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MALDI Investigation of Photooxidation in Aliphatic Polyesters: Poly(butylene succinate)

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ABSTRACT: Matrix-assisted laser desorption ionization mass spectrometry (MALDI-TOF-MS) has been found to be an excellent method to determine the structure of the molecules produced in the photooxidative degradation of poly(butylene succinate) (PBSu) at 60 °C in air. Over 20 compounds are present in the MALDI spectrum of the oxidized sample, as compared to only 4 in the original PBSu sample. The MALDI spectra present many new well-resolved peaks, which provide information on the structure and end groups of the oxidation products. The MALDI peaks correspond to sodiated ions of oxidized oligomers, and they have been assigned to polymer chains containing succinic and malonic acid, butyl ester, ethyl ester, and butyl formate end groups. These oligomers had not been revealed before. The mechanisms accounting for the formation of photooxidation products of PBSu involve the operation of several reactions: (i) oxidation of hydroxyl end groups; (ii) α-H abstraction decomposition; (iii) Norrish I photocleavage. Our results establish the photooxidation mechanisms of PBSu. The novelty of our approach consists of using a nonaveraging technique, such as mass spectrometry, which allows the detection of individual compounds formed during the oxidation process. This is a remarkable result, and it should be expected that future MALDI studies might have an impact on the current views on photooxidation processes of other polymer systems.

Introduction

Aliphatic polyesters are among the most interesting candidates for biodegradable materials[1] in agricultural and sanitary fields as well as in packaging applications. Therefore, several polymers of this type have been recently proposed and their relevant performances are currently under scrutiny.

Such materials, during their normal use, are exposed to sunlight, and therefore, their photoaging becomes of greatest concern. Historically, poly(hydroxybutyrate)s were the first products introduced industrially,[2] whereas more recently poly(butylene succinate), PBSu, and poly(butylene succinate-*co*-butylene adipate), P(BSu-*co*-Ad), have appeared on the market under the trade name of Bionolle.[3]

In this work, PBSu and Bionolle 1001 films were subjected to photoaging and the photooxidation products were analyzed by matrix-assisted laser desorption ionization time-of-flight MS (MALDI). The mechanism of photooxidation is crucial for the understanding of natural aging of aliphatic polyesters, and several studies have appeared quite recently in the literature on the photooxidation process of this class of polymers.[4−9] Information on the photooxidation products of several types of industrial polymers 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.[10] However, molecules formed in the photooxidation processes are often very reactive, do not accumulate, and are present only in minor amounts among the reaction products. UV and IR techniques provide structural information only on functional groups or segments of molecules and not on the full molecule. These techniques might therefore prove inadequate in providing exhaustive information on the molecular structure of the complex mixture of compounds present in the photooxidized polymer samples.

In the past decade the analysis of polymers has taken advantage of the development of MALDI, a high-sensitivity, nonaveraging technique that allows the direct determination of the individual molecules contained in a polymer sample.[11,12] Applications of MALDI to the study of polymer photo- and thermooxidation are quite recent[13−18] 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 so far investigated by MALDI[13−18] are extremely highly informative, as compared with previous studies based on conventional techniques, yielding precise information on the size, structure, and end groups of molecules originated in the oxidation process. According to the structure of the oxidation products identified in this work, three photooxidation processes have been unambiguously ascertained to occur in PBSu. They have been summarized in Scheme 1 and shall be discussed below. Besides the hydrogen abstraction and subsequent hydroperoxide formation, a process active in several other polymeric materials, two other cleavage processes appear to be operating in PBSu, i.e., the chain cleavage reaction Norrish I and the hydroxyl end groups oxidation (Scheme 1).

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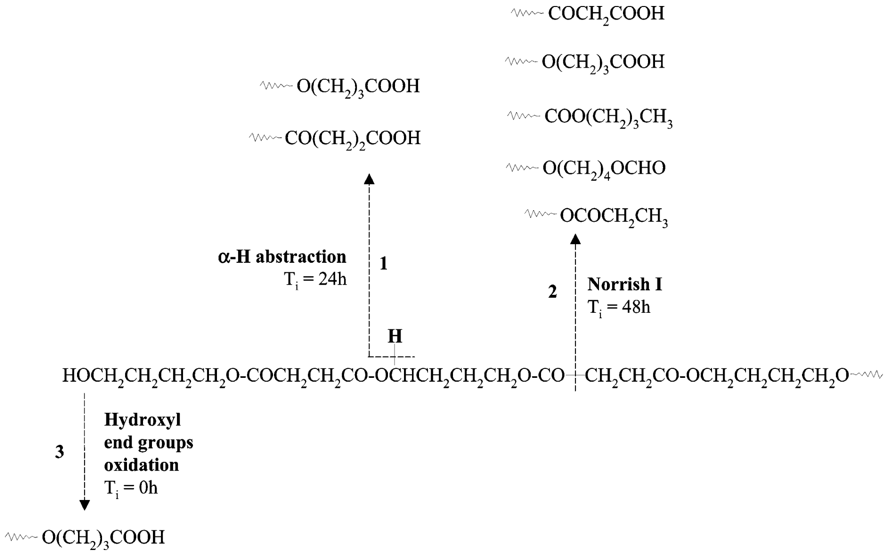
Scheme 1. Overall Photooxidation Processes in PBSu (T_i = Induction Period)



Experimental Section

Materials. Dimethyl succinate and titanium(IV) butoxide were purchased from Sigma-Aldrich (Milan, Italy) whereas 1,4-butanediol was purchased from Janssen Chimica. The reagents were purified by vacuum distillation before use. Showa Denko (Dusseldorf, Germany) provided the commercial polyester with the trade name Bionolle 1001. Bionolle 1001 was dissolved in $CHCl_3$, precipitated in CH_3OH, filtered out, washed with methanol, and dried at 40 °C under vacuum, before use. 2-(4-Hydroxyphenilazo)benzoic acid (HABA) was obtained from Sigma-Aldrich Chemical Co. and used as supplied.

Synthesis of PBSu. Poly(butylene succinate) was synthesized by melt polymerization starting from dimethyl esters of succinic acid and 1,4-butanediol, using an excess of 10% of diol, in the presence of titanium(IV) butoxide as esterification catalyst, as reported previously.[19] The polyester was dissolved in the minimum amount of $CHCl_3$ and precipitated into methanol to remove the residual catalyst and the low molecular mass oligomers. The solid material was filtered out, washed with methanol, and dried at 40 °C under vacuum.

Films. PBSu and Bionolle 1001 films (thickness range: 0.080−0.120 mm ± 0.01 mm) were obtained by hot pressing for a minute under a pressure of 200−250 Kg/cm^2 (Carver C27 laboratory press) the polymer powder between two Teflon plates, at 30−35 °C above the melting temperature.

Photooxidation Procedure. Photooxidative degradation of polyester films was carried out on a QUV PANEL apparatus at 60 °C with continued exposure to UV radiation for up to 8 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 were analyzed by SEC and by MALDI-TOF MS, and the results were found to be quite consistent for the two series of films.

SEC Analysis and Molar Mass Calculations. Polymer Lab Caliber software was used to compute the average molar masses of all the samples (Table 1) by means of the calibration curve obtained with a set of primary polystyrene standards.

MALDI-TOF MS Analysis. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were recorded in reflector mode using a Voyager-DE STR (Applied Biosystem) mass spectrometer equipped with a nitrogen laser emitting at 337 nm with a 3-ns pulse width and working in positive ion mode. The accelerating voltage was 20 kV; the grid voltage and the delay time were optimized for each sample to achieve the higher molar mass values. The laser irradiance was maintained slightly above threshold. 2-(4-Hydroxyphenilazo)benzoic acid (HABA) (0.1 M in THF/$CHCl_3$) was used as matrix. Appropriate volumes of polymer solution (5 mg/mL in $CHCl_3$) and matrix solution were mixed to obtain a 2:1, 1:1, and 1:2 ratios (sample/matrix v/v). An aliquot (1 μL) of a 0.1 M solution of sodium trifluoroacetate (NaTFA) in THF was added to aid cationization; 1 μL of each sample/matrix mixture was spotted on the MALDI sample holder and slowly dried to allow matrix crystallization.

Table 1. Molar Mass of PBSu and Bionolle 1001 Films as a Function of the Exposure Time

sample	T (°C)	exposure time (h)	M_w[b]	M_n[b]	D[c]
PBSu	60	0	45 959	25 558	1.8
		24	27 991	15 026	1.9
		48	11 860	6 951	1.7
		72	8 523	5 882	1.4
		96	12 678	6 889	1.8
		120	12 228	6 855	1.8
		144	8 985	5 910	1.5
		168	5 707	5 292	1.1
		192	7 340	5 407	1.4
Bionolle 1001	60	0	130 560	70 930	1.8
		96	30 000	8 900	3.4
		240	13 500	5 670	2.4
		264	21 550	6 700	3.2
		288	27 800	7 730	3.6
		384	9 020	4 700	1.9
		432	7 130	3 550	2.0

[a] Poly(butylene succinate) = $-[O(CH_2)_4OCO(CH_2)_2CO]-$. [b] Weight-average and number-average molar masses determined using the calibration curve obtained with PS standards in $CHCl_3$. [c] $D = (M_w/M_n)$ dispersion index.

The resolution of the MALDI spectra reported in the text is about 7000 fwhm, and the mass accuracy, determined by external calibration, was lower than 200 ppm 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 2 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.[15b] Some plausible structures were also derived according to those proposed by previous studies.[4−9]

UV Analysis. The original and photooxidized samples were dissolved in $CHCl_3$ and the absorption spectra were recorded using a UV 1601 Shimadzu spectrometer.

Table 2. Structural Assignments of Ions Appearing in the MALDI-TOF Spectra of Photooxidized PBSu and Bionolle1001 Samples[a]

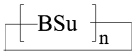
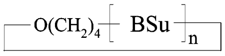
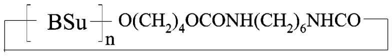
Symbols	Structures	n	$M\cdot Na^+$	$M\cdot K^+$
A	 $[\text{BSu}]_n$ (cyclic) $HOOC(CH_2)_2OC-[\text{BSu}]_n-O(CH_2)_2CH{=}CH_2$	7	1228	1244
B	$HOOCCH_2CO-[\text{BSu}]_n-O(CH_2)_4OH$	6	1232	
C	$H-[\text{BSu}]_n-OH$ $HOOCCH_2CO-[\text{BSu}]_n-O(CH_2)_3COOH$	7	1246	
D	$CH_3CH_2OC-[\text{BSu}]_n-O(CH_2)_4OCOCH_2CH_3$	6	1258	
E	$HOOC(CH_2)_2OC-[\text{BSu}]_n-O(CH_2)_3COOH$	6	1260	
C'	$H-[\text{BSu}]_n-O^-Na^+$ $HOOCCH_2CO-[\text{BSu}]_n-O(CH_2)_3COO^-Na^+$	7	1268	
F	$H_2N(CH_2)_6NHOC-[\text{BSu}]_n-O(CH_2)_3CH_3$	6	1273	
G	$HCO-[\text{BSu}]_n-OH$	7	1274	
E'	$HOOC(CH_2)_2OC-[\text{BSu}]_n-O(CH_2)_3COO^-\ Na^+$ $CH_2{=}CH(CH_2)_2OCO(CH_2)_2CO-[\text{BSu}]_n-O(CH_2)_2CH{=}CH_2$	6	1282	
H	$CH_3CH_2CO-[\text{BSu}]_n-O(CH_2)_4OCOCH_2COOH$	6	1288	
I	$H_2NCO-[\text{BSu}]_n-OH$	7	1289	
E''	$Na^+\ {}^-OOCCH_2CO-[\text{BSu}]_n-O(CH_2)_3COO^-Na^+$	7	1290	
L	 $-O(CH_2)_4-[\text{BSu}]_n-$ (cyclic)	7	1300	
M	$CH_3CH_2OC-[\text{BSu}]_n-OH$ $H-[\text{BSu}]-O(CH_2)_3CH_3$	7	1302	
H'	$CH_3CH_2CO-[\text{BSu}]_n-O(CH_2)_4OCOCH_2COO^-\ Na^+$	6	1310	
N	 $[\text{BSu}]_n-O(CH_2)_4OCONH(CH_2)_6NHCO-$ (cyclic)	6	1314	
O	$HOOC(CH_2)_3OCO(CH_2)_2CO-[\text{BSu}]_n-O(CH_2)_3CH_3$	6	1316	

Table 2 (Continued)

Symbols	Structures	n	M·Na$^+$	M·K$^+$
P	$\mathrm{H{-}[BSu]_{n}O(CH_2)_4OH}$	7	1318	
Q	$\mathrm{OHC{-}[BSu]_{n}O(CH_2)_3CH_3}$	7	1330	
R	$\mathrm{H{-}[BSu]_{n}O(CH_2)_3COOH}$ $\mathrm{HOCOCH_2OC{-}[BSu]_{n}OH}$	7	1332	
S	$\mathrm{HOOC(CH_2)_2CO{-}[BSu]_{n}OH}$ $\mathrm{OHC{-}[BSu]_{n}O(CH_2)_4OH}$	7	1346	1362
T	$\mathrm{OHC{-}[BSu]_{n}O(CH_2)_3COOH}$	7	1360	
S’	$\mathrm{HOOC(CH_2)_2OC{-}[BSu]_{n}O^{-}\,Na^{+}}$	7	1368	
U	$\mathrm{CH_2{=}CHCO{-}[BSu]_{n}O(CH_2)_4OH}$	7	1372	
V	$\mathrm{CH_3CH_2CO{-}[BSu]_{n}O(CH_2)_4OH}$	7	1374	
W	$\mathrm{H_2NOC{-}[BSu]_{n}O(CH_2)_3COOH}$	7	1375	
Z	$\mathrm{CH_3CH_2CO{-}[BSu]_{n}O(CH_2)_3COOH}$ $\mathrm{HOOCCH_2CO{-}[BSu]_{n}O(CH_2)_3CH_3}$	7	1388	
S’’	$\mathrm{Na^{+}\,{}^{-}OOC(CH_2)_2CO{-}[BSu]_{n}O^{-}\,Na^{+}}$	7	1390	

[a] BSu = $-[O(CH_2)_4OCO(CH_2)_2CO]-$.

Results and Discussion

Two polyester samples (Table 1) were used for this study. Moulded films with a thickness of about 100 μm were subjected to accelerated photoaging treatment by using a QUV PANEL test at 60 °C, in atmospheric air, up to 192 h. The photooxidative process was fairly rapid producing a severe reduction of the average molar mass with the irradiation time already after 24 h (Table 1).

The entire MALDI spectrum of PBSu is reported in Figure 1S (Supporting Information), so that in Figure 1a−c are shown only expanded portions of the MALDI spectra of the PBSu samples irradiated for 0, 96, and 192 h, respectively. These portions span over a mass range of 350−400 Da (about two PBSu repeat units). From the inspection of the spectra in Figure 1b,c it is possible to observe a gradual increment of peaks with respect to the original sample in Figure 1a. This indicates that photooxidation reactions have occurred, producing new compounds that are detected and differentiated by the MALDI analysis. The favorable event here is that the MALDI spectra present many new well-resolved peaks, which provide potential information on the structure and end groups of the oxidation products.

Due to the effect of isotopic resolution, the identity and relative intensity of peaks in Figure 1a−c are not easily assessed, and therefore, in Figure 2 the PBSu spectra are shown after the deisotoping procedure. The latter implies the use of a deisotoping program to suppress the contributions of the M + 1 and M + 2 peaks. All the peaks correspond to PBSu oligomers with a variety of end groups, and they have been assigned (Table 2) to specific oligomer structures. The identification of the structure and of end groups attached to the oligomers produced in the oxidation process is of outmost importance, since the end groups may reveal the particular mechanism that has been active in the oxidation process. In Figure 2 are shown the MALDI

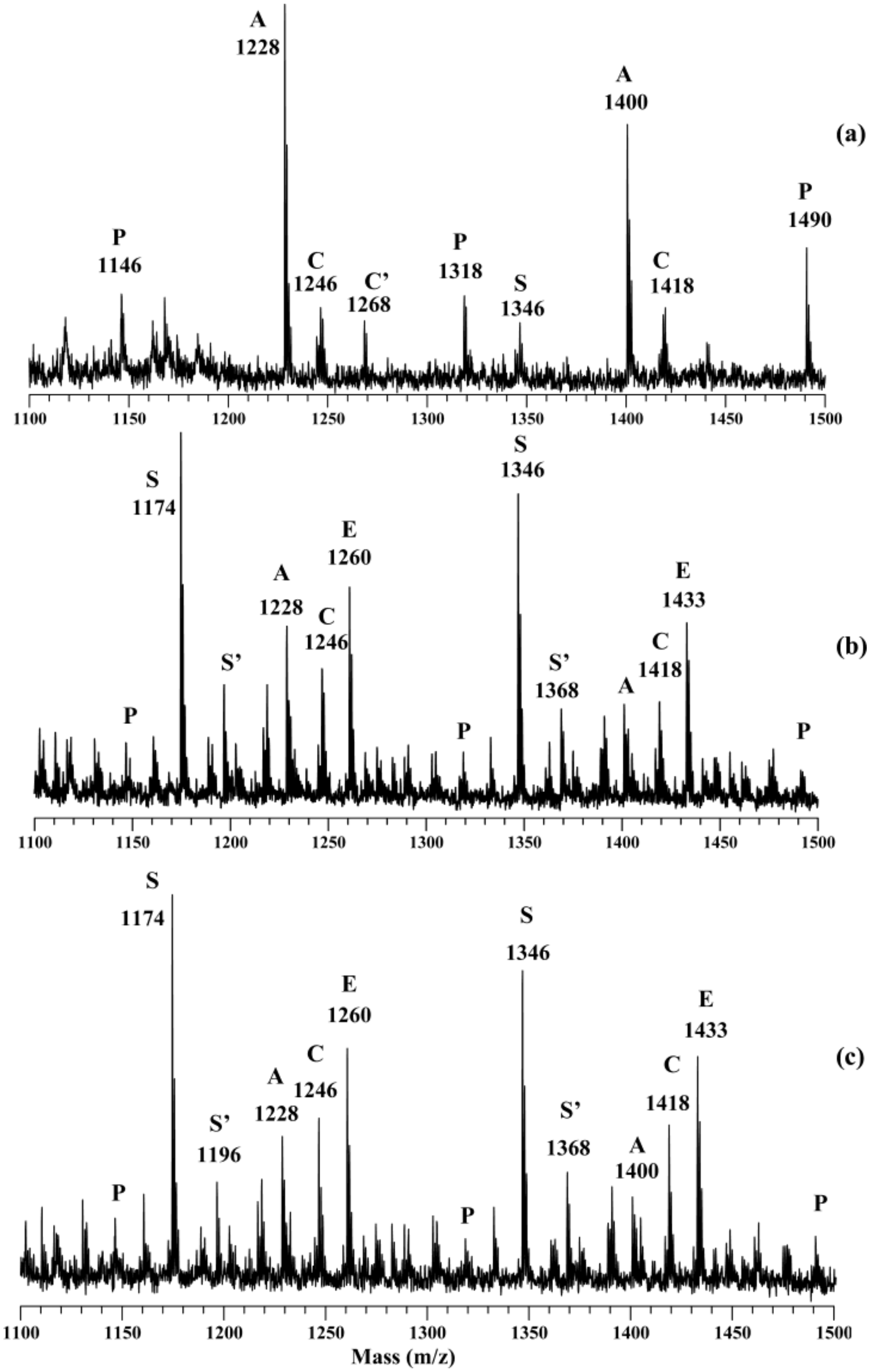


Figure 1. Enlarged portions of the MALDI-TOF mass spectra of PBSu sample photooxidized at 60 °C for 0 (a), 96 (b), and 192 h (c).

spectra of the PBSu sample, original (a) and after 24 h of irradiation (b). The six MALDI peaks in Figure 2a are due to only four oligomers: (i) sodiated ions of cyclic PBSu chains (species A Na^+; *m*/*z* 1228) and potassiated ions of cyclic PBSu chains (species A K^+; *m*/*z* 1244); ii) sodiated ions of linear oligomers terminated with carboxyl at one end and with hydroxyl groups at the other end (species C Na^+; *m*/*z* 1246) and the corresponding sodium salt of the same species (C′ Na^+; *m*/*z* 1268); (iii) sodiated ions of linear oligomers terminated with hydroxyl groups at both ends (species P Na^+; *m*/*z* 1318); (iv) sodiated ions of linear oligomers terminated with carboxyl groups at both ends (species E Na^+; *m*/*z* 1346). The structure of each oligomer is identified in the inset of Figure 2.

Although the peak at 1228 Da, due to the cyclic oligomer, appears the most intense in Figure 2, the relative abundance of the cyclic oligomers ions decreases rapidly at higher mass (Figure 1S), as it is usually observed for synthetic polymers.[11] Therefore, the MALDI spectrum of the original PBSu can be safely taken as indicating that the sample under investigation, although containing a sizable amount of cycles, is mainly constituted of linear chains terminated with carboxyl and hydroxyl groups (peaks at 1246, 1318, and 1346 Da, Figure 2 and Table 2).

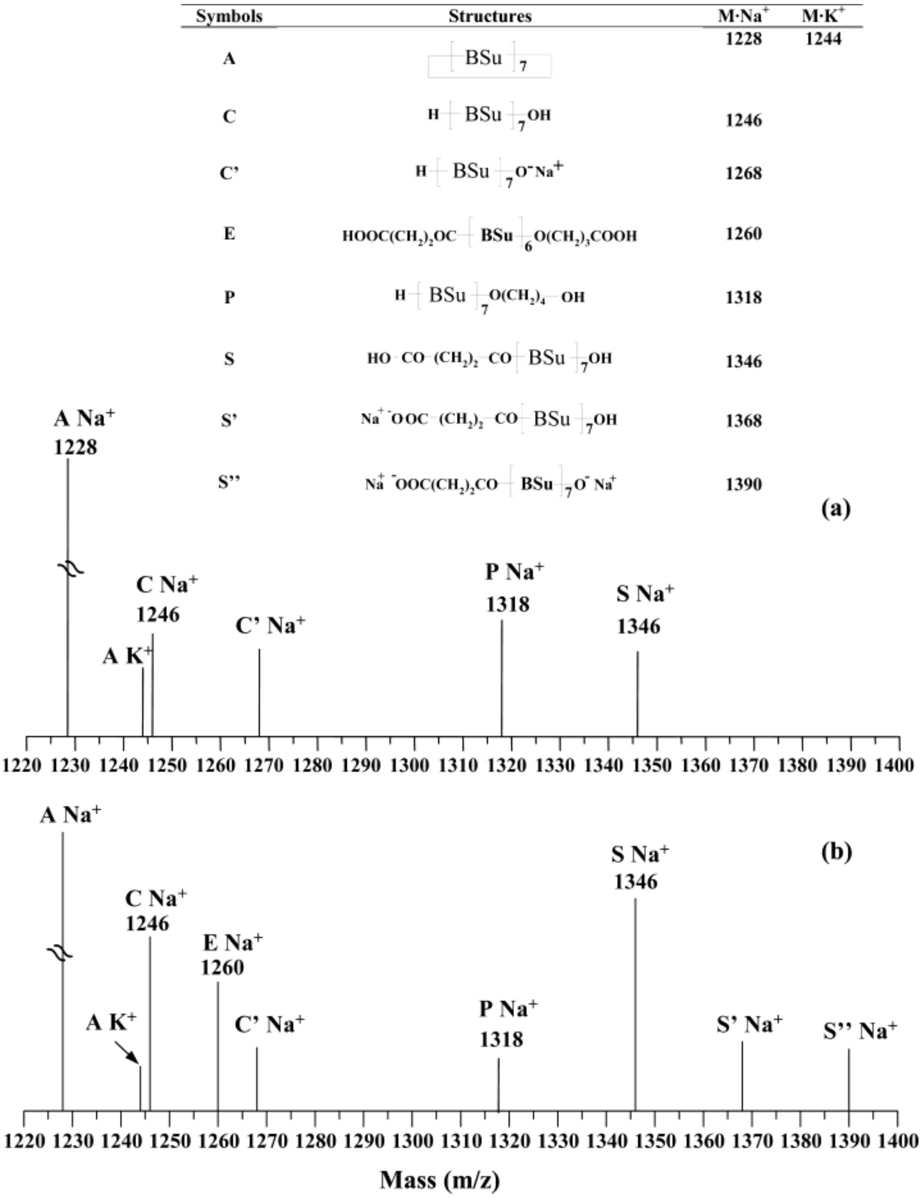


Figure 2. Deisotoping MALDI-TOF mass spectra, in the mass range of 1220−1400 Da, of the original PBSu sample (a) and photooxidized for 24 h at 60 °C (b).

The MALDI spectrum (after deisotoping) of the PBSu sample irradiated for 24 h at 60 °C is reported in Figure 2b. In Figure 2S is reported the same mass spectrum before deisotoping. We notice the appearance of a new peak at 1260 Da (a linear oligomer terminated with malonic acid at one end and succinic acid at the other end; Table 2), originated by the oxidation of the alcoholic chain end of the oligomer at 1246 Da (eq 1, Scheme 1).[20]

$$\sim\!\sim O(CH_2)_4OH \xrightarrow[h\nu]{O_2} \sim\!\sim O(CH_2)_3COOH \qquad (1)$$

Also the peak at 1346 Da (a linear oligomer terminated with a carboxyl group at each end; Table 2) appears with increased intensity with respect to the original sample, indicating the early occurrence of an oxidation process. This oxidation reaction (Scheme 1) is also confirmed by the trend of the ion abundance at 1318 Da (a linear oligomer terminated with hydroxyl groups at both ends), which appears in Figure 2b with decreased intensity with respect to the spectrum of the original sample in Figure 2a.

Our mass spectral data provide also an insight on the product distribution changes during the photooxidation reaction.

In Figure 3 are reported the kinetic tracings of three representative oligomers. The relative abundance of the cyclic oligomer peak at *m*/*z* 1228 Da (Table 2) steadily decreases to about one-fifth of its initial value already after 72 h of irradiation. On the contrary, the relative abundance of the linear oligomer ions at 1260 Da, bearing carboxyl groups at both ends (Table 2), shows a noticeable increment with the irradiation time. The progressive decrement of the intensity of the peak at 1318 Da, shown in Figure 3, is in agreement with the above-mentioned oxidation of the alcoholic end groups (Scheme 1).

In Figure 4a is shown the MALDI spectrum (mass range of 1220−1400 Da, after deisotoping) of the PBSu sample irradiated for 48 h. In Figure 3S is reported the same spectrum non-deisotopized. The most interesting change with respect to the sample irradiated for 24 h (Figure 2b) is given by the appearance of a new peak at 1332 Da, whose structure (species R, Table 2) suggests

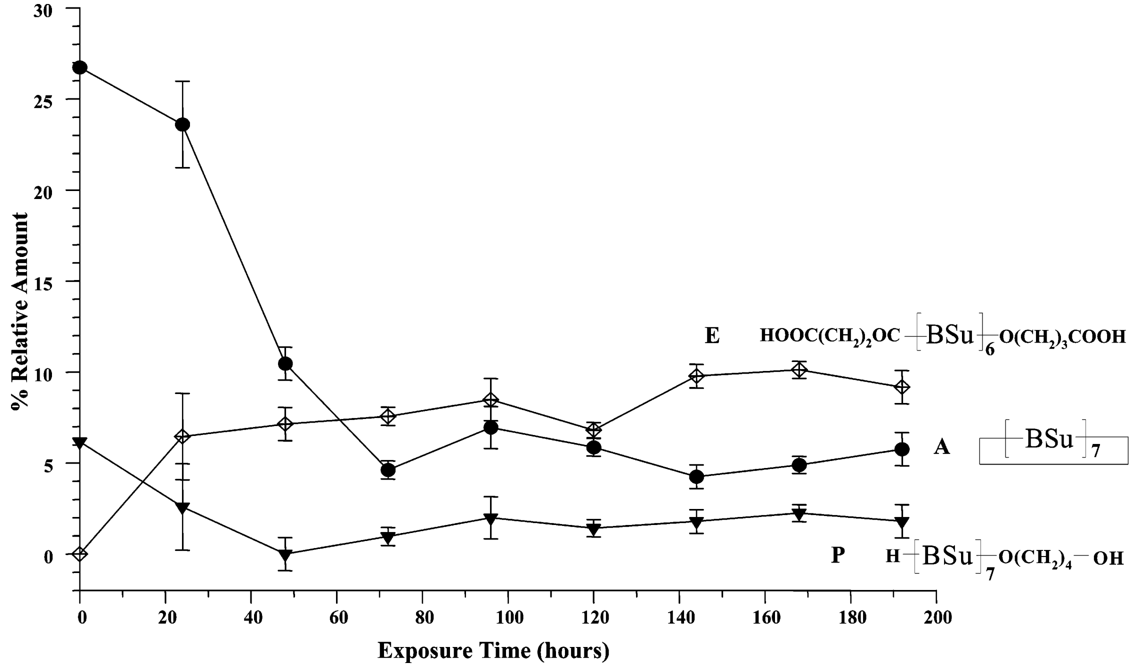


Figure 3. Relative amount vs exposure time of oligomers E, A, and P (Table 2), obtained from the MALDI spectra of the photooxidized PBSu sample.

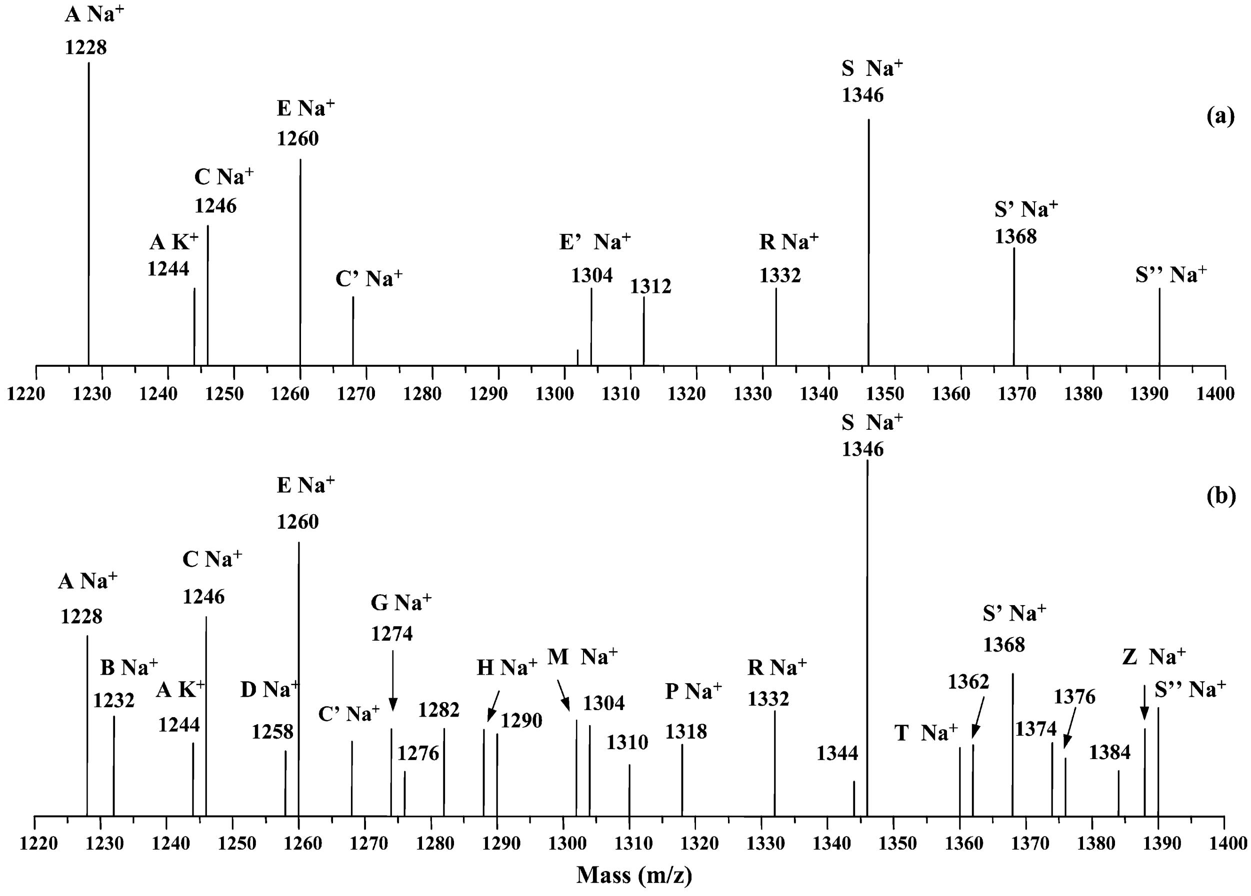


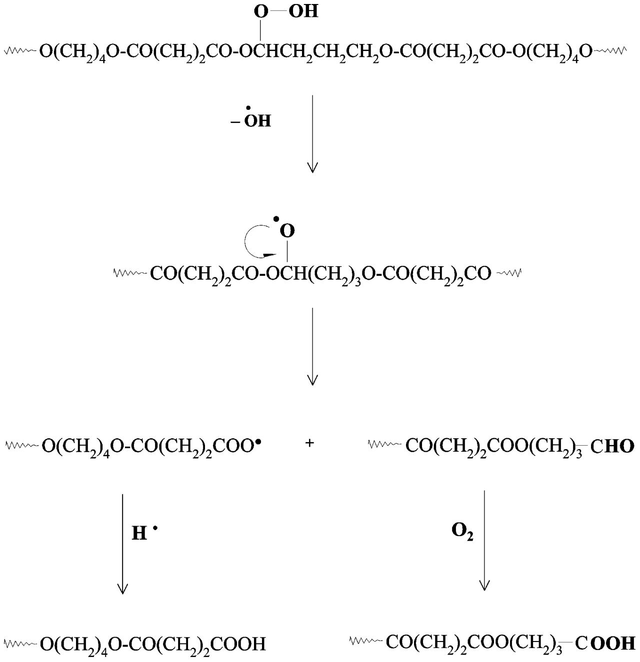
Figure 4. Deisotoping MALDI-TOF mass spectra, in the mass range 1220−1400 Da, of the PBSu sample photooxidized at 60 °C for 48 (a) and 192 h (b).

that the well-known[10] α-H abstraction process is already active.

$H\text{-}[BSu]_n\text{-}O(CH_2)_3COOH$ 1332Da

The initial step in this process consists of a hydrogen abstraction from the methylene group adjacent to the ester linkage, leading then to the formation of a hydroperoxide intermediate. The latter decomposes (Scheme 2) by radical rearrangement reactions and generates the PBSu oxidation products observed in the MALDI spectra (Figure 4a,b, Table 2, Scheme 2). The MALDI spectrum (after deisotoping) of the PBSu sample irradiated for 192 h is reported in Figure 4b. The original

Scheme 2. Photodecomposition of the Hydroperoxides of PBSu Formed via the α-Hydrogen Abstraction



spectrum is shown in Figure 4S. In addition to the oligomers present in the previous spectra, several new compounds can be identified (Table 2) in this spectrum. Among them, the peak at 1274 Da (species G, Table 2),

$$\mathrm{HCO}\!-\!\!\left[\mathrm{BSu}\right]_n\!\!-\mathrm{OH}$$

having a butyl formate and a succinic acid as the chain ends, is diagnostic for the occurrence of the Norrish I cleavage reaction, as reported in Scheme 3.

The Norrish I cleavage reaction (Scheme 3) yields oligomers with end groups such as butyl formate, ethyl ester, butyl ester, and malonic acid that correspond to peaks at 1258, 1274, 1288, 1310, and 1360 Da.

The other peaks appearing in Figure 4b have been assigned to oligomers bearing end groups that can derive from all the processes considered here and consequently are not unequivocally connected to a specific photooxidation process.

The appearance of several compounds produced at higher irradiation times (Figure 4a,b), with respect to the only one new photooxidation product present in Figure 2b (species E), points out that the new oxidation reactions experience an induction period before becoming active.

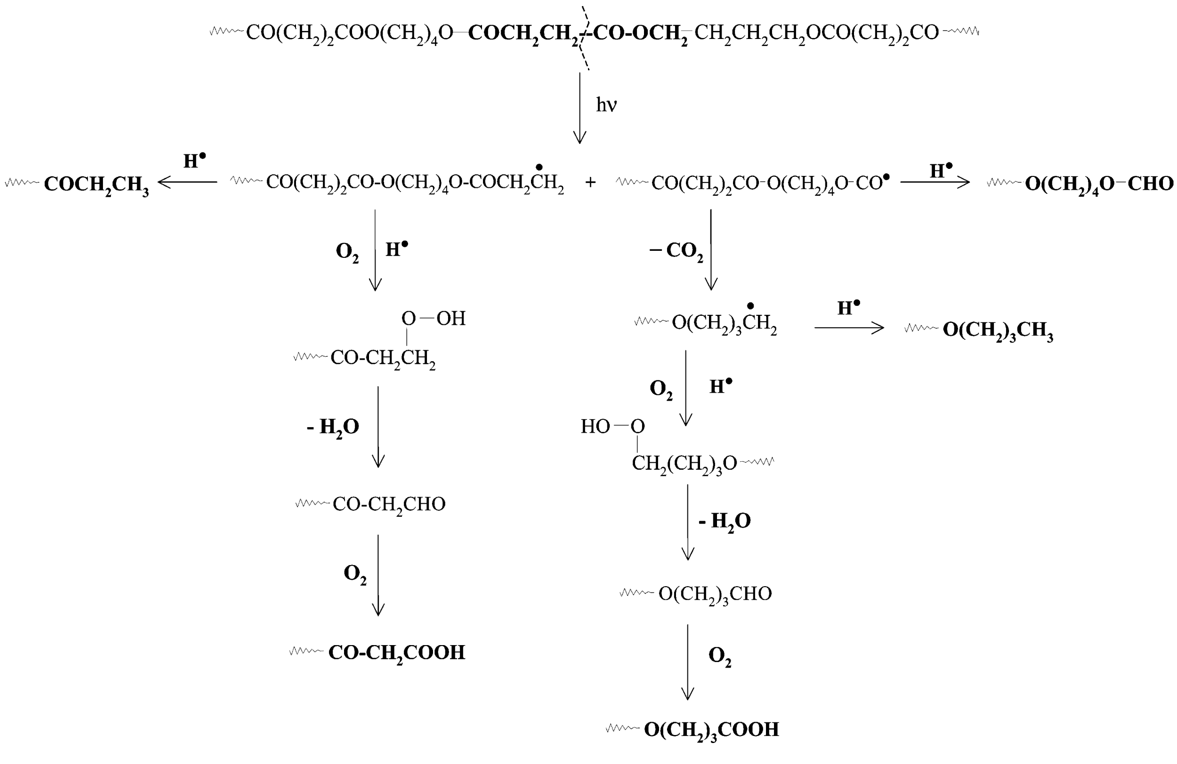
This fact can be accounted for looking at the increasing amount of UV light absorbed by the polyester films as a function of the exposure time.

The UV spectrum (Figure 5) of the unexposed PBSu films shows a broad absorption band with a maximum at about 240−300 nm, which nearly doubles its intensity and widens toward the longer wavelengths with the exposure time, most likely due to the presence of the photooxidation products. Therefore, the irradiated films absorb a higher amount of light, allowing the occurrence of new oxidation processes and justifying the presence of an induction period for their appearance (Figures 2, 4, and 6).

In Figure 6 are reported the kinetic tracings relative to the relative ions abundance of some oxidation products representative of the two chain cleavage oxidation mechanisms found to be operating. These photoproducts appear after an induction period (T_i, Scheme 1), contrary to the oligomers shown in Figure 3, which are immediately subject to variation.

Remarkably, the induction period for the appearance of the oxidation products from the Norrish I reaction is 48 h (Figure 6b,c), whereas the induction period for the appearance of the oxidation products from the hydroperoxide decomposition is 24 h (Figure 6a).

Scheme 3. Photodecomposition of PBSu via the Norrish I Reaction



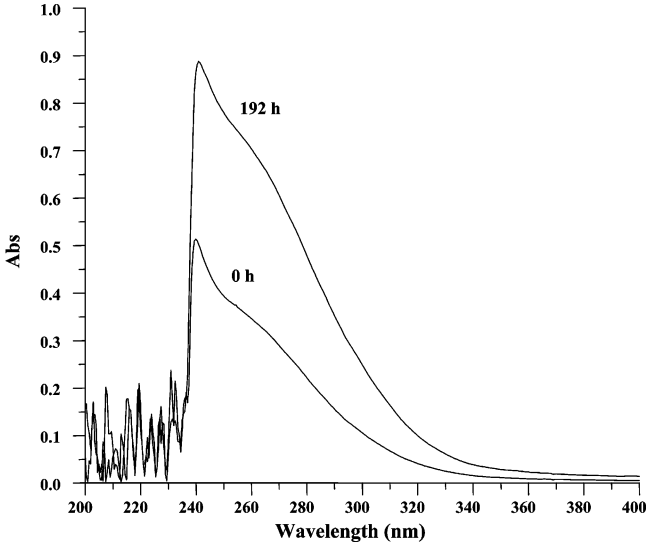


Figure 5. UV spectra of PBSu sample photooxidized for 0 and 192 h.

Kinetic data in Figures 3 and 6 have an obvious relevance in describing the relative importance and succession of the oxidation events in aliphatic polyesters. It should not remain unnoticed that these data provide an additional discrimination criterion for the spectral peaks assignment reported in Table 2, especially where isobar structures could be drawn from the mass of some oligomers.

A decarboxylation reaction has been proposed[7] to occur in aliphatic polyesters. However, this process would produce the same oligomers originating from the Norrish I reaction, except for the oligomer corresponding to the peak at 1274 Da, which is diagnostic for the Norrish I reaction. Therefore, the occurrence of a decarboxylation reaction cannot be established unambiguously by our mass spectrometric evidence.

We lack also of specific evidence for the occurrence of extensive hydrolytic reactions during the photoirradiation of PBSu.

According to some recent literature reports,[4−7] the main photodegradation mechanism of PBSu is the β-hydrogen transfer. This process would lead to the formation of linear oligomers with carboxyl and unsaturated end groups, but these oligomers are isobaric with the cycles (species A, Table 2) and with another oligomer type (species E′, Table 2). Therefore, the occurrence of this reaction cannot be established here. However, on the basis of the evidence presented above, if occurring, the β-hydrogen transfer reaction cannot be considered the major photodegradation process active in PBSu. In fact, if the β-hydrogen transfer mechanism were active, reasonably the relative intensity of the peak at 1228 Da (species A, Table 2) should increase; Figure 3 shows that it does not happen.

In Figure 7a,b are shown expanded portions of the MALDI spectra of the Bionolle 1001 sample irradiated for 0 and 96 h, respectively. In Figures 5S and 6S (Supporting Information) are reported the non-deisotopized mass spectra. The spectrum of the original Bionolle 1001 sample is similar to that of PBSu in Figure 2a, except for the intense peak appearing at 1314 Da, which has been unambiguously as-

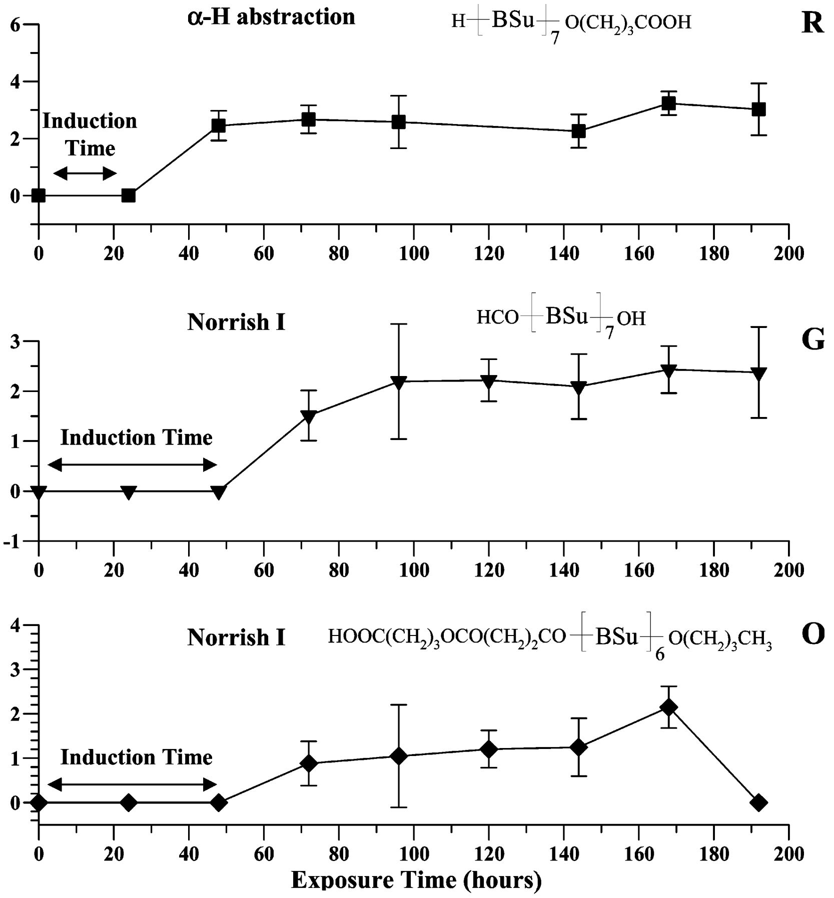


Figure 6. Relative amount vs exposure time of species R, G, and O (Table 2), obtained from the MALDI spectra of the photooxidized PBSu sample.

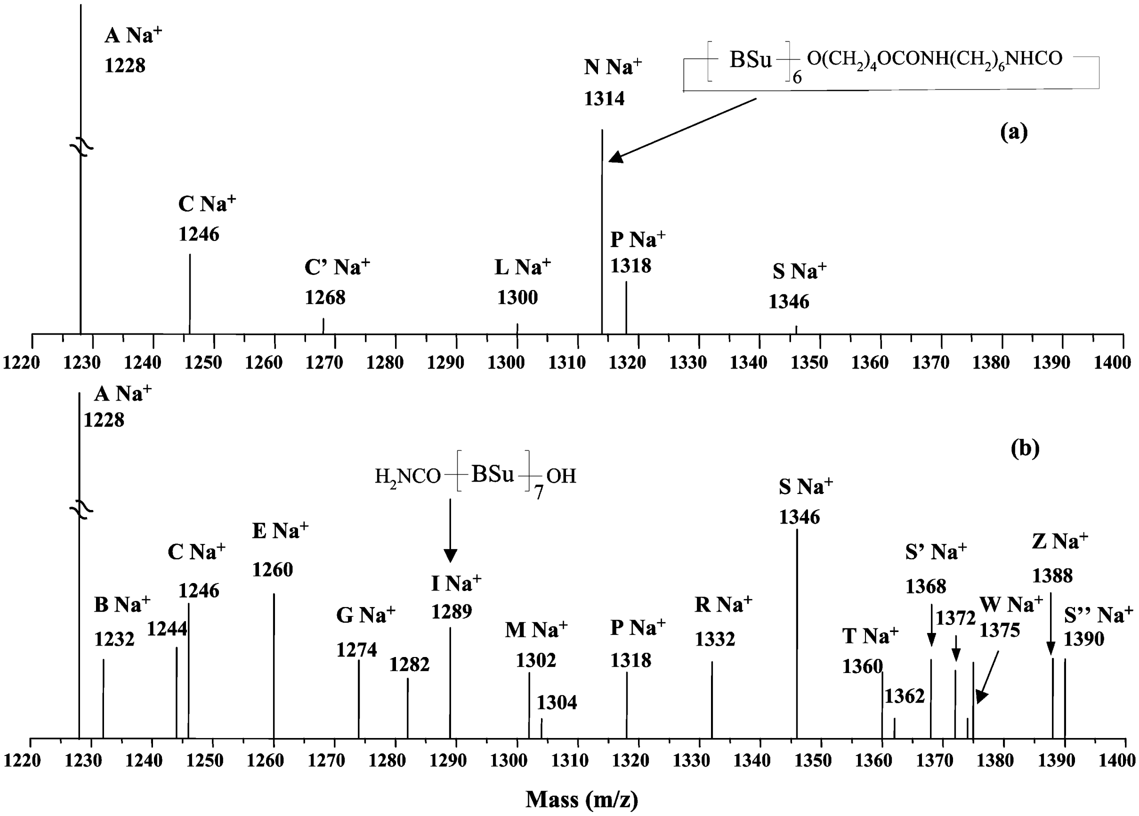
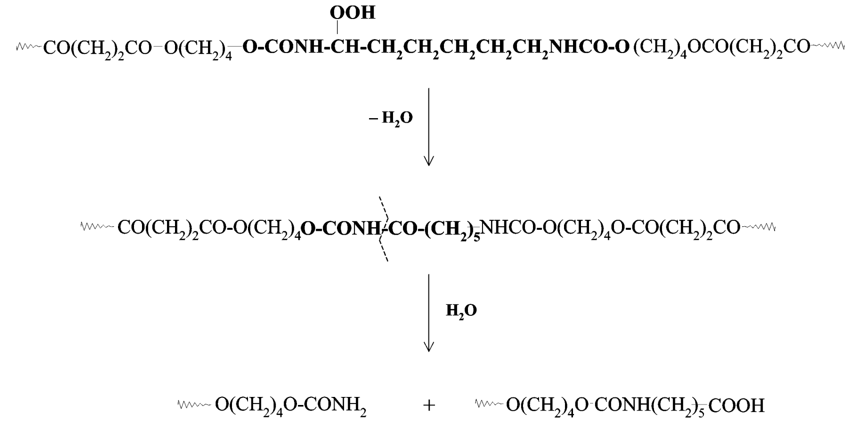


Figure 7. Deisotoping MALDI-TOF mass spectra, in the mass range of 1220–1400 Da, of the original Bionolle 1001 sample (a) and photooxidized for 96 h at 60 °C (b).

Scheme 4. Photodecomposition of the Hydroperoxides Formed from the Urethane Units in Bionolle 1001 via the α-Hydrogen Abstraction



signed to an oligomer bearing urethane units (Table 2), and the peak at *m/z* 1310 (species L, Table 2),

$$\left[O(CH_2)_4OCO(CH_2)_2CO\right]_n O(CH_2)_4OCONH(CH_2)_6NHCO$$

assigned to cycles bearing ether bond units. The presence of urethane linkage (species N, Table 2) confirms that hexamethylene diisocyanate was used in the synthetic procedure as chain extender to increase the molar mass of this industrial polymer (Table 1).

The fate of these urethane units in the photooxidation process is described in Scheme 4. Following to the hydrogen abstraction process, the hydroperoxide decomposition occurs with loss of water molecules and chain scission, reaching the ultimate step with the formation of two oligomers at 1289 and 1375 Da (Figure 7b):

$$H_2NCO\left[O(CH_2)_4OCO(CH_2)_2CO\right]_n OH \qquad 1289\text{Da}$$

$$H_2NCO\left[O(CH_2)_4OCO(CH_2)_2CO\right]_n O(CH_2)_3COOH \qquad 1275\text{Da}$$

This photooxidation process has already been described in the literature for polyurethanes[9,10] and is quite similar to that occurring in Nylon 6.[15b]

Except for this particular difference, originating from the different synthetic procedures, the MALDI spectra of PBSu and Bionolle 1001 (Figures 2a and 7a) are nearly identical, indicating that the same photooxidation processes do occur in these aliphatic polyesters.

Conclusions

In summary of our results, a relevant amount of structural information on the photooxidation products of PBSu has been extracted from the MALDI spectra reported herewith. The novelty of our approach consists of using a nonaveraging technique (mass spectrometry), which allows the detection and monitoring of each oligomer during the oxidation process.

In fact, the present MALDI investigation allowed the detection of many products, formed in the photooxidative degradation of PBSu, which had escaped previous studies.

Photoirradiation produced a sensible reduction of the molar mass of the polyesters (Table 1), promoting the formation of PBSu oligomers with different end groups (Table 2).

According to the structure of the oxidation products identified, three photooxidation processes have been unambiguously ascertained to occur in PBSu.

Beside the hydrogen abstraction and subsequent hydroperoxide formation, a process active in several other polymeric materials, two other cleavage processes appear to be operating in PBSu, i.e., the chain cleavage reaction Norrish I and the hydroxyl end groups oxidation (Scheme 1).

Remarkably, these three processes have been revealed to be time-resolved, each showing a different induction period before appearance.

Photooxidation of the PBSu alcoholic end groups, leading to oligomers with carboxyl chain ends (route 3, Scheme 1), is the first process to occur. Then, the hydroperoxides, formed from PBSu chains by α-H abstraction, undergo thermal degradation to produce different oligomers (route 1, Scheme 1). The last process is a Norrish I chain cleavage reaction, which generates specific oxidation products (route 2, Scheme 1).

The data collected are sufficiently diagnostic to discriminate among different oxidative pathways proposed in the literature[4−9] and provide the first solid evidence about the photooxidation mechanisms operating in PBSu.

Overall, our results introduce new concepts and extend the general knowledge of photooxidation reactions in aliphatic polyesters, and it should be expected that future MALDI studies might have an impact on the current views on photodegradation processes of other polymer systems.

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Supporting Information Available: Figures 1S, presenting the entire MALDI-TOF mass spectrum of the original PBSu sample, Figures 2S, showing the MALDI-TOF mass spectrum, in the mass range 1220−1400 Da, of the PBSu sample photooxidized at 60 °C for 24 h, Figures 3S, presenting the MALDI-TOF mass spectrum, in the mass range 1220−1400 Da, of the PBSu sample photooxidized at 60 °C for 48 h, Figures 4S, showing the MALDI-TOF mass spectrum, in the mass range 1220−1400 Da, of the PBSu sample photooxidized at 60 °C for 192 h, Figure 5S, showing the MALDI-TOF mass spectrum, in the mass range of 1220−1400 Da, of the original Bionolle 1001, and Figure 6S, presenting the MALDI-TOF mass spectrum, in the mass range of 1220−1400 Da, of the Bionolle 1001 sample photooxidized for 96 h at 60 °C. This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) A reviewer has suggested that the oxidation of the alcohol chain end may involve a hydrogen abstraction of the methylene group in α position to the hydroxyl end group, followed by a classical hydroperoxidation and further decomposition.

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