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Comparison of Photooxidation and Thermal Oxidation Processes in Poly(ether imide)

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ABSTRACT: Thermal oxidation and photooxidation processes occurring in poly 2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride−1,3-phenylendiamine copolymer (ULTEM), were investigated and compared. The study aimed at finding possible differences in the oxidation pathways of this complex polymer by using the analytical power of MALDI techniques. ULTEM films were subjected to photooxidation by exposure at 60 °C in a UV accelerated chamber (Q-UV Panel) in atmospheric air, and the oxidative process was followed as a function of the exposure time. Relevant structural information on the photooxidized ULTEM species was extracted from the MALDI spectra. These data show the presence of polymer chains containing acetophenone, phenyl acetic acid, phenols, benzoic acid, phthalic anhydride, and phthalic acid end groups. The mechanisms accounting for the formation of photooxidation products of Ultem involve several reactions: (i) photocleavage of methyl groups of the *N*-methyl phthalimide terminal units; (ii) photooxidative degradation of the isopropylidene bridge of BPA units; (iii) photooxidation of phthalimide units to phthalic anhydride and phthalic acid end groups. Some of these cleavage pathways are specific for the photooxidation process and the oligomers deriving from them are absent in the thermal by oxidized Ultem samples, whereas the thermal cleavage of the diphenyl ether units appears to occur only in the thermal oxidation process.

Introduction

In the preceding paper,[1] we have reported the study of the thermooxidation process of ULTEM exposed at 350 °C in air. Here we have investigated the photooxidation processes occurring in this poly(ether imide).

Our study aimed at finding differences in the thermal oxidation and photooxidation pathways of this complex polymer by taking advantage of the analytical power of MALDI−TOF techniques (matrix assisted laser desorption ionization−time-of-flight mass spectrometry).

The distinct advantage of mass spectrometry over other analytical techniques is that it reveals the structure of the whole oligomer (molar mass, elemental composition, inner functional groups, end groups), allowing discrimination among possible oxidation mechanisms.

ULTEM films were subjected to photooxidation by exposure at 60 °C in a UV accelerated chamber (QUV Panel) in atmospheric air, and the oxidative process was followed as a function of the exposure time.

Valuable structural information on the photooxidized ULTEM species was extracted from the analysis of MALDI spectra. These results show the presence of polymer chains containing acetophenone, phenyl acetic acid, phenols, benzoic acid, phthalic anhydride, and phthalic acid end groups.

The mechanisms accounting for the formation of photooxidation products of ULTEM involve several reactions: (i) photocleavage of methyl groups of the *N*-methyl phthalimide terminal units; (ii) oxidative degradation of the isopropylidene bridge of BPA units; (iii) photooxidation of phthalimide units to phthalic anhydride and phthalic acid end groups.

Some of these cleavage pathways are specific for the photooxidation process and the oligomers deriving from them are absent in the thermal oxidized ULTEM samples, whereas the thermal cleavage of the diphenyl ether units appears to occur only in the thermal oxidation process.

Experimental Section

Materials. Basic materials were commercial products appropriately purified before use. Poly{2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride−1,3-phenylendiamine} copolymer (ULTEM) and 2-(4-hydroxyphenylazo)benzoic acid (HABA) were obtained from Sigma-Aldrich Chemical Co (Italy) and used as supplied.

MALDI—TOF Analysis. Matrix assisted laser desorptiotion ionization time-of-flight (MALDI−TOF) mass spectra were recorded in *linear and reflectron mode* by using a Voyager-DE STR instrument. The instrument is equipped with a nitrogen laser emitting at 337 nm and working in positive ion mode. The accelerating voltage was 20−25 kV, and the grid voltage and delay time (delayed extraction, time lag) were optimized for each sample to obtain the higher molar mass values. The laser irradiance was maintained slightly above threshold.

The resolution of the MALDI spectra reported in the text, ranges between 7000 and18000 full width at half-maximum (fwhm), depending on molar mass distribution, purity, and oxidation level of the samples. Mass accuracy, determined by external calibration, was lower than 200 ppm for masses in the range of 1000−2000 Da.

Sample preparation for MALDI analysis involved mixing of adequate volumes of the matrix solution (HABA, 0.1 M in THF/$CHCl_3$) and polymer solution (2 mg/mL in $CHCl_3$) to obtain a 1:1 or 1:3 ratio (sample/matrix, v/v). A solution of sodium trifluoroacetate (NaTFA) or potassium trifluoroacetate

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(KTFA) (1 μL of a 0.1 M) in $CHCl_3$ was added to permit a specific cationization. Then 1 μL of each sample/matrix mixture was spotted on the MALDI sample holder and slowly dried to allow matrix crystallization.

Photooxidative Degradation. The photooxidation was performed on films of ULTEM with a uniform thickness of 10−15 μm. The films were obtained by casting from 2% $CHCl_3$ solution. Photooxidative degradation of ULTEM was carried out on a QUV PANEL apparatus at 60 °C with continued exposure to UV radiation (UVA 340 lamps). At least two separate films were analyzed at each exposure time.

Results and Discussion

The present study is aimed at finding possible differences between the photooxidation and thermal oxidation pathways of ULTEM, by making a comparative investigation on the oligomers produced in the photooxidation and thermal oxidation of ULTEM.

A MALDI study of the photooxidation products generated in poly(ether imide) ULTEM has been previously reported,[2] and we make reference to that work for a detailed account on the photooxidation process. We have now obtained MALDI spectra at higher resolution ((8000 fhwm) with respect to those reported in the previous work[2] (2000 fhwm). Therefore, we have added here the new data when necessary to clarify further the photooxidation process. The peak assignments pertaining to the high-resolution MALDI spectra are reported in Table 1.

In Figure 1 is reported the MALDI spectrum in the region 1000−5000 Da of an ULTEM sample photooxidized at 60 °C for 72 h. The spectrum, obtained in reflectron mode, shows peaks with well-resolved isotopic distribution profiles.

The inset in Figure 1 displays an expanded portion of the peaks in the region of 1200−1800 Da, showing the presence of several new peaks with respect to the seven present in the original sample[1].

All these peaks correspond to sodiated ions of oxidized ULTEM oligomers, and they have been assigned (Table 1) to oligomers containing ULTEM repeat units terminated by different end groups.

The cyclic oligomer at 1207.3 Da (peak A, inset of Figure 1) and the peak at *m/z* 1576.4 Da (peak B, inset of Figure 1), corresponding to a linear oligomer with phenyl−phthalimide end groups at both ends are still present in the MALDI spectrum of the photooxidized ULTEM sample. Oligomers of type B appear with reduced intensity with respect to the original sample,[1] indicating the early occurrence of the photooxidation process. The most intense peak in Figure 1, appearing at *m/z* 1355.3Da, can be assigned to species C (Table 1). The latter are also present in the spectrum of the original ULTEM sample,[1] and correspond to sodiated ions terminated with phenylphthalimide at one end and phthalic anhydride groups at the other end.

In Figure 2 are reported enlarged portions of the MALDI spectra of an ULTEM sample irradiated at 60 °C for (a) 0, (b) 24, and (c) 72 h, which show the kinetics of the photooxidation process.

The intensity of the peak at *m/z* 1368.4.6Da, labeled D in Figure 2a, decreased dramatically upon irradiation (Figure 2b), until it peak disappeared after 72 h of irradiation (Figure 2c).

Peaks of type D correspond to oligomers bearing phenylphthalimide at one end and *N*-methylphthalimide terminal groups at the other end (mass series D, Table 1), and their disappearance is due to the photocleavage of the methyl group, as indicated in Scheme 1. This effect is due to a specific photodegradation reaction most likely occurring through the rupture of C−N bonds and loss of *N*-methyl groups and then producing ULTEM chains terminated with N−H phthalimide groups (Scheme 1).

Another noticeable in the MALDI spectra of ULTEM change induced by the irradiation can be observed in Figure 2a−c where the intensity of peaks labeled C and H (Table 1) increases noticeably with the exposure time.

Peaks of type C correspond to sodiated ions terminated with phenylphthalimide at one end and phthalic anhydride groups at the other end (mass series C, Table 1), and their increment is due to the photooxidation of phthalimide inner units to phthalic anhydride end groups (Scheme 1).

The appearance of phthalic anhydride end groups can be explained through the reaction pathway shown in Scheme 1, which is supported by a detailed photophysical study of the photocleavage of *N*-phenylphthalimide.[3] This process involves the photocleavage of the C−N bond to yield a diradical, which reacts with oxygen to give a peroxide intermediate. The decomposition of this species leads to the formation of oligomers with phthalic anhydride terminal groups.[3]

The presence of oligomers containing phthalic acid end groups (mass series H, Table 1), suggests that, at 60 °C, the hydrolysis of phthalic anhydride end groups is also occurring during the photooxidation process.

Inspection of Figure 2 also allows the identification of further features of the photooxidation process. Thus, in Figure 2, the growing intensity of peak C1 with exposure time is evident. Oligomers corresponding to these C1 peaks have the same structure as peaks of type C but they contain an additional oxygen atom (mass series C1, Table 1).

The introduction of one or more additional oxygen atoms into the ULTEM oligomers can be explained (Scheme 2) by the decomposition of the hydroperoxide I (formed by hydrogen abstraction from a methyl group of the isopropylidene unit [4] of ULTEM), to yield the tertiary alcohol structure II (Scheme 2).

In the previous study,[2] two isobaric structures were considered possible for these oligomers, because the mass spectrometric analysis is not able to distinguish between them. However, in a recent paper [5] the presence of structure II among the products from the γ-radiolysis of ULTEM was identified by NMR analysis.

This oxidation pathway is also observed for other oligomers (labeled G1, B1, B2, B3, and R1, in Table 1) which differ from oligomers of type C1 only by their end groups.

The importance of this particular photooxidation process is most evident in the case of linear oligomers of type B (Table 1), which are the most abundant species present in the original ULTEM sample.[1,2]

Pertinent sections of the MALDI spectra of an unexposed ULTEM films and of the same films after 24 h exposure are compared in Figure 3. The original peak B appears at 1575.4 Da in Figure 3a, whereas after 24 h of exposure (Figure 3b), the spectrum shows the appearance of the photooxidized oligomers. In fact, peak B is now accompanied by three peaks, B1, B2, and B3, 16 mass units removed from each other, corresponding to oligomers incorporating one, two, and three oxygen atoms in their structure (Table 1).

Table 1. Structural Assignments of Sodiated Ions Appearing in the MALDI−TOF Spectra of Photooxidized ULTEM Sample

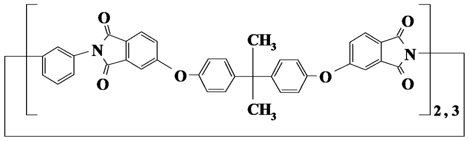
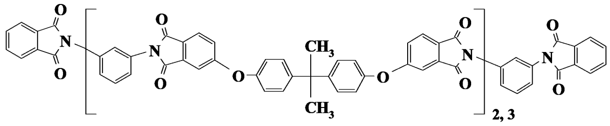
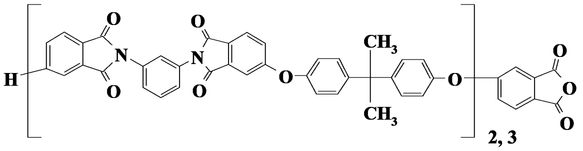
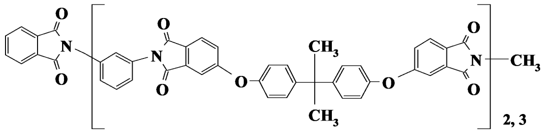
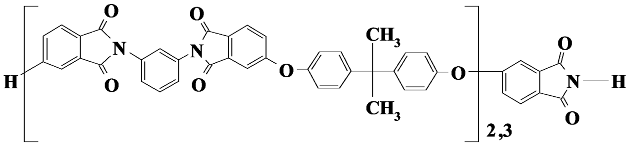
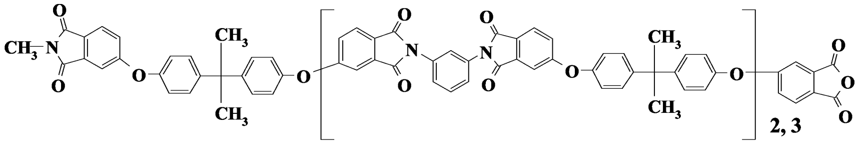
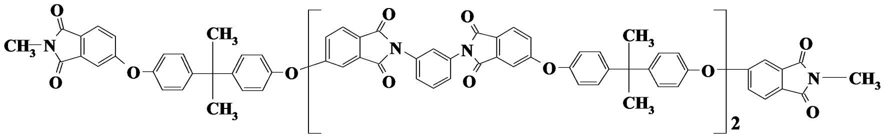
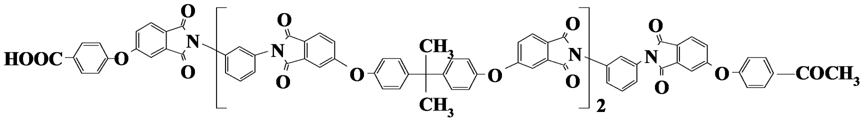
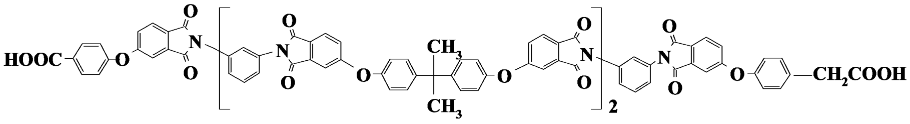
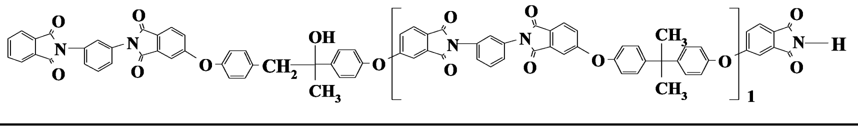
Series Mass	Structures	MNa^+	Photo-oxidation processes
A		1207.3 1799.5	E
B		1575.4 2167.5	E
C		1355.3 1947.5	E
D		1368.4 1960.5	E
G		1370.4 1962.5	E
E		1740.5 2332.6	E
F		1753.5 2345.6	E
M		1253.4	P3-P3
Y		1269.4	P3-P3
G1		1370.4	E-P4-P2

Table 1 (Continued)

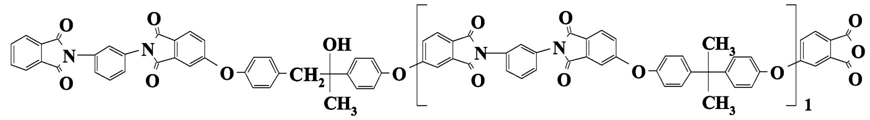
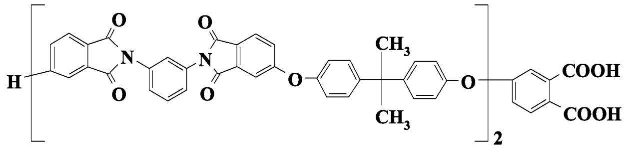
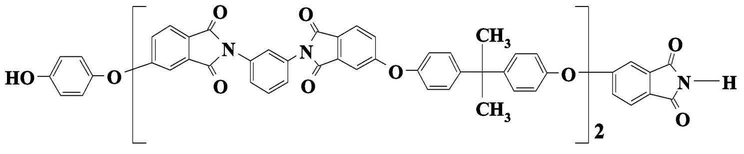
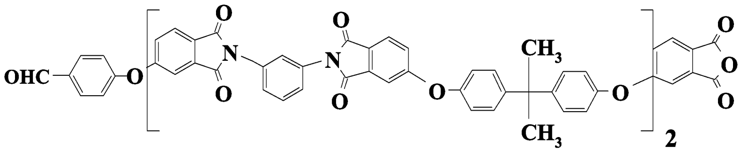
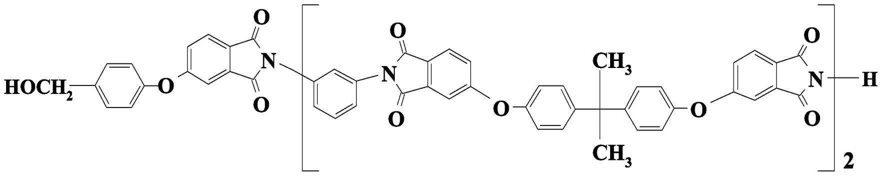
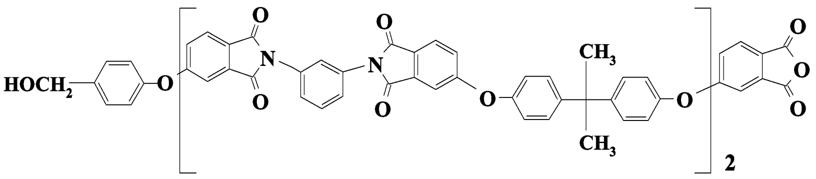
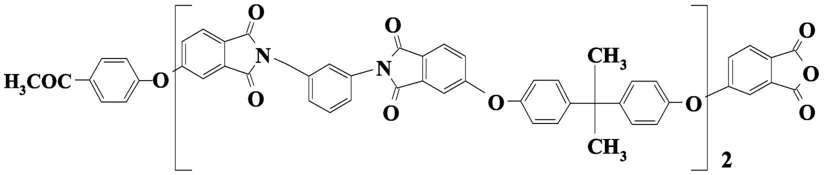
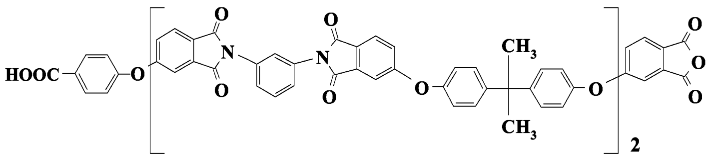
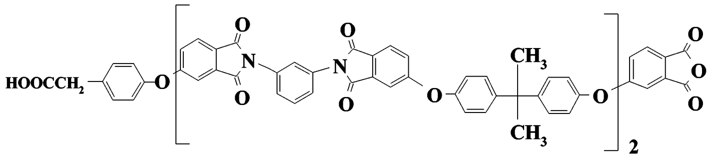
C1		1371.4	E-P4-P1
H		1373.3	E-P1
K		1462.4	P3-P2
		1475.4	P3-P1
L		1476.4	P3-P2
		1477.4	P3-P1
		1489.4	P3-P1
N		1491.4	P3-P1
O		1505.4	P3-P1

Table 1 (Continued)

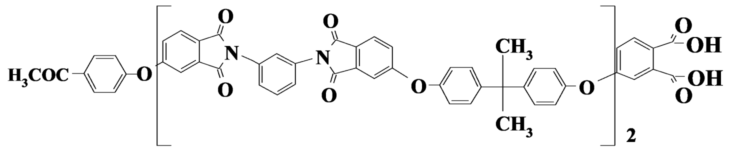
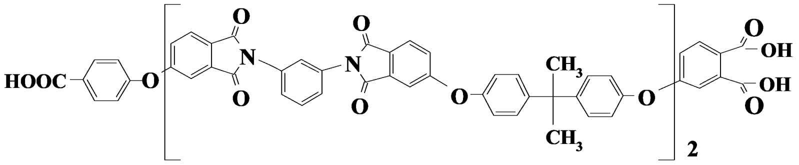
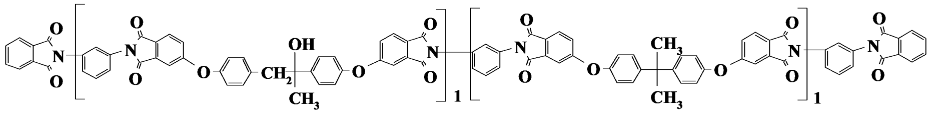
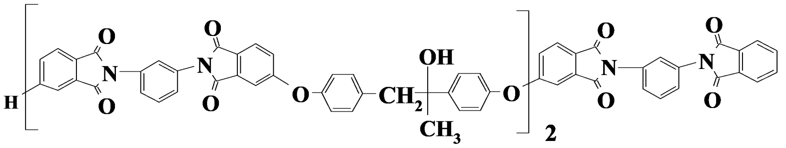
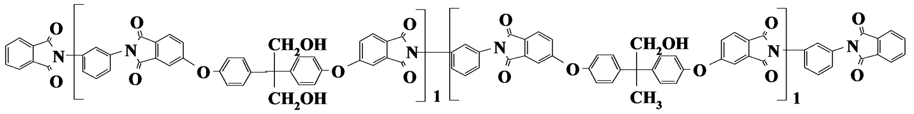
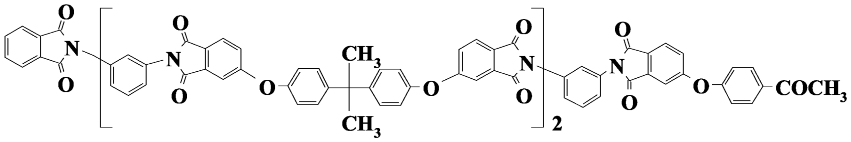
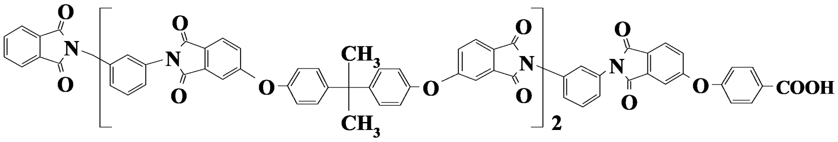
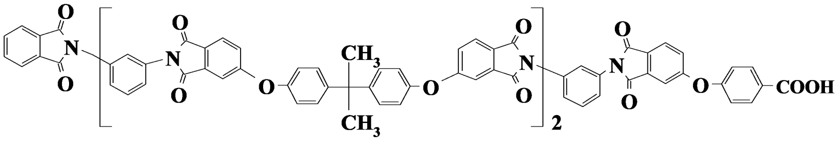
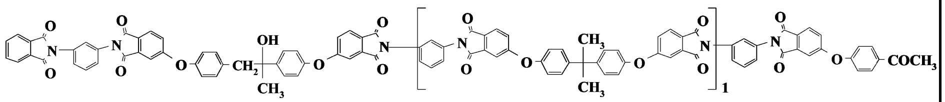
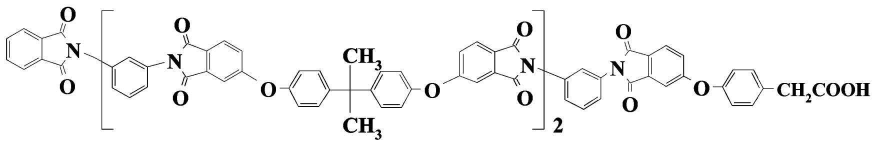
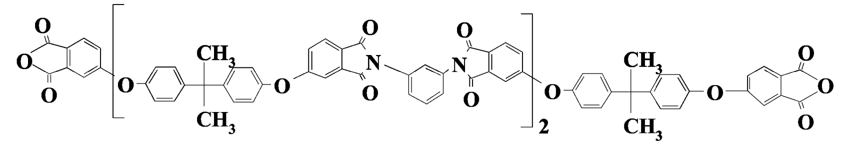
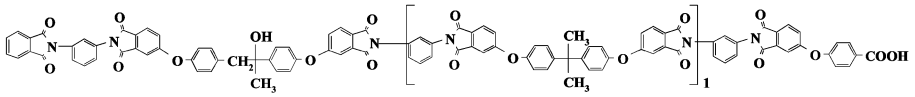
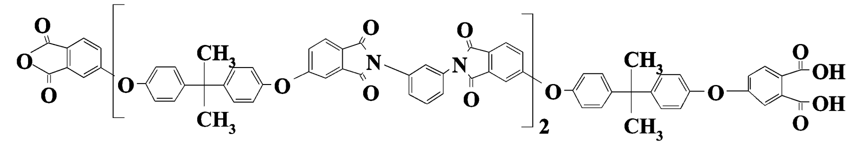
		1507.4	P3-P1
P		1509.4	P3-P1
B1		1591.4	E-P4-E
B2		1607.4	E-P4-E
B3		1623.4	E-P4-E
R		1709.4	E-P3
		1711.4	E-P3
		1711.4	E-P3
R1	 	1725.4	P4-P3 E-P3

Table 1 (Continued)

U		1727.4	**P1-P1**
			**E-P3**
V		1745.4	**P1-P1**

From the foregoing discussion it can be recognized that there are different reactions involved in the photoprocess. To make the photooxidation products easily recognizable, Table 1 specifies which decomposition pathway is responsible for the formation of each new oligomer produced in the thermal oxidation process.

Thus, symbol P_1 specifies the photocleavage of phenylphthalimide units to yield phthalimide and phthalic anhydride end groups, symbol P_2 specifies the photocleavage of the *N*-methyl end group, producing ULTEM chains terminated with N−H phthalimide groups, symbol P_3 specifies the thermal oxidative degradation of the isopropylidene bridge of BPA units to yield benzyl alcohol, acetophenone, phenyl-substituted acetone, phenyl acetic acid, phenol, benzoic acid, end groups, and symbol P_4 means that along the oligomer chain a further oxidation step has occurred, leading to the formation of a tertiary alcohol structure without chain scission, whereas the symbol E indicates just one of the end groups present in the original ULTEM sample (Table 1).

Because each oligomer has two ends, the notation P_1-P_3, for instance, means that a chain cleavage process

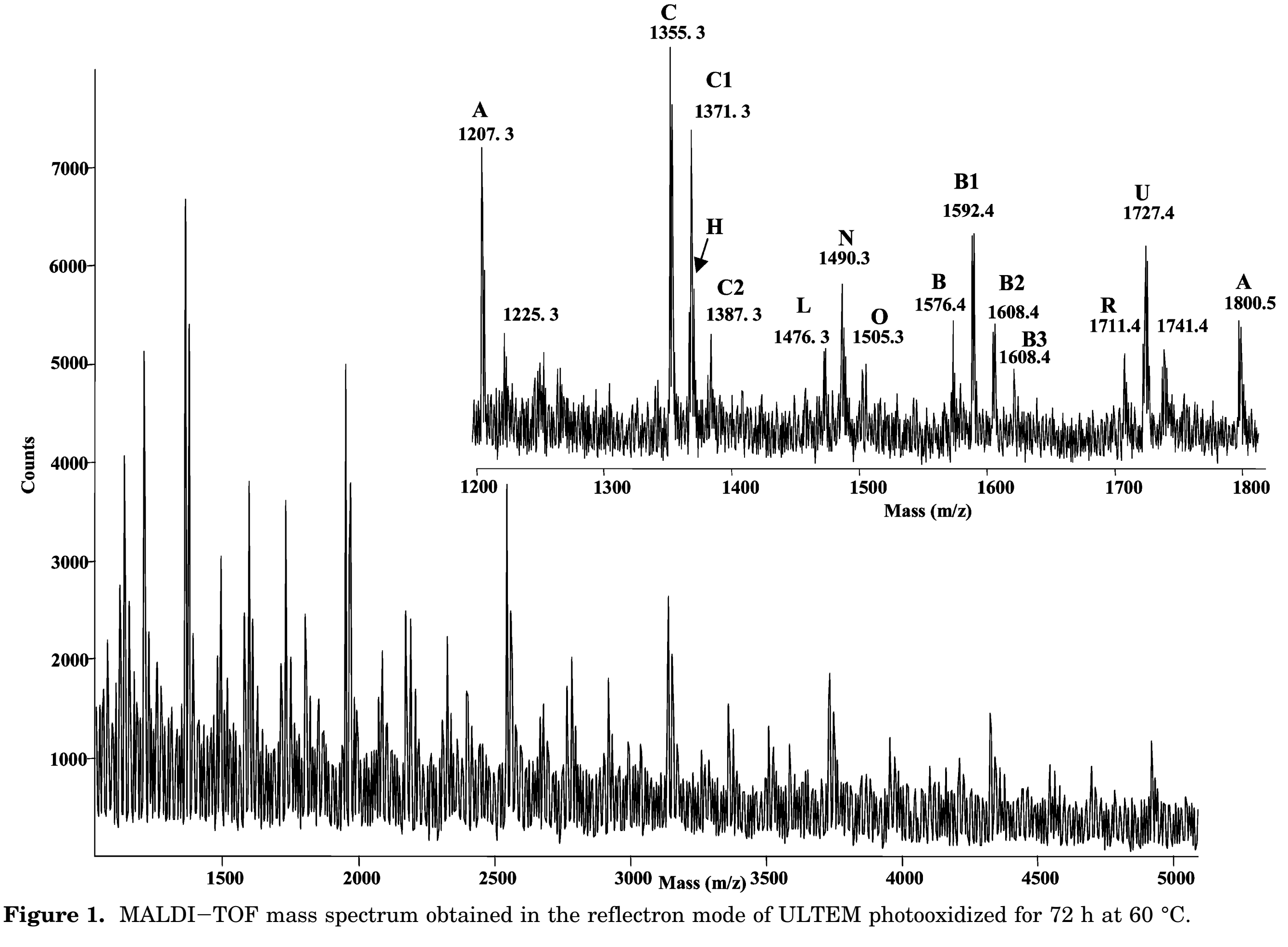


Figure 1. MALDI−TOF mass spectrum obtained in the reflectron mode of ULTEM photooxidized for 72 h at 60 °C.

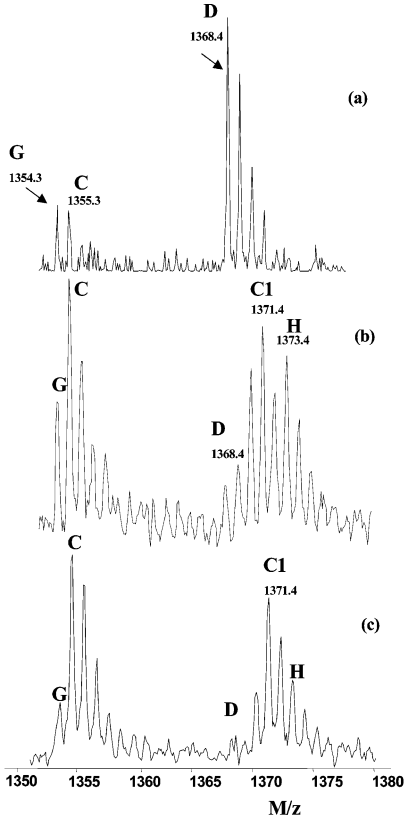
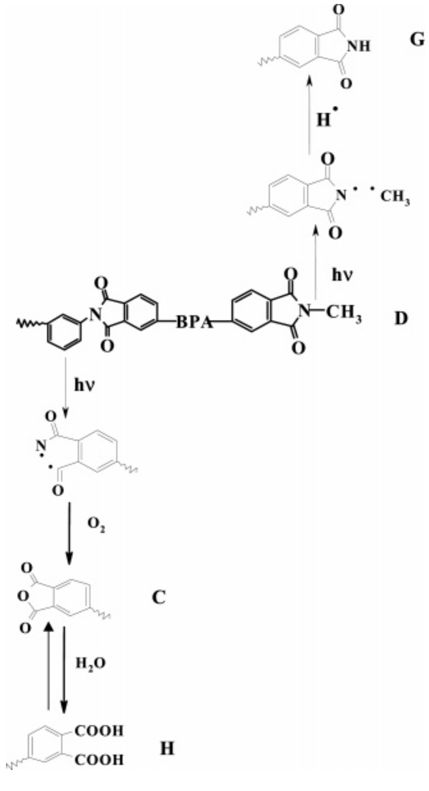


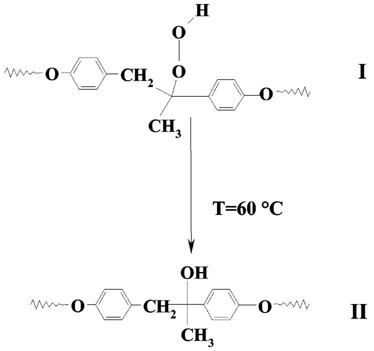
Figure 2. Enlarged portions of the MALDI−TOF mass spectra of ULTEM photooxidized at 60 °C for 0 (a), 24 (b), and 72 h (c).

Scheme 1. Photooxidation Mechanisms in Polyethereimide (ULTEM)



involving the decomposition of phenylphthalimide units to yield phthalic anhydride and phthalic acid groups occurred at one end, whereas the oxidative degradation of the isopropylidene bridge occurred at the other end.

Scheme 2. Decomposition Product of the Hydroperoxide at 60 °C



Moreover, three letters label some oligomers in Table 1 (for instance: the E−P_4−E, peak at *m/z* 1371.4Da). The external letter E retains the meaning of end group existing in the unexposed ULTEM sample, whereas the intermediate letter P_4 means that along the oligomer chain a further oxidation step has occurred, leading to the formation of a tertiary alcohol structure, without chain scission.

According to the structure of the major oxidation products detected by MALDI (Table 1), four photooxidation processes can be postulated, as pictured in Scheme 3: (i) photooxidation of phthalimide units to phthalic anhydride end groups (P_1 in Scheme 3); (ii) photocleavage of methyl groups of the *N*-methyl phthalimide terminal units (P_2 in Scheme 3); (iii) oxidative degradation of the isopropylidene bridge of BPA units (P_3 in Scheme 3); (iv) photooxidation reaction introducing one oxygen atom in several isopropylidene bridges along the main chain (P_4 in Scheme 3).

The photooxidative degradation of the isopropylidene bridge (pathway P_3, Scheme 3), leads to the production of the same oligomers observed in the thermal oxidation of ULTEM at 350 °C.[1]

In fact, both thermal process and photoprocess are initiated[1] by the extraction of a methyl hydrogen atom,

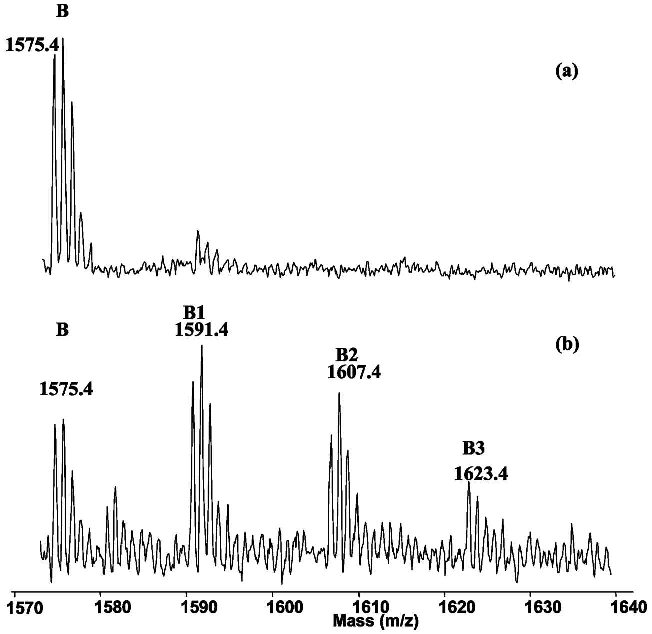
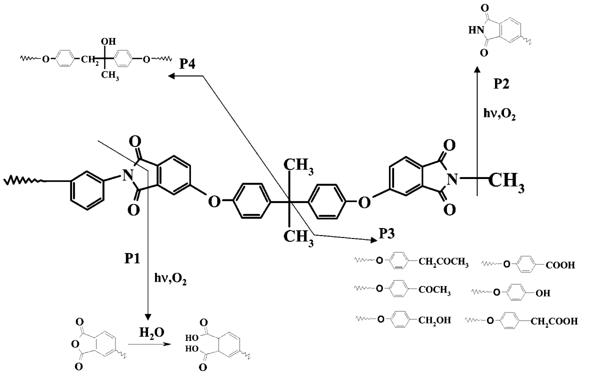


Figure 3. Enlarged portions of the MALDI−TOF mass spectra of ULTEM photooxidized at 60 °C for 0 (a), and 24 h (b).

Scheme 3. Overall Photooxidation Processes in Polyethereimide (ULTEM)



yielding a methylene radical which reacts with oxygen to form the hydroperoxide shown in Scheme 2.

The decomposition of this hydroperoxide, when occurring at 350 °C, leads directly to the same oligomers listed in pathway P_3, Scheme 3. However, when the photooxidation is performed at 60 °C, the formation of further oxidation products such as B1, B2, B3 can be detected (pathway P_4, Scheme 3).

Another apparent difference between the two processes is that the scission of the diphenyl ether units is not observed in the photooxidation process at 60 °C (Scheme 3), whereas the cleavage of the diphenyl ether units was detected in the thermal oxidation process at 350 °C.[1]

This scission is a pure thermal process and it has been shown to occur in the pyrolysis of ULTEM.[6]

Conclusions

Clarification of the mechanisms of oxidation are crucial to understanding the aging processes in polymers. However, most of the mechanisms reported in the literature are simply inferred from the observation of relatively few end products by applying general free-radical chemical concepts. Molecules formed by oxidation are often very reactive, do not accumulate, and are present only in minor amounts among the reaction products. Conventional techniques (IR, for instance) may yield information on functional groups, but not on the structure and end groups of the whole molecule.

On the contrary, MALDI mass spectra yield precise information on the size, structure and end groups of oligomers originated in the oxidation process, allowing discrimination among possible oxidation pathways.

These results open new vistas in the understanding of polymer degradation.

Summarizing our results, it should be remarked that the structural analysis of the oxidation products provided by MALDI allowed construction of a detailed map of the thermal and photooxidation mechanisms of poly(ether imide) ULTEM.

Two photocleavage pathways appear due to the high UV absorption of the phthalimide unit, which absorbs most of the light irradiated by the Q-panel (max at 340 nm). These are: the cleavage of the phthalimide unit to yield phthalic anhydride (P_1 in Scheme 3), and the cleavage of the phthalimide N−CH$_3$ bond (P_2 in Scheme 3). In both cases, the structural changes are due to the cleavage of C−N bonds, as shown in detail in Scheme 1.

On the contrary, the photoscission of the isopropylidene bridge (P_3 in Scheme 3), leads to the formation of degradation products similar to those observed in the thermal oxidation. In fact, the cleavage of the isopropylidene bridge is a nonspecific oxidation process, occurring each time the molecule is excited by any kind of energy (thermal or photo).

However, when the photooxidation is performed at 60 °C, the formation of further oxidation products can be detected (pathway P_4, Scheme 3).

It is also worth noting that the photooxidative degradation process produces a significant reduction of the molar mass of the ULTEM samples,[2] whereas this is not observed in the thermal oxidation reaction at 350 °C.[1] Most likely this difference is due to the abundant cross-linked insoluble residue formed during the thermal oxidation, whereas no insoluble residue is formed in the photooxidative process at 60 °C.

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