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New Vistas in the Photo-Oxidation of Nylon 6

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ABSTRACT: Matrix-assisted laser desorption ionization mass spectrometry (MALDI) is an excellent method to use in determining the structure of the molecules produced in the photo-oxidative degradation of nylon 6 at 60 °C in air. The MALDI spectra of photo-oxidized nylon 6 (Ny6) show the presence of over 40 compounds, as compared to only 3 in the blank Ny6 sample. The extremely favorable event here is that the MALDI spectra present so many new well-resolved peaks, which provide information on the structure and end groups of the oxidation products. The structural analysis of the photo-oxidation products provided by the MALDI spectra allowed us to draw a detailed map of the photo-oxidation mechanisms of Ny6 (Schemes 1−4). The presence of the majority of the oligomers listed in Table 1 had not been revealed before. Our results extend and modify the currently accepted picture for the photo-oxidation mechanisms of Ny6. In fact, our results confirm previous insights that the hydrogen abstraction and subsequent formation of a hydroperoxide intermediate actually occur but also reveal that Norrish I and Norrish II chain-cleavage reactions play an important role in the photo-oxidation process of Ny6. This essential feature of the process had been missed in previous studies focused on UV and IR techniques. The peculiarity of our approach consists of using a high-sensitivity and nonaveraging technique such as mass spectrometry, which allows the detection and monitoring of each new oligomers formed during the oxidation process. This is a remarkable result, and it should be expected that future MALDI studies may have an impact on the current views of photo-oxidation processes of other polymer systems.

Introduction

Aliphatic polyamides find wide application as engineering plastics and fiber materials, and during their normal use, they are exposed to sunlight. Photoaging of this class of polyamides is of greatest concern because many security devices are made from this high-performance material.

The mechanism of photo-oxidation is crucial to the understanding of the natural aging of aliphatic polyamides, and it has been widely studied.[1−8]

Remarkable information on the photo-oxidation of nylon 6 (Ny6) has been provided in the past by investigations that used mainly UV, IR, and wet chemistry methods to follow the process and to identify the products formed.[1−8]

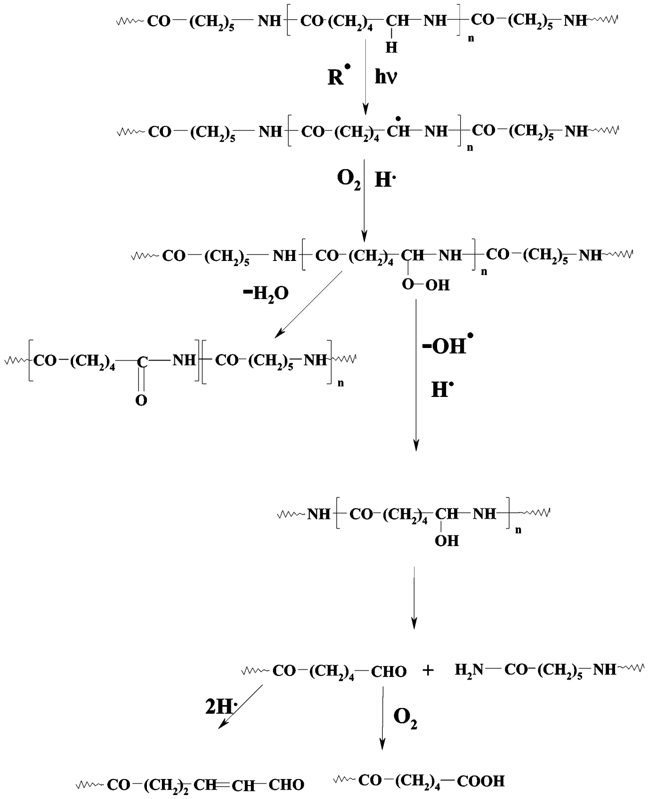
A detailed pathway for the photo-oxidation of Ny6 was derived from the oxidation products identified, and this has been assumed up to the present to be the only oxidation mechanism operating in the case of Ny6.[1−8]

According to the mechanism reported in Scheme 1, the main step of the process consists of a hydrogen abstraction from the methylene group adjacent to the amide NH, leading then to the formation of a hydroperoxide intermediate.

The decomposition of this hydroperoxide generates the actual products of Ny6 photo-oxidation by radical rearrangement reactions, shown in Scheme 1.

However, molecules formed in the photo-oxidation processes are often very reactive, do not accumulate, and are present only in minor amounts among the reaction products.

Scheme 1. Photodecomposition of Ny6 Hydroperoxides



Conventional analytical techniques as UV and IR might prove to be inadequate in providing exhaustive information on the molecular structure of the complex

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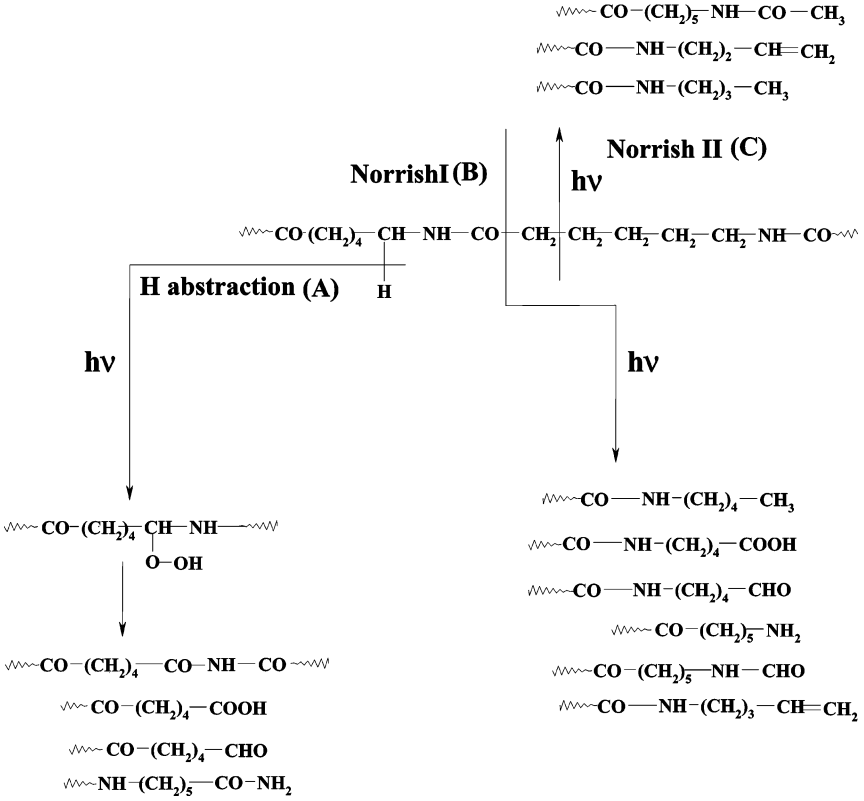
Scheme 2. Overall Photo-Oxidation Processes in Ny6



mixture of compounds present in the photo-oxidized Ny6 samples, therefore leaving room for more detailed investigations.

In the past decade, the analysis of polymers has taken advantage of the development of matrix-assisted laser desorption ionization time-of-flight MS (MALDI), a high sensitivity, nonaveraging technique that allows the direct determination of the individual species contained in a polymer sample.[9,10]

Applications of MALDI to the study of polymer oxidation are quite recent[11−17] and involve the collection of MALDI spectra at different irradiation times and/or temperatures to observe the structural changes induced by heat or light under an oxidizing atmosphere. The polymer sample can be directly analyzed, and the recorded MALDI spectrum arises from a mixture of nonoxidized and oxidized chains.

The results obtained for the systems investigated[12−15] so far are surprisingly highly informative, as compared with previous studies based on conventional techniques.

In fact, MALDI spectra yield precise information on the size, structure, and end groups of molecules originating in the oxidation process, allowing discrimination among possible oxidation mechanisms.

This opens new vistas in studying polymer oxidation processes and deserves careful exploration because of the relevance of these phenomena in everyday practice.

In the present work, Ny6 films were subjected to photoaging, and the photo-oxidation products were analyzed by MALDI. The spectra carry an extremely rich mass of structural information on the products of the photo-oxidation of Ny6, and the new results allow us to extend and redefine the oxidation mechanisms of nylon 6.

According to the structure of the products identified in the present investigation, three photo-oxidation processes are simultaneously occurring in Ny6. They have been summarized in Scheme 2 and shall be discussed in detail below.

Besides the hydrogen abstraction and subsequent hydroperoxide formation, which had been established in previous studies,[1−8] two other major processes appear to be operating in Ny6 (i.e., chain-cleavage reactions Norrish type I and Norrish type II (Scheme 2)).

Experimental Section

Materials. 2-(4-Hydroxyphenilazo)benzoic acid (HABA) and trifluoroethanol were analytical-grade materials, purchased from Sigma-Aldrich Chemical Co. (Italy) and used as supplied. Ny6 (M_v 19 000) was supplied by Sigma-Aldrich, and it was dried at 80 °C under vacuum for 2 days.

Photo-Oxidation Procedure. The photo-oxidation was performed on films of nylon 6 with uniform thicknesses of 10 and 40 μm. The films were obtained by casting from a 2% trifluoroethanol solution. Photo-oxidative degradation of nylon 6 films was carried out on a QUV PANEL apparatus at 60 °C with continued exposure to UV radiation for up to 19 days. At least two separate films were analyzed at each exposure time. The irradiance of the UV lamps (UVA 340 lamps) has a broad band with a maximum at 340 nm. Films of 10 and 40 μm thickness were analyzed by MALDI (see below), and the results were found to be quite consistent for the two series of films.

MALDI: Sample Preparation and Analysis Procedures. Samples for the MALDI analyses were prepared by mixing adequate volumes of the matrix solution (HABA, 0.1 M in TFE) and polymer solution (2 mg/mL in TFE) to obtain a 1:1 or 1:3 ratio (sample/matrix v/v). An aliquot (1 μL) of a 0.1 M solution of sodium trifluoroacetate (NaTFA) in TFE was added to aid cationization; 1 μL of each sample/matrix mixture was then spotted on the MALDI sample holder and slowly dried to allow matrix crystallization.

Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were obtained using Voyager-DE STR instrument equipped with a nitrogen laser emitting at 337 nm with a 3-ns pulse width and working in positive ion

Table 1. Structural Assignments of Sodiated Ions Appearing in the MALDI-TOF Spectra of Photo-Oxidized Ny6 Samples[a]

photo-oxidation processes a)	Structures	M + Na$^+$
B—E	$\mathrm{H_2C{=}CH{-}(CH_2)_3{-}HN{-}[CO{-}(CH_2)_5{-}NH]_8{-}H}$	1013
B—A **C—A**	$\mathrm{H_3C{-}(CH_2)_4{-}HN{-}[CO{-}(CH_2)_5{-}NH]_7{-}CO{-}(CH_2)_4{-}CHO}$ $\mathrm{H_2C{=}HC{-}(CH_2)_2{-}HN{-}[CO{-}(CH_2)_5{-}NH]_7{-}CO{-}(CH_2)_4{-}COOH}$	1014
B—E	$\mathrm{H_3C{-}(CH_2)_4{-}HN{-}[CO{-}(CH_2)_5{-}NH]_8{-}H}$	1015
C—A	$\mathrm{H_3C{-}(CH_2)_3{-}HN{-}[CO{-}(CH_2)_5{-}NH]{-}CO{-}(CH_2)_4{-}COOH}$	1016
B—E	$\mathrm{OHC{-}HC{=}HC{-}(CH_2)_2{-}HN{-}[CO{-}(CH_2)_5{-}NH]_8{-}H}$	1027
B—A	$\mathrm{OHC{-}(CH_2)_4{-}HN{-}[CO{-}(CH_2)_5{-}NH]_7{-}CO{-}(CH_2)_4{-}CHO}$	1028
B—E	$\mathrm{OHC{-}(CH_2)_4{-}HN{-}[CO{-}(CH_2)_5{-}NH]_8{-}H}$	1029
B—A	$\mathrm{H_3C{-}(CH_2)_4{-}HN{-}[CO{-}(CH_2)_5{-}NH]_7{-}CO{-}(CH_2)_4{-}COOH}$	1030
cyclic Ny6	$\boxed{\mathrm{[CO{-}(CH_2)_5{-}NH]_9}}$	1041
C—C	$\mathrm{H_3C{-}(CH_2)_3{-}HN{-}[CO{-}(CH_2)_5{-}NH]_8{-}CO{-}CH_3}$	1043
B-A-A	$\mathrm{H_3C{-}(CH_2)_3{-}CO{-}HN{-}[CO{-}(CH_2)_5{-}NH]_7{-}CO{-}(CH_2)_4{-}COOH}$	1044
B—E	$\mathrm{HOOC{-}(CH_2)_4{-}HN{-}[CO{-}(CH_2)_5{-}NH]_8{-}H}$	1045
A—A	$\mathrm{H_2N{-}[CO{-}(CH_2)_5{-}NH]_8{-}CO{-}CH_2{-}CH_2{-}CH{=}CH{-}CHO}$	1055
E—A	$\mathrm{HO{-}[CO{-}(CH_2)_5{-}NH]_8{-}CO{-}CH_2{-}CH_2{-}CH{=}CH{-}CHO}$	1056
A—A **B—C**	$\mathrm{H_2N{-}[CO{-}(CH_2)_5{-}NH]_8{-}CO{-}(CH_2)_4{-}CHO}$ $\mathrm{H_3C{-}(CH_2)_4{-}HN{-}[CO{-}(CH_2)_5{-}NH]_8{-}CO{-}CH_3}$	1057
A—E **E—A**	$\mathrm{H_2N{-}[CO{-}(CH_2)_5{-}NH]_9{-}H}$ $\mathrm{HO{-}[CO{-}(CH_2)_5{-}NH]_8{-}CO{-}(CH_2)_4{-}CHO}$	1058
linear Ny 6	$\mathrm{HO{-}[CO{-}(CH_2)_5{-}NH]_9{-}H}$	1059
B—C	$\mathrm{OHC{-}CH{=}HC{-}(CH_2)_2{-}HN{-}[CO{-}(CH_2)_5{-}NH]_8{-}CO{-}CH_3}$	1069
E-A-A	$\mathrm{HO{-}[OC{-}(CH_2)_4{-}CO{-}NH]_2{-}[CO{-}(CH_2)_5{-}NH]_6{-}CO{-}(CH_2)_2{-}CH{=}CH{-}CHO}$	1070
B—C	$\mathrm{OHC{-}(CH_2)_4{-}HN{-}[CO{-}(CH_2)_5{-}NH]_8{-}CO{-}CH_3}$	1071
A—A **E-A-A**	$\mathrm{H_2N{-}[CO{-}(CH_2)_5{-}NH]_8{-}CO{-}(CH_2)_4{-}CO{-}NH_2}$ $\mathrm{HO{-}[OC{-}(CH_2)_4{-}CO{-}NH][CO{-}(CH_2)_5{-}NH]_7{-}CO{-}(CH_2)_4{-}CHO}$	1072
A—A	$\mathrm{H_2N{-}[CO{-}(CH_2)_5{-}NH]_8{-}CO{-}(CH_2)_4{-}COOH}$	1073
E—A	$\mathrm{HO{-}[CO{-}(CH_2)_5{-}NH]_8{-}CO{-}(CH_2)_4{-}COOH}$	1074
B-A-C	$\mathrm{OHC{-}CH{=}CH{-}(CH_2)_2{-}NH{-}[CO{-}(CH_2)_4{-}CO{-}NH]{-}[CO{-}(CH_2)_5{-}NH]_7{-}CO{-}CH_3}$	1083
B-A-C	$\mathrm{OHC{-}(CH_2)_4{-}NH{-}[CO{-}(CH_2)_4{-}CO{-}NH][CO{-}(CH_2)_5{-}NH]_7{-}CO{-}CH_3}$	1085
A—B	$\mathrm{H_2N{-}[CO{-}(CH_2)_5{-}NH]_9{-}CHO}$	1086
B—C **E—B**	$\mathrm{HOOC{-}(CH_2)_4{-}HN{-}[CO{-}(CH_2)_5{-}NH]_8{-}CO{-}CH_3}$ $\mathrm{HO{-}[CO{-}(CH_2)_5{-}NH]_9{-}CHO}$	1087
E-A-A	$\mathrm{HO{-}[OC{-}(CH_2)_4{-}CO{-}NH][CO{-}(CH_2)_5{-}NH]_7{-}CO{-}(CH_2)_4{-}COOH}$	1088
A—C	$\mathrm{H_2N{-}[CO{-}(CH_2)_5{-}NH]_9{-}CO{-}CH_3}$	1100
E—C	$\mathrm{HO{-}[CO{-}(CH_2)_5{-}NH]_9{-}CO{-}CH_3}$	1101
E-A-A	$\mathrm{HO{-}[OC{-}(CH_2)_4{-}CO{-}NH]_2{-}[CO{-}(CH_2)_5{-}NH]_6{-}CO{-}(CH_2)_4{-}COOH}$	1102
C—A -A	$\mathrm{H_2C{=}CH{-}(CH_2)_2{-}NH{-}[CO{-}(CH_2)_5{-}NH]_8{-}CO{-}(CH_2)_4{-}CHO}$	1111
C—E -E	$\mathrm{H_2C{=}CH{-}(CH_2)_2{-}NH{-}[CO{-}(CH_2)_5{-}NH]_9{-}H}$	1112
C—A -A	$\mathrm{H_3C{-}(CH_2)_3{-}NH{-}[CO{-}(CH_2)_5{-}NH]_8{-}CO{-}(CH_2)_4{-}CHO}$	1113
C—E -E	$\mathrm{H_3C{-}(CH_2)_3{-}NH{-}[CO{-}(CH_2)_5{-}NH]_9{-}H}$	1114
E-A-C -C	$\mathrm{HO{-}[CO{-}(CH_2)_4{-}CO{-}NH]{-}[CO{-}(CH_2)_5{-}NH]_8{-}COCH_3}$	1115

[a] Terminal groups originated by specific photo-oxidation processes: A = hydroperoxides; B = Norrish I; C = Norrish II; E = end groups of the unexposed nylon 6.

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 the threshold.

The resolution of the MALDI spectra reported in the text is about 7000 fwhm, and the accuracy of mass determination was lower than 0.5 amu for masses in the range of 1000−2000 Da.

To distinguish and separate between the contributions of isotopic peaks M + 1 and M + 2 and peaks due to isobaric structures, a deisotoping program (Mariner Lab) was used. This program produces a theoretical spectrum for each species and subtracts from the experimental spectrum the intensity calculated values of M + 1 and M + 2 isotopic peaks. Thus, the deisotoping spectrum shows only the first mass peaks M for each species.

The structural identification of MALDI peaks in Table 1 was mainly made on the basis of empirical formulas. However, isotopic resolution helps considerably in the peak-assignment process through the comparison of the relative intensities of isotopic peaks corresponding to oligomers of increasing molar mass.[17] Some plausible structures were also derived from previous studies.[1−17]

As an example, the structure of the α-β unsaturated aldehydes (Table 1) could be unsaturated anywhere in the chain, in the absence of corroborating information.[4,5]

Assignments in Table 1 are therefore strongly suggestive but not absolute.

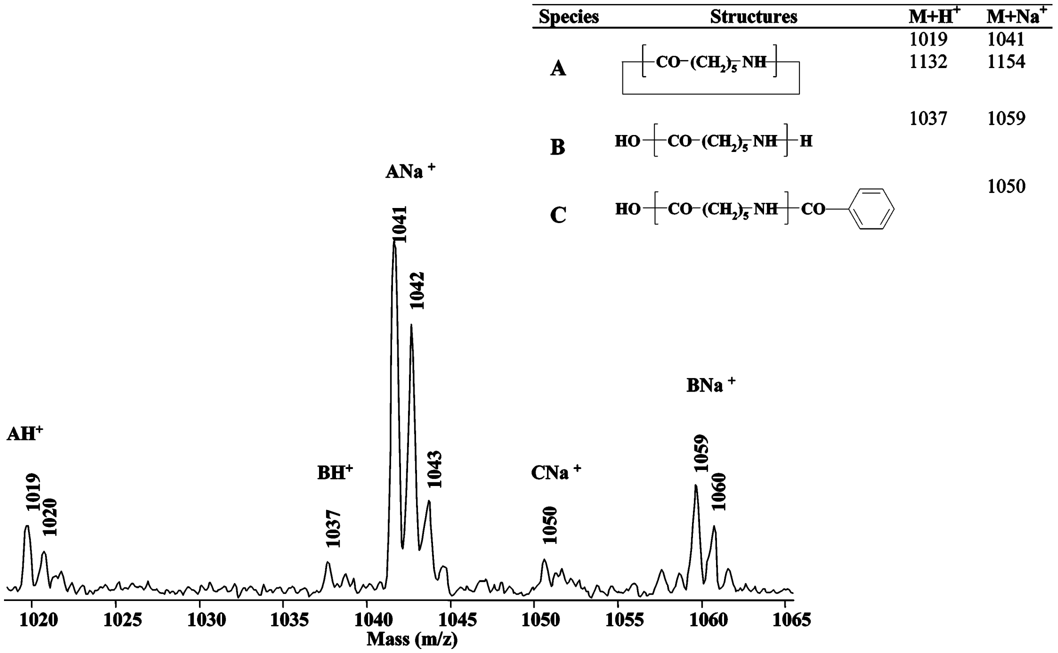


Figure 1. Expanded MALDI-TOF mass spectrum of a Ny6 sample in the mass range of 1010−1065 Da obtained in reflectron mode.

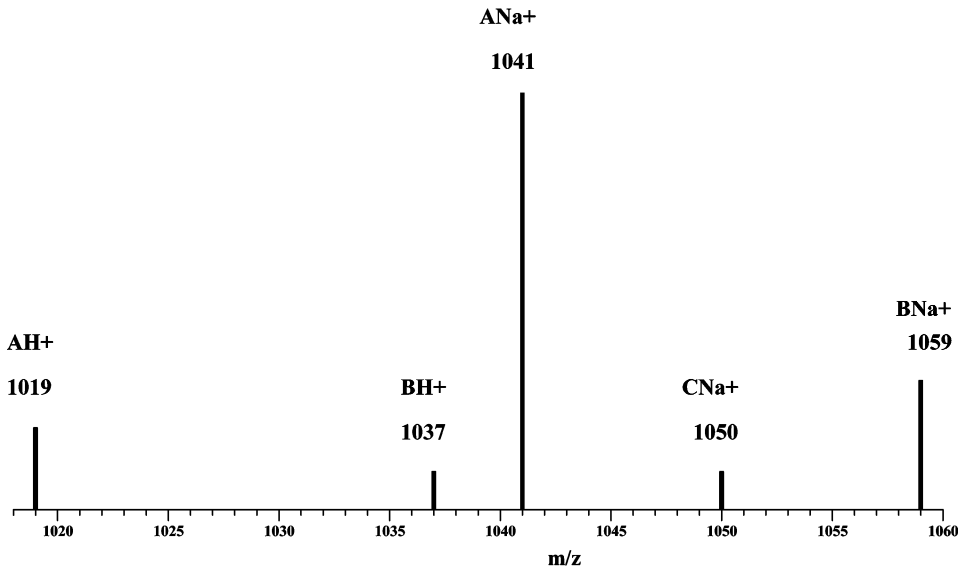


Figure 2. Deisotoping MALDI-TOF mass spectrum of a Ny6 sample in the mass range of 1010−1065 Da.

Determination of Molar Masses. Molar mass values were calculated from viscosity measurements. The solution viscosity was measured to be 25 ± 0.1 °C with an Ubbelhode viscometer employing a concentration of 0.5 g/dL in an 85% aqueous solution of HCOOH. The Mark−Houwink coefficient for nylon 6 in HCOOH[18] used to calculate M_v values (reported below) is $[\eta] = 22.6 \times 10^3\ M_v^{0.82}$.

The M_v values of nylon 6 40-μm films photo-oxidized at 60 °C are initial, M_v 19 000; 240 h irradiation, M_v 15 000; and 458 h irradiation, M_v 10 500.

For the 10-μm films, the values are 11 h of exposure, M_v 13 600; 24 h of exposure, M_v 8650; 48 h of exposure, M_v 5700; 96 h of exposure, M_v 2300; and 120 h of exposure, M_v 1500.

Results and Discussion

A nylon 6 sample with a number-average molar mass of 19 000 was used for this study. Ny6 films were subjected to accelerated photoaging treatment by using a QUV PANEL test at 60 °C in air for 4, 10, 12, and 19 days for the 40-μm films. Instead, films with a thickness of 10 μm were exposed for 11, 24, 48, 96, 120, and 168 h. Under these conditions, the photo-oxidative process is fairly rapid, producing a reduction of the molar mass with reaction time of up to 10.500 for 458 h of exposure in the first set of films (40 μm) and M_v = 1500 for 120 h of irradiance in the latter set of films (10 μm).

The blank nylon 6 sample and the TFE soluble photo-oxidation products of nylon 6 were analyzed by MALDI-TOF mass spectrometry using HABA as a matrix.

The MALDI spectrum of nylon 6 has already been reported,[13] so in Figure 1 we shown only an expanded portion of the total spectrum, spanning over a mass range of 113 Da (the Ny6 repeat unit).

The spectrum in Figure 1 shows mass peaks with isotopic resolution, whereas in Figure 2 we show the spectrum after the deisotoping procedure. The latter

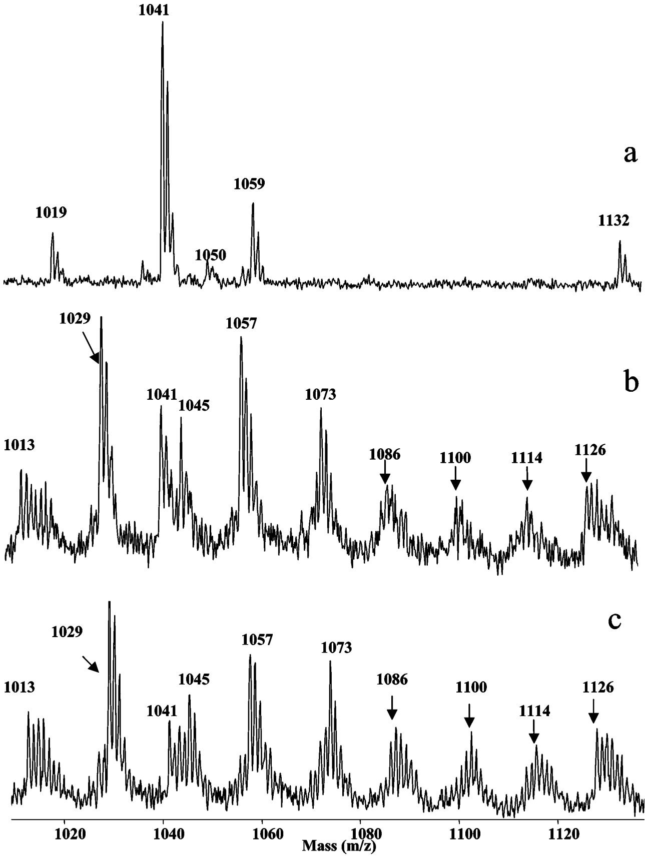


Figure 3. MALDI-TOF mass spectra obtained in reflectron mode in the mass range of 1010–1130 Da of 40-μm Ny6 photo-oxidized for (a) 0 h, (b) 96 h, and (c) 289 h.

implies the use of a deisotoping program to suppress the contributions of the M + 1 and M + 2 peaks.

The five MALDI peaks in Figure 2 are due to only three oligomers: (i) sodiated ions of cyclic nylon 6 chains (species ANa$^+$, *m/z* 1041), (ii) sodiated ions of linear oligomers terminated with carboxyl at one end and amino groups at the other end (species BNa$^+$, *m/z* 1059), and (iii) sodiated ions of linear oligomers terminated with carboxyl at one end and benzoyl groups (capping agent) at the other end (species CNa$^+$, *m/z* 1050).

The two peaks that appear at *m/z* 1019 and 1037 correspond to protonated ions of the linear and cyclic oligomers. The structure of each oligomer is identified in the inset of Figure 1.

The intensity of the protonated peaks at *m/z* 1019 + 113.15 Da and *m/z* 1037 + 113.15 Da and the intensity of the peaks corresponding to the end-capped oligomers at *m/z* 1050 + 113.15 Da decrease sensibly at higher masses.

Therefore, the MALDI spectrum of the blank Ny6 indicates that the sample under investigation is mainly constituted of linear chains terminated with carboxyl groups at one end and amino groups at the other end.

In Figure 3a–c, we report expanded portions of the MALDI spectra of 40-μm Ny6 samples irradiated for 0, 96, and 289 h, respectively.

From the inspection of the spectra in Figure 3b and c, it is possible to observe a spectacular increment of peaks with respect to the blank sample in Figure 3a. This indicates that photo-oxidation reactions have occurred in nylon 6, producing new compounds that are detected and differentiated by MALDI analysis. The spectra sequel (Figure 3a–c) permits us to appreciate the evolution of the oxidation process.

The extremely favorable event here is that the MALDI spectra present so many new well-resolved peaks, which provide potential information on the structure and end groups of the oxidation products.

Because of the effect of isotopic resolution, the identity and relative intensity of peaks in Figure 3 are not easily assessed; therefore, Figure 4 shows the spectrum of a Ny6 sample irradiated for 289 h after deisotoping.

More than 40 compounds are present in the mass spectrum of the oxidized sample, as compared to only 3 in the blank Ny6 sample.

All of these peaks correspond to sodiated ions of oxidized Ny6 oligomers, and they have been assigned (Table 1) to specific oligomer structures and to specific oxidation pathways.

The identification of the end groups attached to the oligomers produced in the oxidation process is of outmost importance because the end groups may reveal the particular mechanism that has been active in the oxidation process.

According to the structure of the major oxidation products identified, three photo-oxidation processes appear to be simultaneously occurring in Ny6, as summarized in Scheme 2.

Besides the hydrogen abstraction and subsequent hydroperoxide formation, two other processes appear to be operating in Ny6 (i.e., the chain-cleavage reactions Norrish I and Norrish type II (Scheme 2)).

A detailed map of the processes and of the end groups generated by the hydroperoxide decomposition in Ny6 molecules (route A) is given in Scheme 1. The initially formed hydroperoxides undergo thermal degradation to produce imide units inside the chain, plus aldehyde, α-β unsaturated aldehyde, *N*-1-hydroxylated, acid, and amide end groups.

Schemes 3 and 4 illustrate the oxidation processes occurring when chain cleavage is promoted by the well-known Norrish type I and Norrish type II reactions (routes B and C, respectively).

The Norrish type I cleavage reaction (route B) yields amine, alkylic, alkenic, aldehyde, acid, α-β unsaturated aldehyde, and *N*-formamide end groups (Scheme 3).

The Norrish type II reaction (route C) yields NH–CO–CH_3 butylenes and butylics end groups (Scheme 4).

In Table 1, we specify which photo-oxidation mechanism is responsible for the formation of each new oligomer. We have adopted a particular code to specify the relationship between each oligomer end group and the photo-oxidation mechanism from which it originates.

Thus, A (Table 1) specifies any end group generated by the decomposition of the hydroperoxides (Scheme 1), B specifies any end group generated by Norrish type I chain cleavage (Scheme 3), C specifies any end group generated by Norrish type II chain cleavage (Scheme 4), and E indicates just one of the end groups present in the original Ny6 sample.

Because each oligomer has two ends, the notation B–A, for instance, means that a Norrish type I chain cleavage occurred at one end and that hydroperoxide decomposition occurred at the other end. Moreover, three letters label some oligomers in Table 1 (for instance, B-A-C; peak at *m/z* 1085). End letters B and

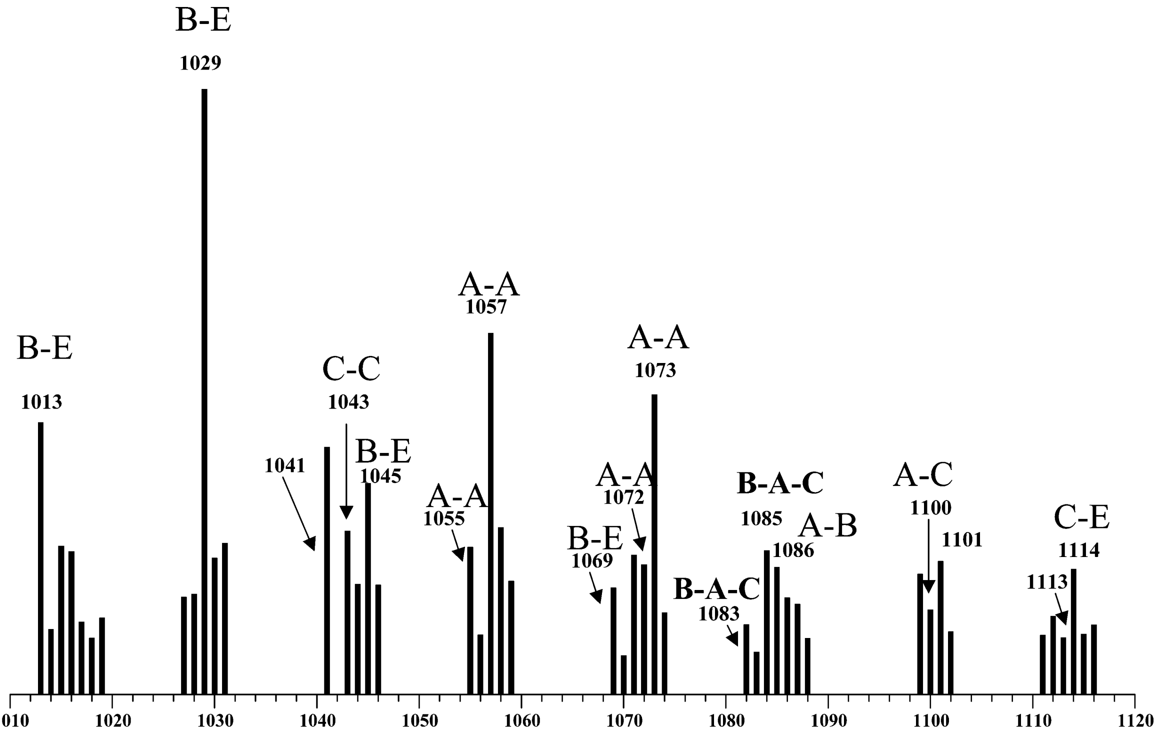
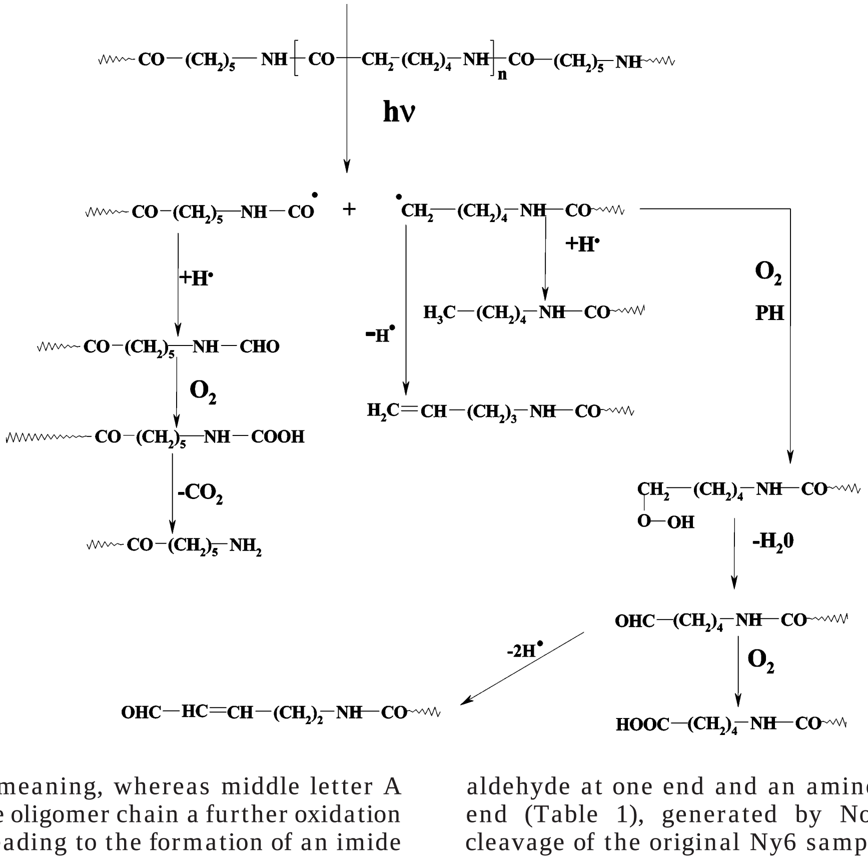


Figure 4. Deisotoping MALDI-TOF mass spectrum in the mass range of 1010−1120 Da of a photo-oxidized 40-μm Ny6 sample for 289 h.

Scheme 3. Photodecomposition of Ny6 via the Norrish I Reaction



C retain the above meaning, whereas middle letter A means that along the oligomer chain a further oxidation step has occurred, leading to the formation of an imide group (Scheme 1) without chain scission.

The inspection of the spectrum in Figure 4 reveals that the cyclic oligomer at *m/z* 1041 Da and the linear oligomer at *m/z* 1059, which belong to the original Ny6 sample, are still present in the photo-oxidized sample.

The most prominent peak appearing in Figure 4 (*m/z* 1029 Da) was univocally assigned to oligomers with an aldehyde at one end and an amine group at the other end (Table 1), generated by Norrish type I chain cleavage of the original Ny6 sample (Scheme 3).

Also, the peaks at *m/z* 1013, 1015, 1027, and 1045 (Table 1) correspond to oligomers unequivocally generated by a single Norrish type I chain cleavage of the original Ny6 sample (Scheme 3).

Peaks appearing in the spectrum in Figure 4 at *m/z* 1056, 1058, 1070, 1072, 1074, 1088, and 1102 belong to oligomers unequivocally generated by the decomposition

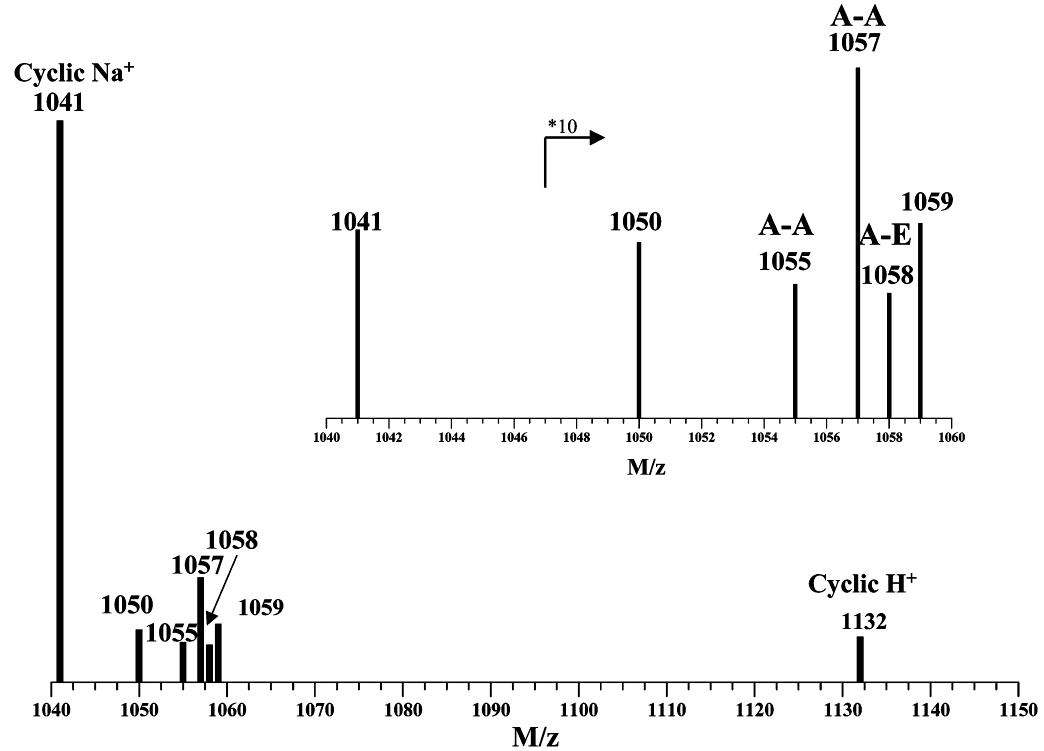
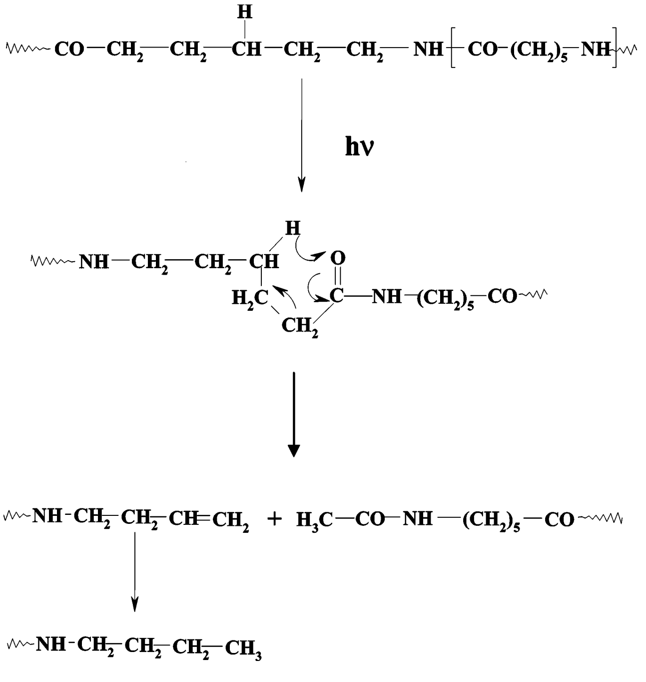


Figure 5. Deisotoping MALDI-TOF mass spectrum in the mass range of 1010−1120 Da of a photo-oxidized 10-μm Ny6 sample for 11 h.

Scheme 4. Photodecomposition of Ny6 via the Norrish II Reaction



of the hydroperoxides and consequent cleavage of the original Ny6 sample (Scheme 1).

These oligomers are primary products of the photo-oxidation and have a strong diagnostic value in assigning a major role to the hydroperoxide cleavage mechanism.

Finally, peaks at *m/z* 1043, 1101, 1112, and 1114 have been unequivocally assigned to photo-oxidation products generated by a single Norrish type II chain cleavage of the original Ny6 sample (Scheme 4). At one chain end, the oligomers at 1101, 1112, and 1114 Da retain the original end group present in the Ny6 chain prior to photo-oxidation, thus they can be assignment to primary photo-oxidation products.

The remaining peaks in Figure 4 correspond to oligomers (Table 1) generated by two (and sometimes three) steps of chain oxidation. These oligomers do not retain any of the end groups existing in the original Ny6 sample and are therefore secondary photo-oxidation products.

In more detail, three peaks in Table 1 have been assigned to two isobar structures. For instance, the intense peak at *m/z* 1057 (Table 1) corresponds to two isobar structures: a macromolecular ion bearing aldehyde and amide end groups and/or an oligomer with an alkyl end group at one end and a methyl-amide end group at the other end. This procedure leaves a degree of uncertainty about the mechanisms responsible for the formation of these specific oligomers.

MALDI provides only semiquantitative information as far as peak intensity data are concerned;[9] therefore, the importance of the three photo-oxidation mechanisms cannot be deduced from the relative intensity of the peaks in Figure 4. However, Norrish type I and hydroperoxide formation photo-oxidation mechanisms appear to be more important than the Norrish type II process.

The presence of end groups due to Norrish I and Norrish II reactions escaped previous investigations.[1−8] This is perhaps due to the fact that the main photo-oxidation products bear aldehyde (1029 *m/z*), α-β unsaturated aldehyde (1027 *m/z*), alkyl (1015 *m/z*), and carboxyl end groups (1045 *m/z*); all compounds originated from hydroperoxide decomposition.

Our results also provide insight into the product distribution changes during the photo-oxidation reaction. In Figure 5, we reported the MALDI spectrum of 10-μm films exposed for only 11 h, which shows the

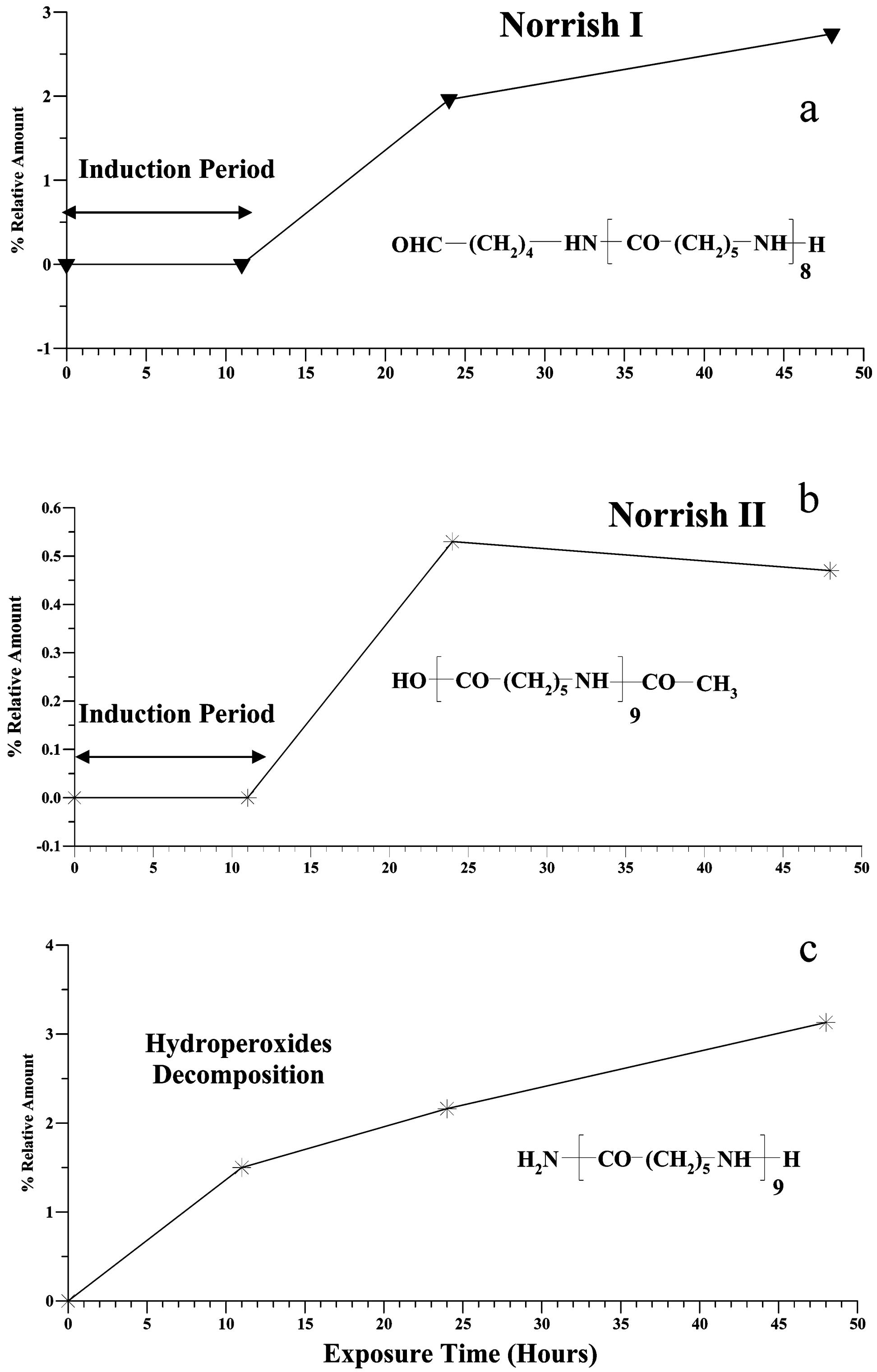


Figure 6. Relative amount vs exposure time of species at *m*/*z* (a) 1029, (b) 1101, and (c)1058 as obtained from the MALDI spectra of photo-oxidized 10-μm Ny6 samples.

appearance of only a few photo-oxidation products, all of which were generated (Table 1) by hydrogen peroxide decomposition (process A, Scheme 1).

This indicates that the chain photocleavage Norrish I and Norrish II type reactions (Scheme 2) do occur at a later stage of irradiation.[19−20]

In Figure 6a−c, we report the kinetic tracings of the oxidation products, representative of the three oxidation mechanisms found to be operating. Both Norrish I and Norrish II photoproducts appear after an induction period, whereas the oligomer generated by hydrogen peroxide decomposition is formed immediately.

The UV absorption of the unexposed Ny6 films shows a weak maximum at about 225 nm, but the UV absorption dramatically increases and widens toward the longer wavelengths with increasing exposure time[4,5] most likely because of the presence of the photo-oxidation products generated by hydrogen peroxide decomposition. A greater amount of light therefore becomes available for film absorption, allowing the occurrence of the Norrish-type processes and justifying the presence of an induction period for their appearance.

Conclusions

Summarizing our results, it should be remarked that an impressive amount of valuable structural information on the photo-oxidation products of Ny6 has been extracted from the (spectacular) MALDI spectra reported in Figures 1−5.

The peculiarity of our approach consists of using a nonaveraging technique (mass spectrometry), which allows the detection and monitoring of each oligomer during the oxidation process.

Let us recall the difference between two stages of the scientific elaboration of data: theory fitting and theory testing.

When the experimental data are insufficient and do not permit us to choose among different theories (models) to describe a phenomenon, the data can still be used to determine if they do not contradict the predictions of a particular theory.

This procedure (theory fitting) does not prove that the theory provides a suitable model to account for the observed facts, and this happened in previous studies.[1−8]

Instead, if the available data are sufficiently diagnostic, then one is in a position to test different theories and to discriminate among them (theory testing), as in the present case.

The present MALDI investigation allowed the detection of many hitherto unidentified products formed in the photo-oxidative degradation of nylon 6.

The collected data show that the photo-oxidation degradation processes produce a sensible reduction of the molar mass of Ny6 and indicate the formation of Ny6 oligomers with different end groups, consequent to chain cleavage due to oxidation.

Five oligomers originate exclusively from Norrish I and four oligomers originate exclusively from Norrish II chain-cleavage reactions. Furthermore, nine peaks are exclusively due to Ny6 oligomers originating only from hydroperoxide decomposition reactions. The presence of the majority of the oligomers listed in Table 1 had not been revealed before.

The structural identification of the photo-oxidation products provided by the MALDI spectra allowed us to draw a detailed map of the photo-oxidation mechanisms of Ny6 (Schemes 1−4).

Our results extend and change the currently accepted picture of the photo-oxidation mechanisms of Ny6. Our results confirm that the hydrogen abstraction and subsequent formation of a hydroperoxide intermediate actually occurs but also reveal that Norrish I and Norrish II chain-cleavage reactions play an important role in the photo-oxidation process of Ny6.

This essential feature had escaped previous studies.

Overall, a remarkable advance has been provided by the present investigation, and it should be expected that future MALDI studies might have an impact on the current views on photo-oxidation processes of other polymer systems.

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