

Infrared analysis of the photochemical behaviour of segmented polyurethanes

3. Aromatic diisocyanate based polymers

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FTi.r. studies of the photooxidation of aromatic diisocyanate (MDI) based polyurethanes are presented. The results obtained show that the photochemical evolution of the aromatic moieties involves a dual mechanism: one is a photo-Fries type reaction whereas the other results in an induced oxidation of the central methylene group of MDI. Direct evidences that these reactions occur are obtained on the basis of the modification of the spectral features resulting from both the rearrangement of urethane functions and the formation of oxidized groups.
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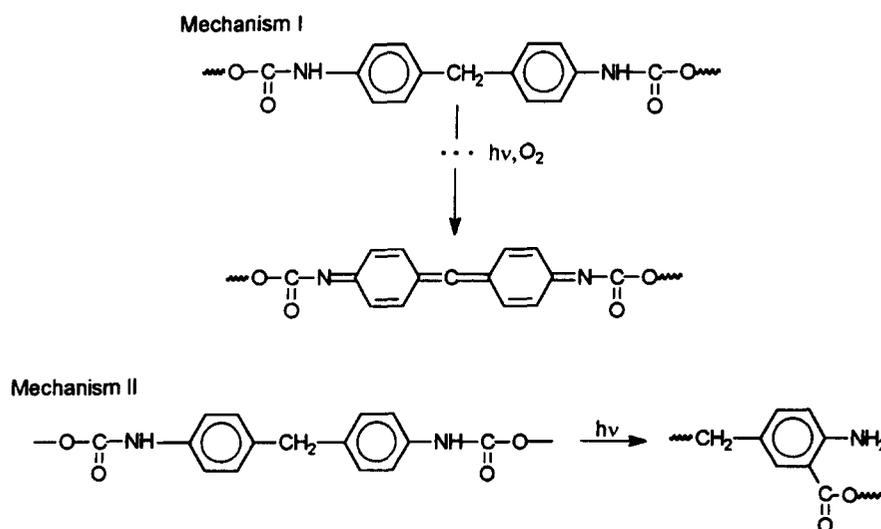
INTRODUCTION

The photooxidation of polyurethanes based on aromatic diisocyanates has been subject of active interest within the last 20 years. These polymers rapidly degrade and undergo yellowing on exposure to u.v. light. Numerous studies have then concerned the u.v. induced photoyellowing and the photochemical processes responsible for the photo-discolouration of these materials have been investigated extensively. It is generally admitted that the yellowing of polyurethanes based on 4,4'-diphenylurethane diisocyanate (MDI) involves two main pathways corresponding to the mechanisms (I) and (II) of Scheme 1^{1–11}. Mechanism I is based on a series of reactions producing quinoid-type

structures by initial oxidation of the central methylene carbon of the bis-arylcarbamate moiety. Mechanism II depicts a classical photo-Fries type rearrangement.

Mechanism I was initially proposed by Schollenberger and coworkers^{1,2}. This mechanism was deduced from the comparison of the behaviour of MDI-based polymers to that of polyurethanes synthesized with antiquinoid diisocyanates. As an example, it has been shown that an isopropyl group used in place of the central methylene group was yielding colour stable polyurethanes.

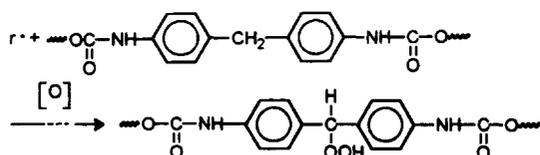
More recently, it has been confirmed in our group⁴ that the photooxidation of MDI based polyurethanes involved the oxidation of the central methylene group to give the formation of hydroperoxides. It was anticipated that these



Scheme 1

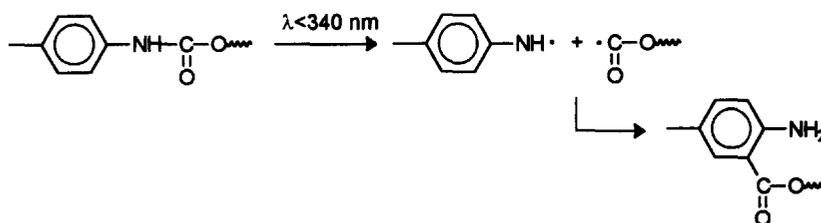
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hydroperoxides were the primary products of the reaction leading to the formation of quinone-imides:



Direct evidence of hydrogen abstraction on the methylene group has been obtained by Hoyle *et al.*¹¹ who have characterized, by flash photolysis of aromatic polyurethanes in solution, the formation of a substituted diphenylmethyl radical.

Laser flash photolysis measurements have been also conducted in order to characterize the N–C cleavage involved in the photo-Fries rearrangement¹¹. This confirmed previous results obtained in our group⁴. Our results had shown that a non-oxidative reaction led to the photodiscolouration of the polymer by direct excitation of the chromophoric groups at wavelengths below 340 nm. By analogy to the work carried out by Beachell and Chang^{5,6}, it had been suggested that u.v. irradiation could provoke a scission of the N–C bond followed by the migration of the radical to the ortho position of the aromatic ring with an hydrogen exchange. This reaction led to the formation of photoproducts with an absorption extending up to the visible region:



In this series of articles, we report on experiments carried out on polyurethanes with structures based on various combinations of aliphatic (HDI) or aromatic (MDI) diisocyanates and polyester (ES) or polyether (ET) soft segments. Four model polymers were studied: ESHDI, ESMDI, ETHDI and ETMDI.

In parts 1 and 2^{12,13}, we have examined the photo-oxidation of ESHDI and ETHDI polymers. The photoproducts formed upon irradiation of these polymers have been characterized by FTi.r. spectrometry. Mechanisms accounting for the formation of the different photoproducts have been proposed. It has been confirmed that the polyester soft segments were rather photostable, and that the oxidative degradation of the ESHDI polymer resulted from the oxidation of the aliphatic urethane segments. Our results have confirmed the high photosensitivity of the polyether segments participating to the structure of ETHDI¹⁴. In these investigations, a peculiar attention has been paid to the ultimate oxidation of the polyether segments.

In the present article, we report on the photooxidation of aromatic diisocyanate-based polyurethanes. Two polymers are studied, ESMDI and ETMDI. Our efforts concentrate on obtaining direct evidence of both the photo-Fries mechanism and the oxidation of the central methylene carbon from analysis of the changes in the FTi.r. spectra.

EXPERIMENTAL

Preparation of the polymers

ESMDI and ETMDI polymers were prepared following the technique of prepolymer synthesis¹⁵. Details on the experimental method have been given previously^{12,13}. Two polyethers with different molecular weights were used as macrodiols (ET: polyoxytetramethylene glycol with $\overline{M}_n = 650 \text{ g l}^{-1}$ or 2000 g l^{-1}) and one polyester (ES: polytetramethylene adipate glycol) with a molecular weight $\overline{M}_n = 2000 \text{ g l}^{-1}$. Four parts of diisocyanate (MDI) were needed for 1 part of macrodiol (ES or ET) and 3 parts of 1,4-butanediol (used as chain extender).

The two polymers ESMDI and ETMDI were studied in the form of free films with a thickness around 8–10 μm .

Irradiation and spectroscopic analysis

Irradiation conditions and the material used for analysing the spectroscopic evolution of the polymeric samples have been described previously^{12,13}.

EXPERIMENTAL RESULTS

Analysis of the photooxidation of ETMDI

Irradiation of ETMDI films at $\lambda > 300 \text{ nm}$ in the presence of oxygen led to important modifications of the IR spectra of the exposed samples. From our previous observations on the photooxidation of the polyether–aliphatic diisocyanate based polyurethanes (ETHDI), the modifications of the IR

spectra could be easily separated into those concerning the evolutions of the polyether component and those dealing with the urethane functions.

Reactivity of the polyether segments. All the absorption bands characteristic of the polyether segments decreased on irradiation:

- in the C–H stretching vibrations domain $3000\text{--}2800 \text{ cm}^{-1}$, one observed an important decrease of the bands attributed to the vibrations of the methylene groups^{16–18};
- in the complex region of the C–O stretching vibrations, the intensity of the band peaking up at 1114 cm^{-1} attributed to the $\nu_a(\text{C–O–C})$ vibrations of the ether groups was strongly reduced on irradiation (Figure 1).

The decrease of the band at 1114 cm^{-1} coincided with the appearance of an absorption band with a maximum at 1174 cm^{-1} . In the domain of the C=O stretching vibrations, one observed the appearance of a band at 1725 cm^{-1} (Figure 2). One observed also the decrease of the C=O bands of the urethane groups ($1731/1703 \text{ cm}^{-1}$). The maxima at 1174 and at 1725 cm^{-1} were attributed to the formation of formates by oxidation of the polyether segments^{13,14}. As reported formerly¹³, these evolutions result from the oxidation of the polyether soft segments.

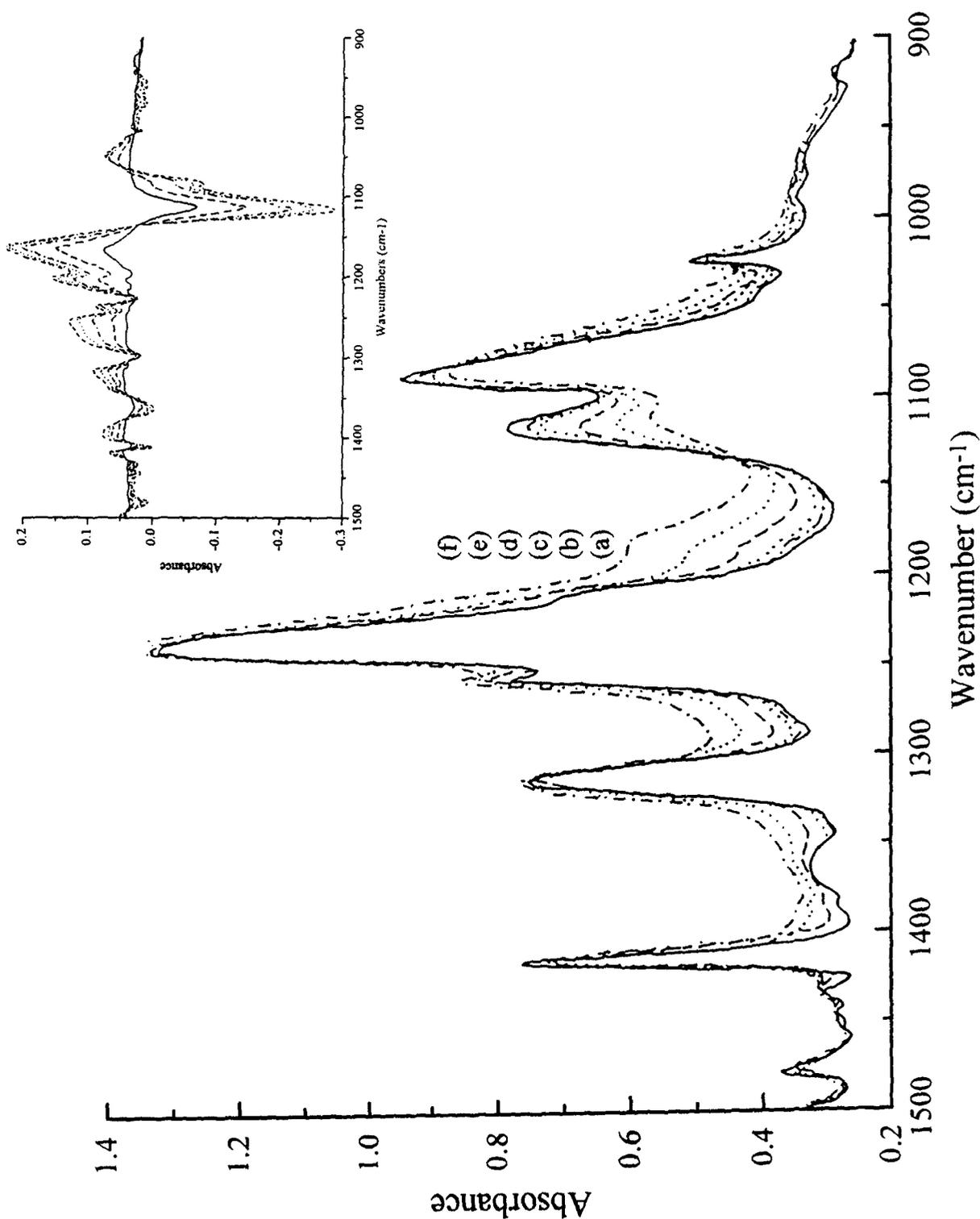


Figure 1 Evolution of the spectrum of an ETMDI sample on irradiation at long wavelengths ($\lambda > 300$ nm) in the domain 1500–900 cm^{-1} : (a) initial; (b) 15.8 h; (c) 23.7 h; (d) 45.1 h; (e) 67.7 h; (f) 91.6 h. Subtraction of the initial spectrum from the spectra of the photooxidized films is shown in the inset

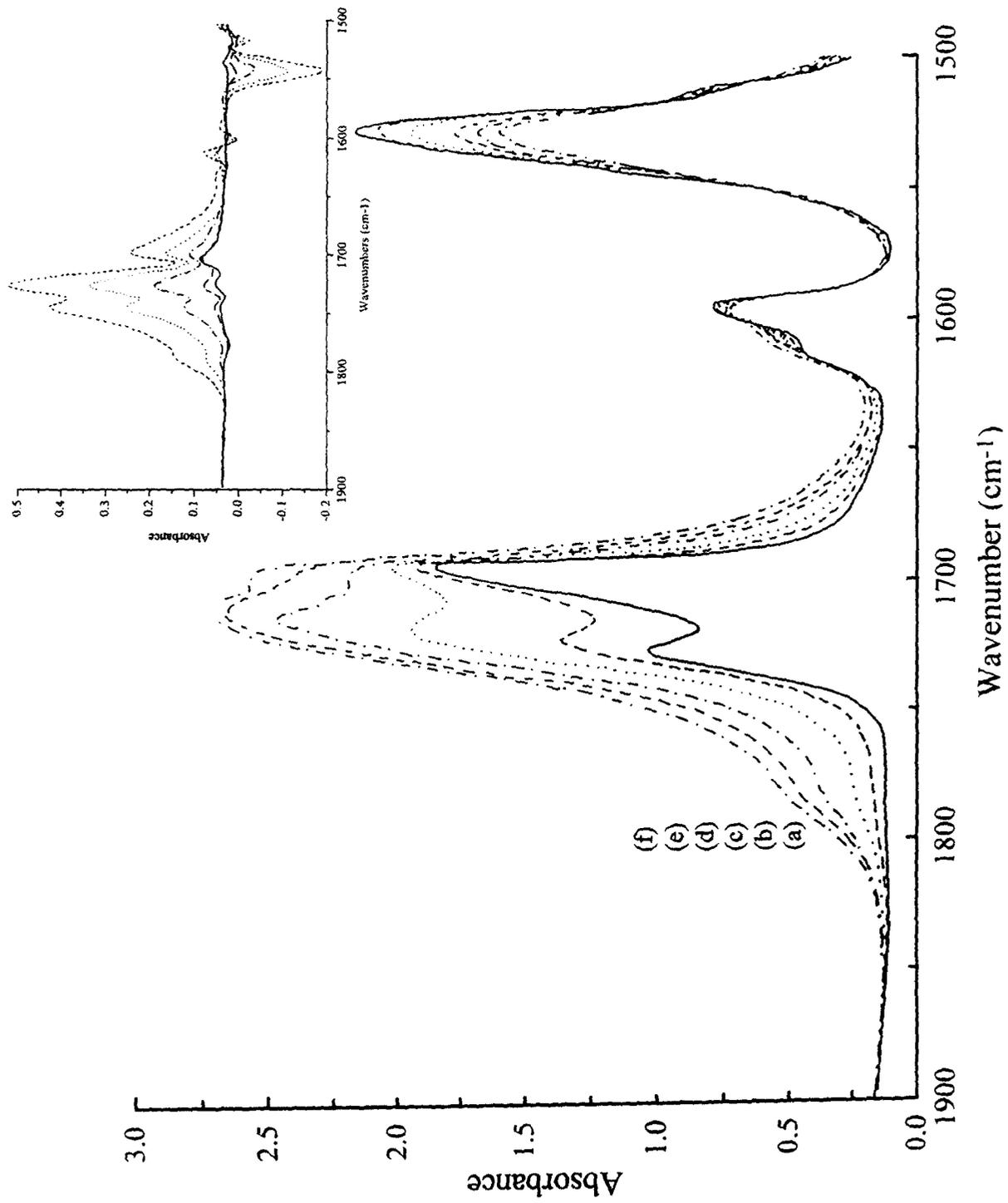


Figure 2 Evolution of the spectrum of an ETMDI sample on irradiation at long wavelengths ($\lambda > 300$ nm) in the domain $1900-1500$ cm^{-1} ; (a) initial; (b) 15.8 h; (c) 23.7 h; (d) 45.1 h; (e) 67.7 h; (f) 91.6 h. Subtraction of the initial spectrum from the spectra of the photooxidized films is shown in the inset

5h>The oxidation rates of ETMDI could be determined from the disappearance of the ether groups measured at 1114 cm^{-1} . Comparing the photooxidation rate of ETMDI to that of ETHDI samples formerly studied¹³ showed that the oxidation rate was more important in the case of the aromatic polymer. This result indicated that light absorption by the aromatic chromophores could induce the oxidation of the polyether segments.

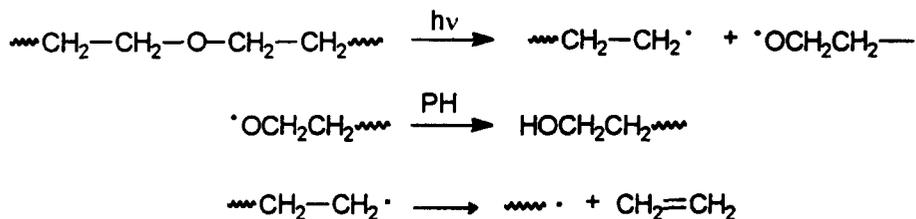
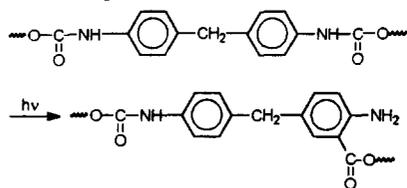
Influence of the molecular weight of the polyether segments. The IR evolutions of ETMDI 2000 and ETMDI 650 were compared on the basis of the decrease of the absorbance at 1114 cm^{-1} . It was observed a faster disappearance of the ether band in the case of the ETMDI 2000 than in the case of the ETMDI 650.

Reactivity of the urethane component. One observed that the photooxidation of ETMDI led to the decrease of all the absorption bands of the urethane component.

- Absorption bands characteristic of the urethane function: one observed a marked decrease of the height of the bands $\nu(\text{N-H})$ at 3331 cm^{-1} , $\nu(\text{C=O})$ free at 1730 cm^{-1} and bonded at 1703 cm^{-1} , amide II at 1534 cm^{-1} , amide III at 1225 cm^{-1} and amide V at 670 cm^{-1} .
- Absorption bands of the aromatic ring: the irradiation of ETMDI provoked the decrease of intensity of the band at 818 cm^{-1} and the appearance of a band with an absorption maximum at 840 cm^{-1} (Figure 3).

The IR spectra of aromatic compounds generally present two or several absorption bands of high intensity between 680 and 900 cm^{-1} , which correspond to the $\delta(\text{CH})$ out-of-plane vibrations of the C-H bonds. The frequency of the absorption maxima depends on both the number and the position of the substituents on the aromatic ring¹⁷. A single hydrogen, as in 1,2,4-tri-substituted rings, absorbs between 910 and 835 cm^{-1} .

It was then anticipated that these evolutions reflected the formation of a product resulting from a photo-Fries type mechanism according to:



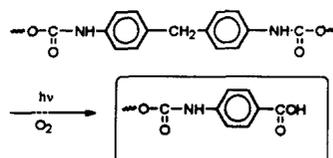
Chemical treatments. Photooxidized ETMDI samples were treated by SF_4 . Derivatization reactions using SF_4 were carried out to characterize the formation of carboxylic acids¹⁹. The reaction of SF_4 with carboxylic acids leads to the formation of acid fluorides²⁰. This reaction provoked the appearance of two bands at 1842 and 1802 cm^{-1} (Figure 4).

Former results²¹ had shown that the band at 1842 cm^{-1} indicated the formation of a fluorinated derivated from a saturated carboxylic acid whereas the band at 1802 cm^{-1} was resulting from the reaction with SF_4 of an aromatic carboxylic acid.

The formation of the saturated carboxylic acid could be unambiguously attributed to the oxidation of the polyether segments¹³ according to the reaction:



The presence of the aromatic acid gave a direct evidence of the oxidation of the bis-arylcarbamate moiety according to the reaction:



Analysis of the photolysis (in absence of oxygen) of ETMDI

Despite the fact that the modifications of the IR spectra of ETMDI samples irradiated in vacuum at $\lambda > 300\text{ nm}$ were very weak even for long irradiation times (1700 h), a decrease of all the absorption bands characteristic of the urethane segments could be observed. This evolution concerned the bands $\nu(\text{NH})$ at 3320 cm^{-1} , amide I at 1534 cm^{-1} , amide II at 1233 cm^{-1} , $\nu(\text{C=O})$ at 1702 cm^{-1} and $\nu(\text{C=C})$ at 1597 , 1505 and 1404 cm^{-1} .

As observed in the case of the photooxidation, the intensity of the band at 818 cm^{-1} decreased whereas a band at 840 cm^{-1} appeared.

On the basis of these modifications of the IR spectra, it could be anticipated that a photo-Fries type rearrangement occurred in the conditions of vacuum photolysis.

Several absorption bands appeared at 3470 , 1340 and 1080 cm^{-1} , indicating the formation of hydroxylated photoproducts. A weak decrease of the intensity of the ether band at 1114 cm^{-1} was observed to occur throughout vacuum photolysis.

The formation of hydroxylated products may be explained by a hydrogen abstraction by the alkoxy radicals formed by homolysis of the ether groups. This reaction could also explain the formation of ethylene, which was detected by analysis of the gas phase¹².

Analysis of the photooxidation of ESMDI

A decrease of the intensity of the absorption bands attributed to the polyester soft segments was observed. The recorded evolutions had a weak amplitude. It is worth recalling that, in the case of aliphatic polyurethanes ESHDI, no modification of the ester bands had been noted¹¹.

An important decrease of the urethane bands was observed, which concerned the amide II band at 1534 cm^{-1} , the carbonyl bands at 1731 and 1703 cm^{-1} and all the urethane bands between 1500 and 900 cm^{-1} . In

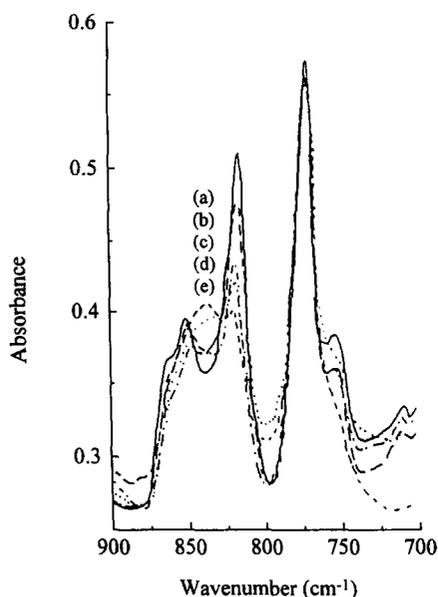


Figure 3 Evolution of the spectrum of an ETMDI sample on irradiation at long wavelengths ($\lambda > 300$ nm) in the domain 900–700 cm^{-1} : (a) initial; (b) 15.8 h; (c) 23.7 h; (d) 45.1 h; (e) 67.7 h

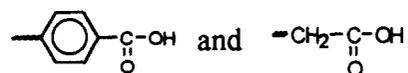
the carbonyl domain, a broad band appeared between 1850 and 1650 cm^{-1} (Figure 5).

Plotting the differences of spectra permitted us to observe an absorption maximum at 1790 cm^{-1} , but the very rapid diminution of the height of the urethane bands prevented from observing any absorption maximum between 1680 and 1750 cm^{-1} .

The modifications of the spectra recorded between 900 and 650 cm^{-1} were similar to those reported above in the case of ETMDI, and showed that the number of substituents on the aromatic rings was increasing on irradiation, which indicates that a photo-Fries reaction could occur.

Treatments of photooxidized samples by SF_4 provoked the decrease of the carbonyl absorbance and led to the formation of two well resolved bands at 1803 and 1841 cm^{-1} , indicating that photooxidation had produced

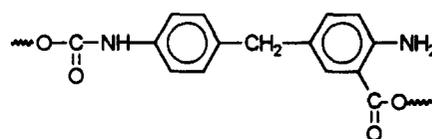
aromatic and aliphatic carboxylic acids (Figure 6):



Analysis of the photolysis of ESMDI

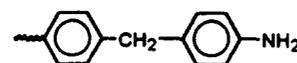
Only weak modifications were observed, even for long irradiation times (1200 h in the SEPAP 12.24). Plotting the difference of spectra facilitated the determination of the spectral evolutions, which were clearly resulting from the homolysis of the N–C bonds.

Comparison with the spectrum of methyl anthranilate permitted the increase of absorbance observed at 1688 cm^{-1} to be attributed to the formation of a product resulting of a photo-Fries reaction and presenting the structure:



A weak absorption was also observed at 1608 cm^{-1} , which corresponded to a $\delta(\text{NH}_2)$ band.

Absorption bands were also appearing at 1530, 1468 and 1174 cm^{-1} . The comparison of these evolutions to the spectrum of dianiline urethane showed a good fit, which permitted us to prove that a primary aromatic amine was formed on photolysis of the ESMDI samples:



Reactions involving the photochemical homolysis of N–C bonds were confirmed from the observation of the decrease of the initial bands at 815 cm^{-1} and the concomitant appearance of a band at 835 cm^{-1} , which

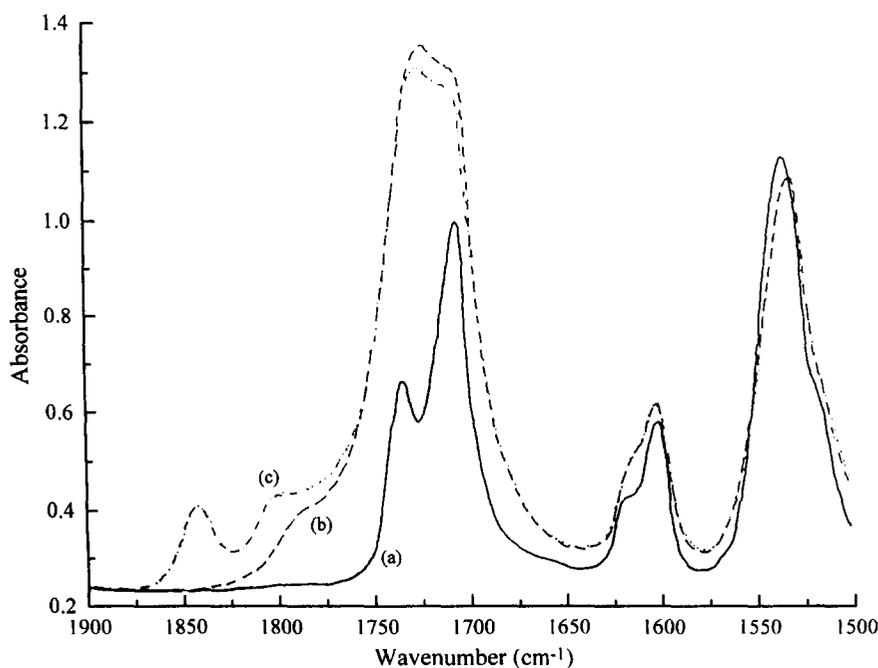


Figure 4 Effect of SF_4 treatment on an ETMDI sample after photooxidation: (a) initial; (b) after 71 h of irradiation; (c) after SF_4 reaction

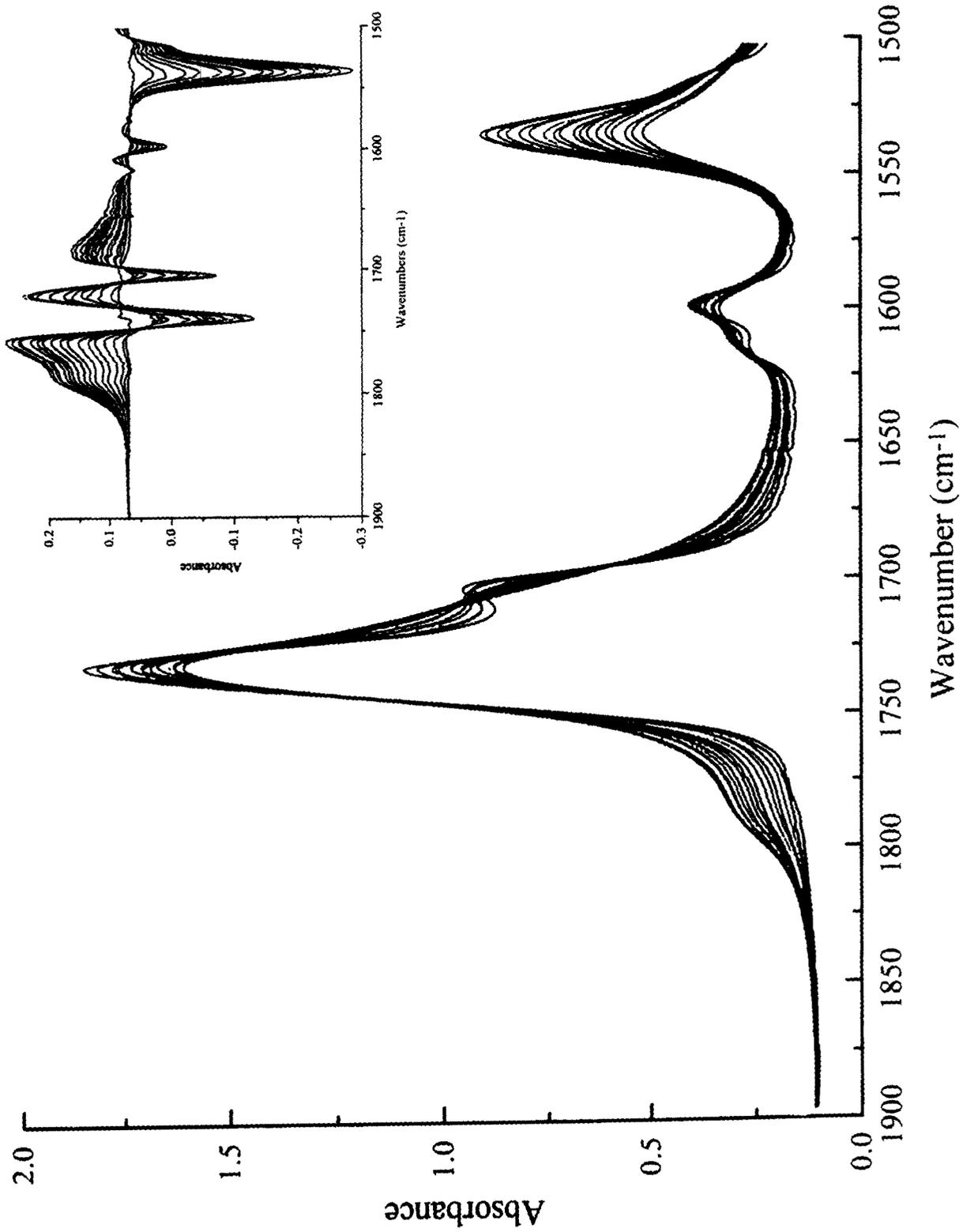
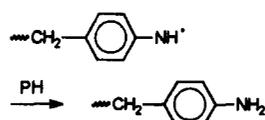


Figure 5 Evolution of the spectrum of an ESMDI sample on irradiation at long wavelengths ($\lambda > 300$ nm) in the domain 1900–1500 cm^{-1} ; spectra recorded every 4 h from 0 to 64 h of irradiation. Subtraction of the initial spectrum from the spectra of the photooxidized films is shown in the inset

radicals (I) lead to an aromatic amine:

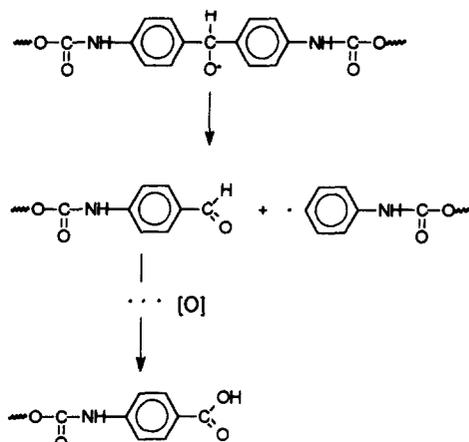


When irradiations are carried out in the presence of oxygen, the behaviour of the polymers is quite different.

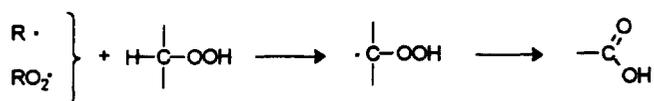
The photo-Fries products whose formation is detected by u.v.-visible spectrophotometric analysis are photooxidized, which contributes to the decrease of absorbance in the visible range.

In the case of polycarbonate, it has been shown that the photooxidation of the photo-Fries products was leading to the formation of acidic groups²⁴.

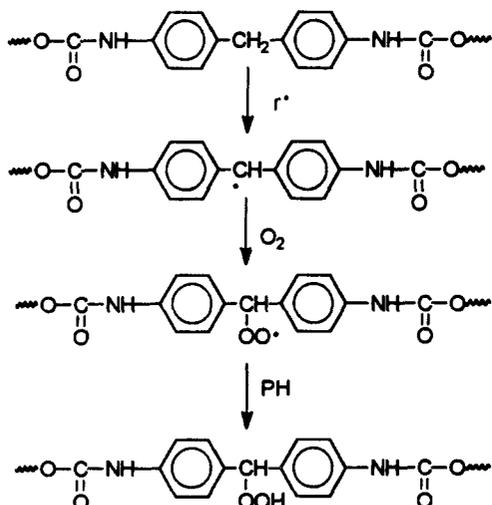
An oxidation of urethane segments occurs. This reaction involves a radical attack on the central methylene carbon of the aromatic structures. Subsequent oxygen addition



Another mechanism that could explain the formation of aromatic carboxylic acids involves a direct decomposition of hydroperoxides, as recently proposed in the case of polyethylene oxidations²⁶:

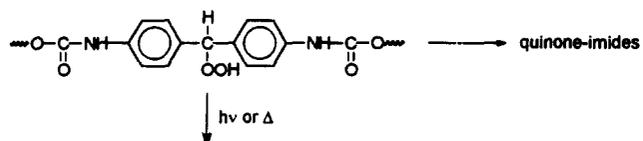


followed by hydrogen abstraction results in the formation of hydroperoxides according to:



The hydroperoxides are photo- and thermo-unstable and reach only low stationary concentrations⁴. The homolysis of the O-O bond gives an alkoxy radical. The evolution of this alkoxy radicals is responsible for the formation of several products, including aromatic carboxylic acids.

The β -scission of the alkoxy radical produces an aldehyde which is in turn oxidized in peracid and leads to benzoic acid²⁵ type end groups.

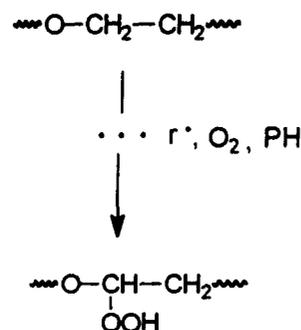


Evidence of the formation of the aromatic carboxylic acid is obtained from the result of SF₄ derivatization.

The formation of such acidic groups proves unambiguously that an induced oxidation of the central methylene occurs, which in turn proves that quinoid-type structures can be formed. This result supports the indirect proofs given previously² for the formation of these coloured photoproducts.

When the polymeric samples are irradiated under polychromatic light, the oxidation can be initiated either by radicals obtained in the photo-Fries reaction up to 340 nm, or by chromophoric defects that absorb at long wavelengths.

The oxidation of the soft segments is very rapid in the case of the polyether-based polyurethanes. The experimental results reported here confirm the high reactivity of the polyether segments. It is briefly recalled that oxidation involves the carbon atom in α -position of the ether groups:



Secondary hydroperoxides are formed and accumulate until important concentrations that can reach 0.8 M⁷. The main way of decomposition of the hydroperoxides is the

