
1465	
1456	(CH_2) bending vibr.
1447	
1436	
1413	
1368	$\alpha(CH_2)$ bending vibr.
1350 ↓ 1200	
1114	antisym. str. (C–O–C)
1050 ↓ 900	
827	sym. str. (C–O–C)
745	rock. vibr. (CH_2)
556	skel. def. vibr. (C–C)

In earlier investigations on the photochemical degradation of polyether based aliphatic polyurethanes[2], we focused on the primary oxidation photoproducts. In this article we report on the whole oxidation mechanism of aliphatic poly(ether-urethane), on the basis of the identification of the different photoproducts until the ultimate degradation of the polymer. Our investigations are based on analysis of changes in the *FT*i.r. spectra of irradiated samples and determination of the volatile products formed upon irradiation. Particular attention was given to the identification of the products formed by oxidation of the polyether component, and particularly to the decomposition pathways of the primary alkyl radical formed by reaction[1].

EXPERIMENTAL

Preparation of the polymer

The polyether/diisocyanate ETHDI was prepared following the technique of prepolymer synthesis[4]. According to this method, the totality of macrodiol polyester was caused to react with the diisocyanate in order to obtain a prepolymer. In a second step the prepolymer reacted with the chain extender. Taking into account the functionalities of the different oligomers used for the synthesis, a 4:1 HDI/PTMG ratio was used to ensure an excess of HDI to produce a diisocyanate 'capped' polyether. Preparation of the prepolymer was carried out in bulk at 80°C for 4 h under N_2 atmosphere. Once the prepolymer was obtained, THF was added with 3 parts of 1,4-butanediol and 0.01% of dibutyltindilaurate (DBTL). The reaction was then carried out for 15 h at 50°C under N_2. The extent of the reaction was periodically monitored by infrared analysis of a sample of the solution. The polymer obtained was precipitated in methanol, filtered and then dried at ambient temperature. The macroglycol used had a molecular weight of $\overline{M_n} = 2000\ \mathrm{g\ mol^{-1}}$.

Very thin films with a thickness below 7–8 μm were prepared. The polymer was at first dissolved in 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) and films were obtained by spreading the solution onto a glass surface. After evaporation of the solvent the films were peeled off from the support.

Irradiation and spectroscopic analysis

Irradiation was carried out in a SEPAP 12.24 apparatus for 'long' wavelength irradiation at $\lambda > 300$ nm. This medium accelerated photoaging device has been described in several papers (see, for instance, Ref. [5]). It allows irradiation at wavelengths above 300 nm with a temperature of the samples of 60°C. Irradiations at 'short' wavelength ($\lambda = 254$ nm) were carried out at room temperature (20°C) in an aging unit equipped with 6 low pressure mercury lamps inside a cylindrical reflecting envelope. For analysis of the gaseous products formed upon irradiation, the polymer sample was placed into a quartz tube linked to a gas cell terminated at both extremities by KBr windows. The whole system was purged with oxygen before irradiation. *FT*i.r. spectra were recorded on a Nicolet 20 SX spectrometer using 64 scan summations at a nominal resolution of 2 cm^{-1}.

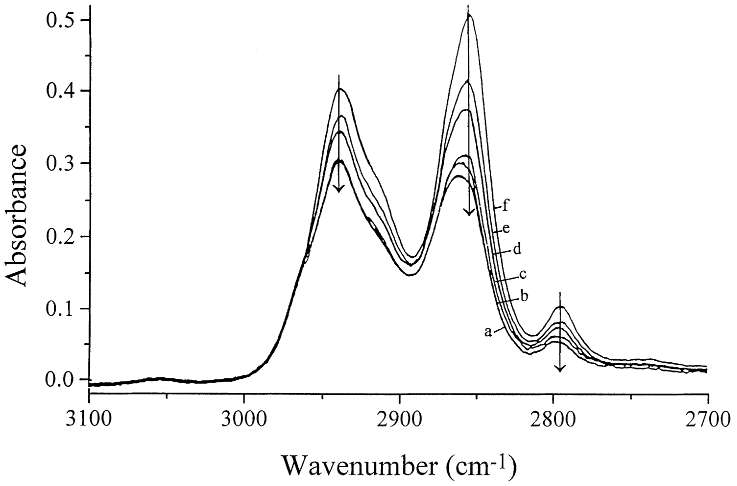


Figure 1 Evolution of the i.r. spectrum of an ETHDI film photooxidized at long wavelengths: (a) initial; (b) 8 h; (c) 12 h; (d) 16 h; (e) 20 h; (f) 28 h in the domain 3100–2700 cm^{-1} (arrows on the spectra indicate decreasing absorbances)

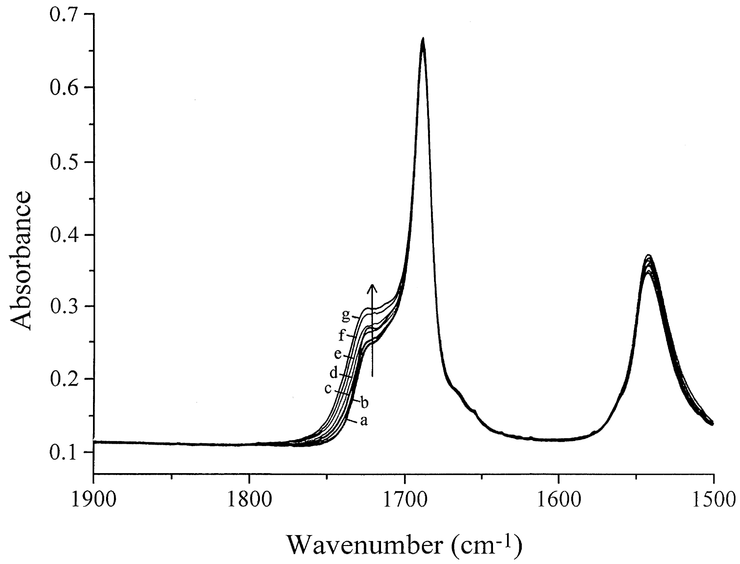


Figure 2 Evolution of the i.r. spectrum of an ETHDI film photooxidized at long wavelengths: (a) initial; (b) 8 h; (c) 12 h; (d) 16 h; (e) 20 h; (f) 24 h; (g) 28 h in the domain 1900–1500 cm^{-1} (arrows on the spectra indicate increasing or decreasing absorbances)

EXPERIMENTAL RESULTS

Analysis of changes in the i.r. spectra requires that the bands composing the spectrum of the polymer before irradiation are identified. The attribution of the bands of the aliphatic urethane segments have been presented previously in the case of the oligourethane HDI-BDO, which does not contain polyether segments[1]. The main spectral features of the polyether component (PTMG) are presented in *Table 1*.

Irradiation was carried out in two different regions: long wavelength irradiation at $\lambda > 300$ nm and short wavelength at $\lambda = 254$ nm. As detailed below, the first results were obtained in conditions of long wavelength irradiation. For practical reasons, the samples had to be irradiated in the form of thin films which permitted us to analyse evolution of the chemical structures by i.r. spectrometry in transmittance mode. As a consequence, irradiation had to be limited to moderate extents of oxidation because the samples were becoming too brittle and were destroyed by the air flux of the fans in the aging device. For that reason, the polymer samples were also submitted to irradiation in a different unit equipped with low pressure mercury lamps that do not require ventilation. The light sources emit a monochromatic light at 253.7 nm. Aging carried out in such a device is not relevant to natural aging if the oxidized polymer presents different photochemical behaviour when exposed to ‘short’ or ‘long’ wavelengths. This situation is often encountered in the case of polymers having aromatic chromophores[8,9]. The polymer whose photooxidation is reported in the present article is not expected to present a wavelength dependent photooxidation mechanism, at least as far the polyether component—the most reactive—is concerned. We have confirmed experimentally this important point.

Irradiation of ETHDI at long wavelengths

Thin films (thickness $\approx 5\,\mu$m) were irradiated in the SEPAP 12.24 unit. Irradiation times were limited to 28 h because oxidation led to the deterioration of the sample for longer times. Important modifications of the infrared spectra of the samples were recorded after irradiation.

In the region of the i.r. spectrum corresponding to C–H stretching vibrations, a noticeable decrease of intensity of the bands at 2796 and 2918 cm^{-1} attributed to the methylene groups α to the oxygen atom of the ether function was observed. The intensity of the bands at 2941 and 2857 cm^{-1} corresponding to the methylene groups α to oxygen also decreased (*Figure 1*).

In the carbonyl domain (*Figure 2*), a band with an absorption maximum at 1725 cm^{-1} increased. This band indicated the formation of formates[3] (C=O stretching). The band at 1534 cm^{-1} (akin to the amide II mode found in polyamides[7]) remained unchanged during irradiation.

Figure 3 shows that, in the domain between 1500 and 900 cm^{-1}, the height of the band at 1368 cm^{-1}, corresponding to the (CH_2) bending vibration of the methylene groups α to the oxygen atom of ether function, decreases. The absorption band at 1114 cm^{-1} corresponding to the antisymmetric (C–O–C) stretching mode was also observed to decrease, whereas an absorption band increased at 1175 cm^{-1}. This band was attributed to the formation of formates (C–O stretching). This evolution led to the formation of an isosbestic point at 1145 cm^{-1}. No change in the intensity of the band at 1264 cm^{-1} (stretch–open mode or ‘amide III’) was noted.

The evolution of the i.r. spectra of ETHDI samples irradiated for 28 h in the SEPAP 12.24 unit corresponded to a decrease by 60% of the absorption bands of the polyether component. No modification of the absorption bands attributed to the urethane component was observed within the 28 h irradiation.

Irradiation of ETHDI at short wavelength

Three different periods had to be discerned:

(1) during the first 4 h of irradiation the evolution of the i.r. spectra were similar to those reported in the case of the long wavelength irradiations, which confirmed that the photooxidation mechanism of the polyether component is not wavelength dependent;

(2) between 4 and 16 h, concerning the urethane functions, a weak decrease of the ‘amide II’ and ‘amide III’ bands was observed. In the carbonyl domain, the shape of the oxidation band peaking at 1725 cm^{-1} was slightly modified by the decrease of the carbonyl band of urethane groups at 1721 cm^{-1};

(3) during the following 24 h upon irradiation (16–40 h)

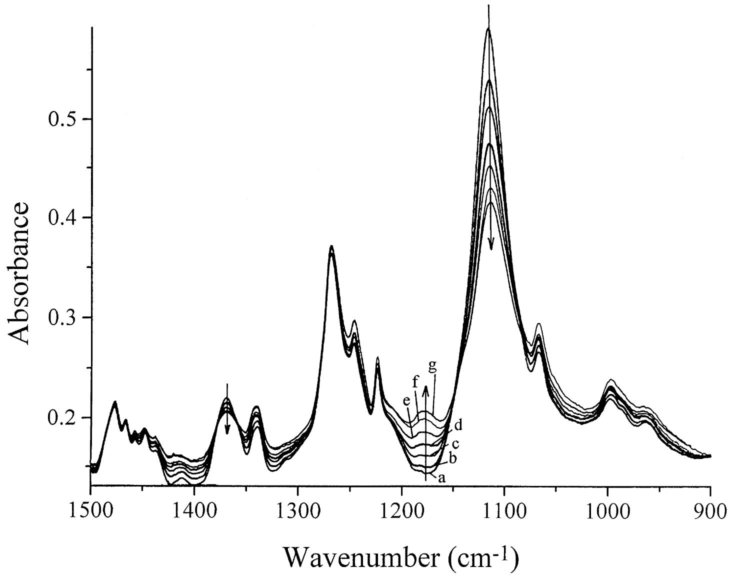


Figure 3 Evolution of the i.r. spectrum of an ETHDI film photooxidized at long wavelengths: (a) initial; (b) 8 h; (c) 12 h; (d) 16 h; (e) 20 h; (f) 24 h; (g) 28 h in the domain 1500–900 cm^{-1} (arrows on the spectra indicate increasing or decreasing absorbances)

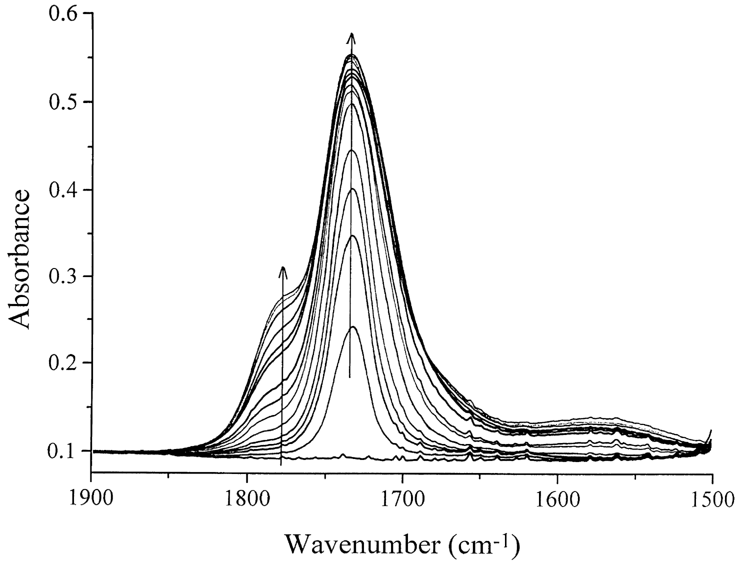


Figure 4 Evolution of the i.r. spectrum of a PTMG film photooxidized at $\lambda = 254$ nm (spectra recorded every 4 h between 0 and 60 h of irradiation) in the domain 1900–1500 cm^{-1} (arrows on the spectra indicate increasing or decreasing absorbances)

the disappearance of the absorption bands of the polyether component was almost total after 40 h. In the domain 1900–1500 cm^{-1}, a broadening of the carbonyl oxidation band and a decrease of the height of the oxidation band at 1725 cm^{-1} were simultaneously observed. A weak band at 1604 cm^{-1}, attributed previously[1] to the (NH_2) deformation band of primary urethane groups, was also observed to increase. This behaviour indicated the commencement of the oxidation of the urethane functions.

When irradiations were carried out for long irradiation times (145 h), one observed changes in the i.r. spectra resulting from the oxidation of the urethane groups. These modifications were similar to those reported previously in the case of an ESHDI polymer based on an aliphatic diisocyanate HDI and a polyester (poly(tetramethylene ethylene adipate)) soft segment[1]. Modifications of the i.r. spectra were characterized by a decrease of the 'amide III' band at 1264 cm^{-1} and the increase of absorbance between 1300 cm^{-1} and 1450 cm^{-1} corresponding to the (CH_2) vibrations. In the domain 1900–1500 cm^{-1} the decrease of the 'amide II' band at 1534 cm^{-1} and the resulting formation of a (NH_2) band at 1604 cm^{-1} were observed. The decrease of the absorption bands at 1685 cm^{-1} and 1721 cm^{-1} gave evidences for the decarboxylation of urethane groups.

As noted above, the mechanisms of polyether photooxidation have been deduced from the results obtained with PTMG[3]. These results were limited to the formation of formates. No detailed study exists on the mechanism of the secondary reactions by which formates are photooxidized once formed by photooxidation of PTMG. For this reason, an experimental study on the ultimate photooxidation of PTMG upon irradiation at 253.7 nm has been carried out.

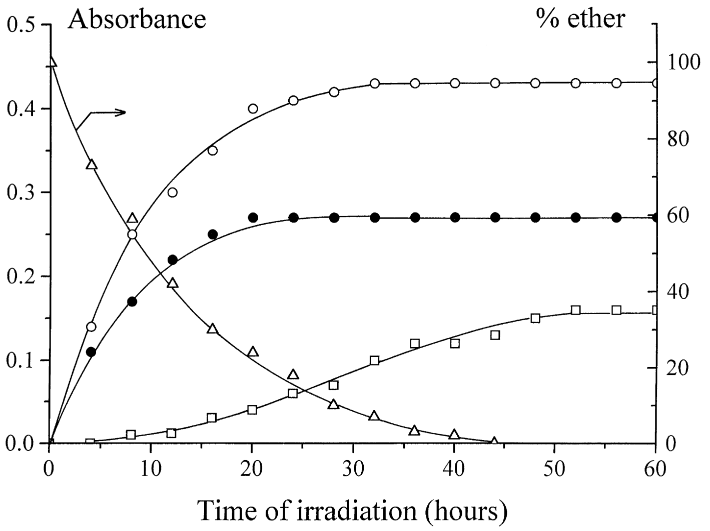


Figure 5 Evolution of absorbance as a function of irradiation time for a PTMG film photooxidized at $\lambda = 254$ nm: (○) 1725 cm^{-1}; (●) 1175 cm^{-1}; (□) 1780 cm^{-1} and decrease of the absorbance of ether groups (△) (given as the percentage of the initial concentration)

Irradiation of PTMG at short wavelength

Analysis of the oxidation of the polymeric matrix by FT*i.r. spectroscopy.* Poly(tetramethylene glycol) was irradiated in the form of thin films spread on KBr windows. The thickness of the obtained films was around 6 microns. The modifications of the *FT*i.r. spectra of photooxidized samples showed that the absorption bands of all the methylene groups decreased dramatically, reaching a total disappearance after 45 h.

Formation of a broad band in the region of the i.r. spectrum between 3600 and 3200 cm^{-1} was obseved. An absorption maximum appeared at 3350 cm^{-1} and shifted to 3300 cm^{-1} at longer irradiation times. The shape of the band was progressively modified because the absorption of the methylene groups and that of the OH terminal groups decreased.

In the carbonyl domain, the absorption band of formates at 1725 cm^{-1} appeared during the first hour. The rate of formation of formates decreased for longer irradiation times, and the maximum of the absorption band was slowly shifted to 1731 cm^{-1}. For longer irradiation times, one observed the appearance of an absorption at 1780 cm^{-1} (*Figure 4*) as a shoulder to the carbonyl band.

In the domain 1500–900 cm^{-1}, the absorption bands at 1368 and 1114 cm^{-1} were observed to increase. The absorption band of the formates at 1175 cm^{-1} appeared.

The kinetics of formation of formates, plotted as the increase of absorbance at 1175 and 1725 cm^{-1}, are given in *Figure 5*. Plotting the variations of absorbance at 1175 cm^{-1} to determine the formation of formates gave a curve with a shape similar to that determined by plotting the variations of absorbance at 1725 cm^{-1}. *Figure 5* shows also the variations of the absorbance at 1780 cm^{-1}, and the diminution of the concentration of the initial ether groups. The disappearance of ether groups was calculated by measuring the height of the bands at 1368 and 1114 cm^{-1}. The curve showing the disappearance of ether groups fits exactly that determined from the decrease of methylene absorption.

Considering the decrease of the ether groups, it is observed that almost all the ether groups have disappeared after 45 h.

The concentration of formates reached a maximum after 20 h, whereas the ether groups had not totally disappeared, indicating that a stationary concentration of formates was established.

The kinetic curve for the product at 1780 cm^{-1} shows that this product appeared after an induction period around 20 h of irradiation and reached a maximal concentration after 50 h.

When irradiations were carried out for a longer time, after the ether groups had totally disappeared, a dramatic decrease of all the absorption bands composing the spectra of the degraded samples was observed, including those corresponding to the formates. The infrared analysis of the solid matrix was then completed by an analysis of the volatile products formed upon irradiation.

Analysis of the gas phase by FT*i.r. spectroscopy.* The i.r. spectra of the gas phase were recorded every 2 h. The spectra presented several absorption bands whose intensities increased with irradiation times:

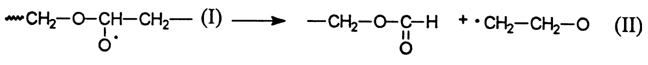
(1) a narrow band peaking at 949 cm^{-1}, which permitted us to identify the product as ethylene;
(2) two bands at 1750 cm^{-1} and 1183 cm^{-1}, corresponding to methyl formate; and
(3) the formation of water, carbon monoxide and dioxide.

DISCUSSION

Mechanism of PTMG photooxidation

Despite the fact that it does not absorb radiation of wavelengths longer than 200 nm, PTMG is very sensitive to photooxidation. The photoinitiation of the degradation can be caused by internal or external impurities resulting from the thermal history of the polymer, which absorb u.v. light and produce radicals which react further with the polymer[10].

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}) (reaction 1):

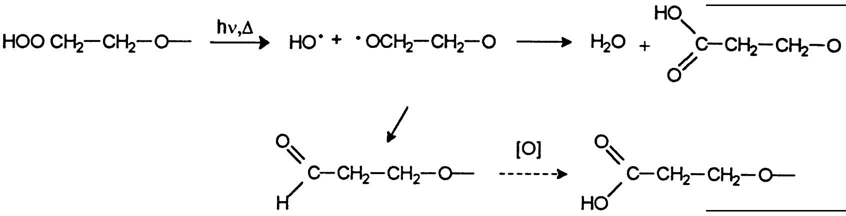


$$\sim CH_2-O-\underset{O^{\bullet}}{\underset{|}{CH}}-CH_2- \ (I) \longrightarrow -CH_2-O-\underset{O}{\underset{\|}{C}}-H + {}^{\bullet}CH_2-CH_2-O \quad (II)$$

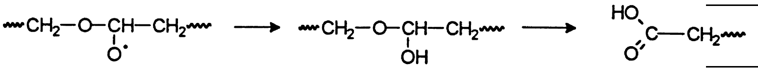
A primary radical (II) •CH_2–CH_2–O– is obtained in this reaction. A possible route of decomposition of this radical is an oxidation leading to primary hydroperoxides.

$$\cdot\,CH_2{-}CH_2{-}O{-}\ (II)\ \xrightarrow{O_2,\ PH}\ HOOCH_2{-}CH_2{-}O{-}$$

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[12].



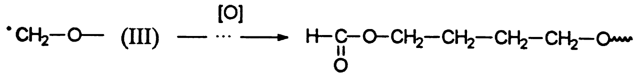
From the shape of the carbonyl band of photooxidized PTMG, it is observed that only very weak concentrations of carboxylic acids are formed. The oxidation pathway of radical (II) to give carboxylic acid has then to be considered as minor, especially if one considers that carboxylic acids can be also formed by oxidation of hemiacetals obtained from the alkoxy radicals (reaction 2).



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

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

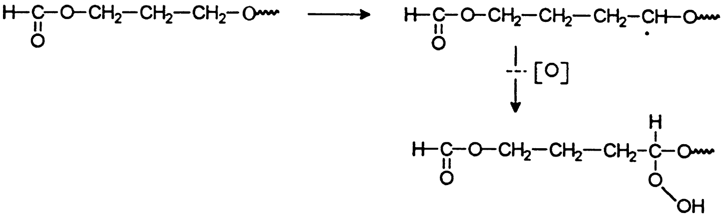
This reaction leads to the formation of ethylene, whose the formation has been observed by i.r. analysis of the gas phase (949 cm^{-1}). The primary radical (III) that is obtained by this reaction may be oxidized to give a formate.



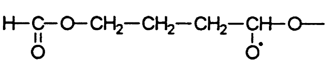
$$\cdot CH_2{-}O{-}\ (III)\ \xrightarrow{[O]}\ H{-}\underset{\underset{O}{\|}}{C}{-}O{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}O\sim$$

This constitutes a supplementary route of formation of formates.

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



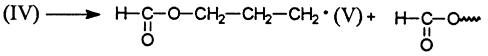
By decomposition of the hydroperoxide, an alkoxy radical (IV)



$$H{-}\underset{\underset{O}{\|}}{C}{-}O{-}CH_2{-}CH_2{-}CH_2{-}\underset{\underset{O\cdot}{|}}{CH}{-}O{-}$$

is obtained.

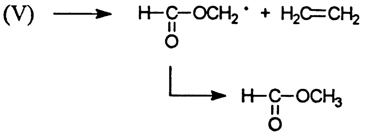
The analysis of the gas phase indicates the formation of methyl formate (1750/1183 cm^{-1}) and ethylene. The formation of these products involves the decomposition of radical (IV) by homolysis of the C–C bond in a β scission process which leads to a primary alkyl radical (V) and regenerates a formate.



$$(IV) \longrightarrow H{-}\underset{\underset{O}{\|}}{C}{-}O{-}CH_2{-}CH_2{-}CH_2\cdot (V) +\ H{-}\underset{\underset{O}{\|}}{C}{-}O\sim$$

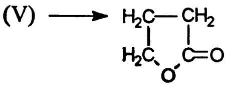
This evolution is in accordance with the kinetic aspects of the oxidation, since it is observed that formates reach a stationary state. By the repetition of this reaction, the chain can be considerably shortened.

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



$$(V) \longrightarrow H{-}\underset{\underset{O}{\|}}{C}{-}OCH_2\cdot + H_2C{=}CH_2 \qquad \longrightarrow H{-}\underset{\underset{O}{\|}}{C}{-}OCH_3$$

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

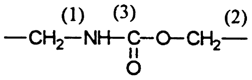


The infrared analysis of the polymeric matrix shows that this product is trapped, at least partially, in the polymer. It appears after a short induction period, whereas formates are detected from the early stages of the oxidative degradation of the polymer.

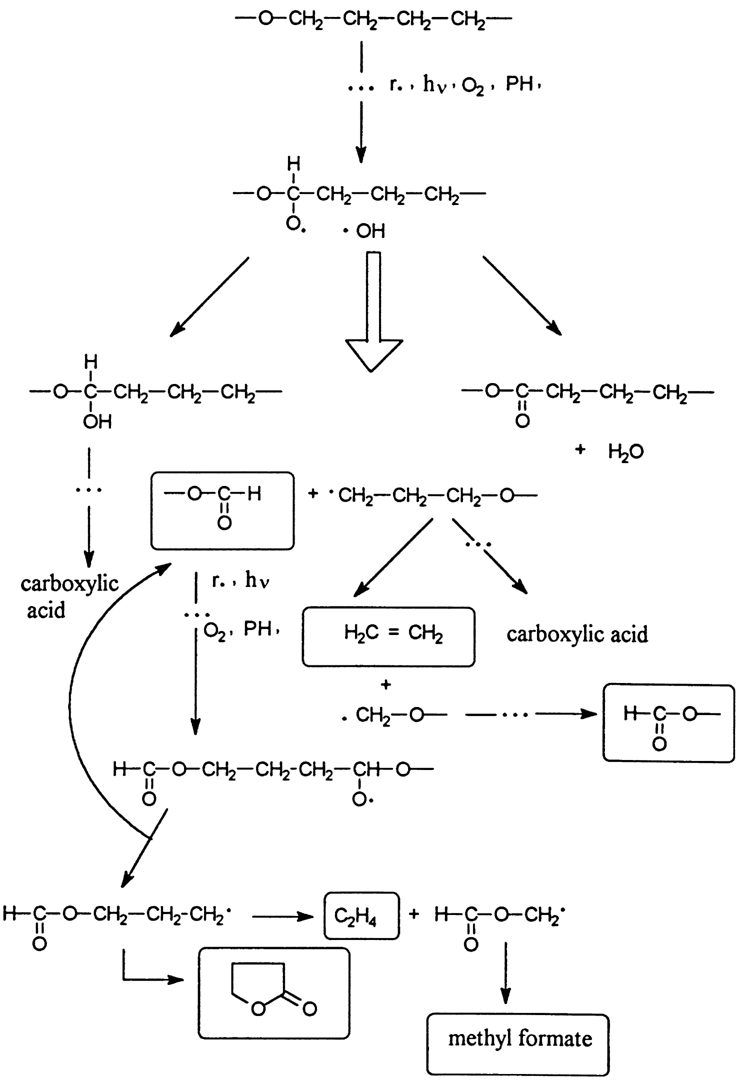
The photochemical evolution of PTMG is described here as involving a succession of reactions. Indeed, one must consider that most of these reactions can occur in a concerted manner. These reactions may be summarized by *Scheme 1*.

Photooxidation of ETHDI

Two different phases have to be considered. The first one corresponds to the oxidation of the polyether component, by far the most oxidizable, which leads to the total disappearance of the ether functions. In the second phase, the oxidation of the urethane component is observed. It is recalled that this reaction involves the oxidation of the methylene groups α to the NH[1].

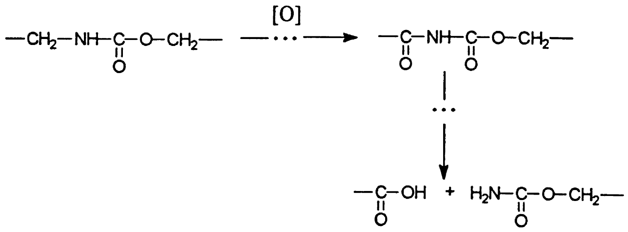


$$\overset{(1)}{{-}CH_2}{-}NH{-}\underset{\underset{O}{\|}}{\overset{(3)}{C}}{-}O{-}\overset{(2)}{CH_2}{-}$$



Scheme 1

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



$$-CH_2-NH-\underset{\overset{\|}{O}}{C}-O-CH_2- \xrightarrow{[O]} -\underset{\overset{\|}{O}}{C}-NH-\underset{\overset{\|}{O}}{C}-O-CH_2- \longrightarrow -\underset{\overset{\|}{O}}{C}-OH + H_2N-\underset{\overset{\|}{O}}{C}-O-CH_2-$$

Short wavelength irradiation can provoke a direct homolysis of the C–N bond[1], C–C bond[2] and N–C bond[3]. A decarboxylation of the urethane groups is observed, and primary amines are formed.

CONCLUSION

The photooxidation of polyether based aliphatic polyurethanes provides evidence for a dual mechanism.

The polyether component is very sensitive to the induced photochemical oxidation. The oxidation of the polyether segments can be studied using the photooxidative degradation of polytetramethyleneglycol as a model. Oxidation leads to the formation of formates as the main photoproducts. Once formed formates can be reoxidized and decompose to form low molecular weight products (including ethylene and methyl formate) that can migrate from the polymeric matrix towards the surrounding atmosphere. The reaction leading to the formation of formates produces a primary alkyl radical that decomposes to form ethylene and regenerates a formate, which is in turn oxidized.

These reactions cause a complete loss of all the infrared absorption bands of both the ether groups and the products formed by photooxidation of the ether groups.

The modifications of the infrared spectrum of the urethane groups, which are far less oxidizable, can be observed once the absorption bands corresponding to the polyether and the products of photooxidation of the soft segments have disappeared. The results obtained confirm the mechanism of photooxidation of the aliphatic urethane formerly proposed[1].

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