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MALDI−TOF MS and DIOS−MS Investigation of the Degradation and Discoloration of Poly(ethylene terephthalate)

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ABSTRACT: In this study, three mass spectrometry techniques matrix-assisted laser desorption ionization mass spectrometry (MALDI−TOF MS) combined with thin-layer chromatography (TLC), laser desorption/ionization on silicon−mass spectrometry (DIOS−MS), and time-of-flight secondary ion mass spectrometry (TOF−SIMS) were used to investigate the thermooxidative degradation and resultant discoloration of poly(ethylene terephthalate) PET that frequently occurs during melt processing. The MALDI−TOF MS spectra of the degraded polymer showed the formation of oligomers containing carboxyl end groups via chain scission at the ether link present in PET. In addition, a variety of cyclic oligomers are found to form via two different mechanisms from the linear oligomers of the virgin PET. Thus, our results not only confirm the oligomers containing carboxyl end groups and cyclic oligomers as the low molecular weight degradation products but also deepen the understanding about their structures, molecular weights, and molecular weight distributions. Furthermore, a MALDI−TOF MS study directly on the TLC plate and DIOS−MS enable us to identify low molecular weight compounds (not detected previously due to matrix interference) that are contributors to color formation.

Introduction

The thermooxidative degradation of poly(ethylene terephthalate) (PET) during melt processing is an undesirable process that adversely affects optical and mechanical properties that are relevant for the end use of the material. This type of degradation produces scission of the polymer chains leading to reduction in molecular weight and formation of various oligomeric compounds.[1] Additionally, the discoloration that accompanies this type of degradation becomes a critical problem for applications where optically clear materials are required. Upon heat treatment, the polymer initially turns green, then dark yellow, and finally brown as the heating is continued. These color changes are ascribed to various chromophores that are generated due to thermal oxidation during melt processing.[2]

The thermooxidative degradation and color formation in virgin PET during melt processing have been previously studied using techniques such as ultraviolet−visible spectroscopy (UV−vis), infrared spectroscopy (IR), nuclear magnetic resonance (NMR) spectroscopy, and X-ray photoelectron spectroscopy (XPS) to understand the degradation process and identify the products.[2−4] Although these methods provide information about the changes in the chemical structure of virgin and degraded polymers, they do not provide information about the molecular weight of the material and the changes in the molecular weight that occur during the thermooxidative degradation, changes that can be linked to discoloration.

In recent years, MALDI−TOF MS has gained importance for studies on thermal and photooxidative behavior of various polymeric materials.[5−15] Detailed information about the molecular weight and structure of the virgin polymer and degradation products can be obtained using this technique. Developed initially for biomaterials characterization,[16−19] MALDI−TOF MS permits a fast identification of the polymer degradation products without time-consuming chromatographic separation.[15] Compared with other mass spectrometry techniques such as direct pyrolysis−mass spectrometry (DP−MS) or time-of-flight secondary ion mass spectrometry (TOF−SIMS), where ionized low mass molecular ions (fragments) are obtained, the MALDI−TOF MS spectra show mainly single charged quasi molecular ions with hardly any fragmentation and, in particular, in the low molecular range exhibit high mass resolution.[15]

Several groups have employed MALDI−TOF MS to analyze various PET samples including the virgin material and PET after thermal, chemical, hydrolytic, or plasma treatment as well as surface treatments.[11,19,20] However to the best of our knowledge, there are no MALDI−TOF MS studies to understand the mechanism of discoloration and the thermooxidative degradation of PET that occurs during melt processing despite its high technological importance. Hence our intention is to use MALDI−TOF MS to obtain detailed information about parameters like molecular weight, end groups, and the structure of the degraded products from the thermooxidative degradation of PET and to gain a better understanding of the mechanism of such degradation and discoloration.

In the present study, the thermal treatment of PET was carried out in air at 280 °C in an aging oven over a period of time to simulate the thermooxidative degradation that occurs during melt processing, and the samples degraded at different time interval were analyzed by MALDI−TOF MS. The degradation products (oligomers) were also extracted and MALDI−TOF MS was performed on the extracts collected from samples at various time intervals. As MALDI−TOF MS requires the use of a matrix reagent, information about the lower molecular weights (under m/z 500) could not be obtained due to the background peaks

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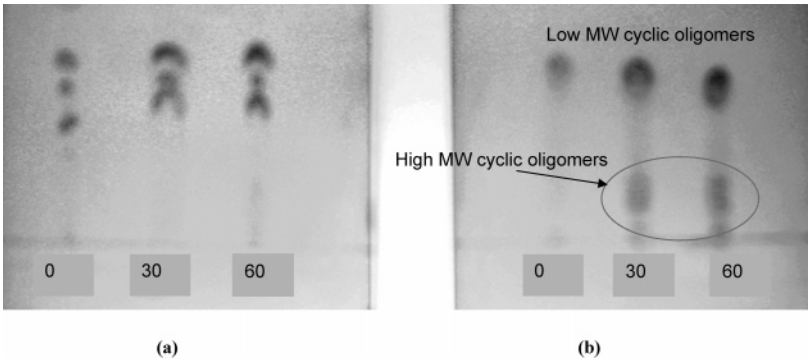
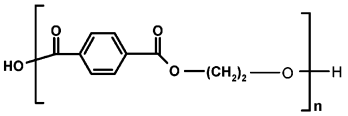
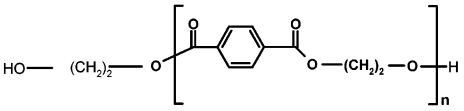
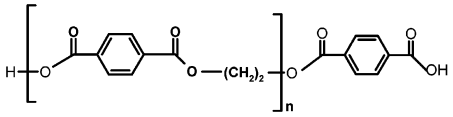


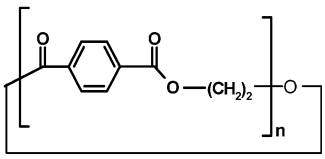
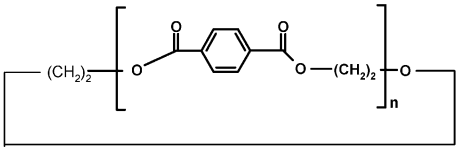
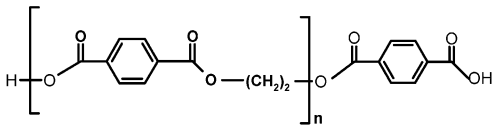
Figure 1. Thin-layer chromatograms of virgin and degraded PET samples: (a) linear oligomers; (b) cyclic oligomers at different times of thermooxidative treatment (0, 30, and 60 min).

Table 1. Structure of the Predominant Ions and Their Molecular Masses in Virgin PET

Oligomer	Structure	m/z (mass of repeating unit (n)= 192)		
	Virgin PET	Observed	Calculated	n
[GT]$_n$ (Heterotelechelic COOH and OH terminated linear oligomer)		[M+H]$^+$	[M+H]$^+$	
		787	787	4
		979	979	5
		1171	1170	6
		1361	1363	7
		1553	1555	8
		1745	1747	9
[GL]$_n$ (Glycol terminated linear oligomer)		[M+H]$^+$	[M+H]$^+$	
		831	831	4
		1024	1023	5
		[M+Na]$^+$	[M+Na]$^+$	
		1429	1430	7
		1621	1622	8
		1813	1814	9
[GC]$_n$ (COOH terminated linear oligomer)		[M+H]$^+$	[M+H]$^+$	
		551	551	2
		743	743	3

originating from the matrix that interfere with the MALDI−TOF MS spectra in the lower mass range. In some cases, optimization of the sample preparation leads to suppression of the matrix signal and can allow unambiguous determination of the analyte peaks.[21] Therefore, thin-layer chromatography (TLC) was used to separate different oligomers from untreated and degraded PET samples and MALDI−TOF MS was performed directly on the spots of the TLC plate. Laser desorption/ionization on porous silicon-mass spectrometry (DIOS−MS), a technique developed by Siuzdak et al.,[22,23] was also used to examine the virgin and degraded polymer samples. This is a novel method that employs direct laser vaporization to create gas-phase ions that can be analyzed. In both techniques, the mass spectra can be obtained without the use of a matrix reagent and obstructive peaks in the lower mass region are not produced[22−25] thus permitting the identification of the low molecular weight polymer degradation products. Finally, TOF−SIMS was used to analyze the surface of the virgin and degraded PET samples.

Table 2. Structure of the Predominant Ions and Their Molecular Masses in Degraded PET

Oligomer	Structure	m/z (mass of repeating unit (n)= 192)		
		Observed	Calculated	n
		$[M+Na]^+$	$[M+Na]^+$	
[GT]$_n$		599	599	3
(Cyclic oligomer)		790	791	4
		983	983	5
		1175	1175	6
		1367	1367	7
[GT]$_n$-G		$[M+Na]^+$	$[M+Na]^+$	
(Cyclic oligomer with an ether linkage in the backbone)		834	835	4
		1028	1027	5
		1220	1219	6
		1412	1411	7
[GC]$_n$		$[M+Na]^+$	$[M+Na]^+$	
(COOH terminated linear oligomer)		551	551	2
		765	766	3
		957	958	4
		1149	1150	5
		1341	1342	6

Experimental

Materials. Virgin PET (intrinsic viscosity ≈ 0.83 dL/g) was obtained from VISY Plastics Australia (supplier: SK Chemicals, Korea). The polymer was dried for several hours in a vacuum oven at 160 °C before use. Trifluoroacetic acid (TFA) and the MALDI−TOF MS matrix compound, 2,5-dihydroxybenzoic acid (DHB), were purchased from Aldrich Chemical Co. Australia. Chloroform and acetone (analytical grade) were supplied by Ajax Finechem, Australia, and used as received.

Thermal Treatment. The model degradation study was carried out in the laboratory for a prolonged time under controlled conditions and a similar discoloration problem was noticed, as is observed in melt processing. Such thermooxidative treatment was performed in an aging oven (Gallenkamph), by heating 5 g of polymer in an aluminum pan in air at 280 °C for 30, 60, and 120 min, respectively. These samples were used for various MALDI−TOF MS, DIOS−MS, and TOF−SIMS analyses.

Sample Preparation for MALDI−TOF MS and DIOS—MS Analyses. In these experiments, 0.2 g of virgin and degraded PET samples were dissolved in 1 mL TFA, and 20 μL of the polymer solution was mixed with 20 μL of the DHB matrix. Then, 1 μL of the mixture was dropped onto a stainless steel MALDI−TOF MS plate and the solvent was evaporated. Also the polymer solutions without the matrix were deposited onto a porous silicon surface for DIOS−MS analysis. Additionally, a PET sample degraded for 60 min was extracted with chloroform using a Soxhlet apparatus, to remove any soluble products for analysis. Then, 1 μL of the extract was deposited onto a porous silicon surface for performing DIOS−MS.

The separation of oligomers was done using a modified literature method.[12] Briefly, 1 g of virgin PET and degraded PET samples were dissolved in 2 mL of TFA. The polymer was then precipitated by successively adding 4 mL of chloroform and 4 mL of acetone. The PET oligomer solution was separated from the precipitated

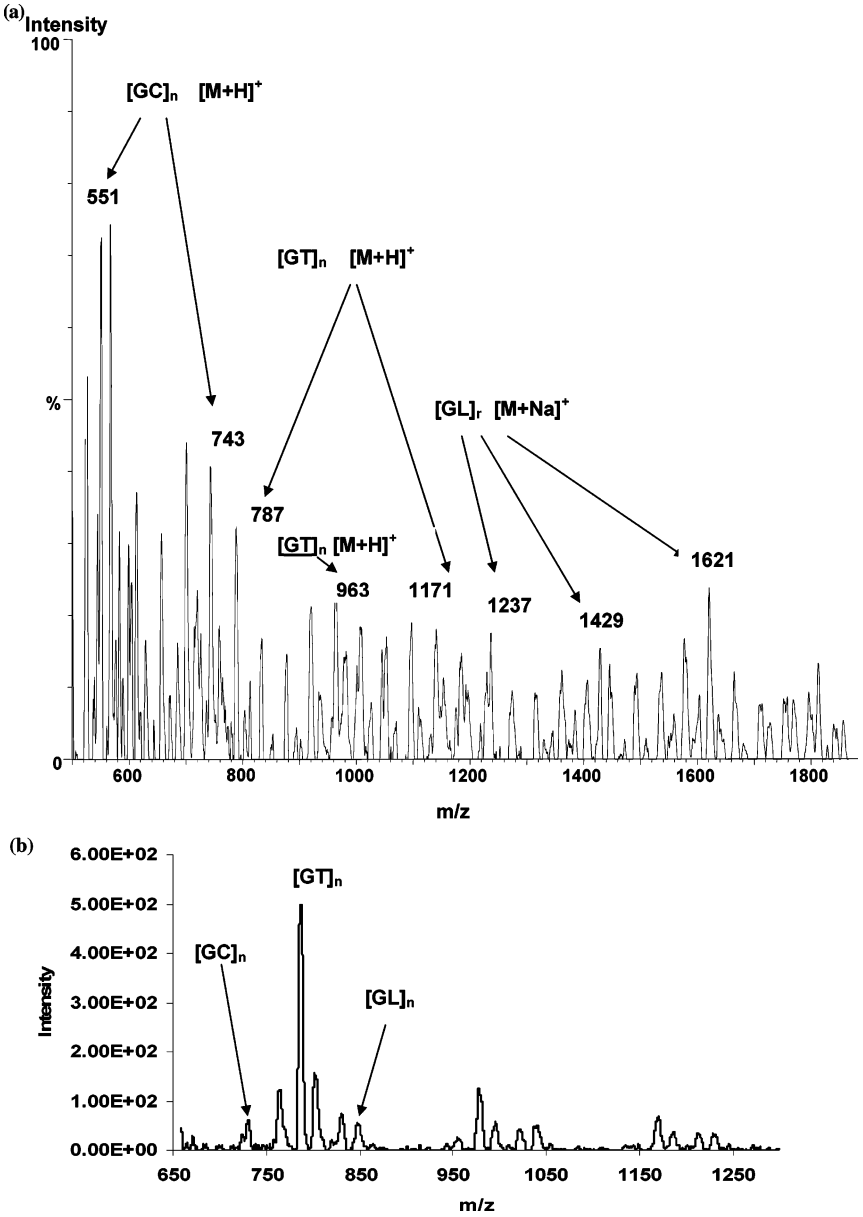


Figure 2. MALDI−TOF mass spectra of virgin PET (a) and oligomers extracted from virgin PET (b).

polymer by filtration. The samples for MALDI−TOF MS analysis were prepared by mixing 20 μL of oligomer solution with 20 μL of DHB matrix. Then, 1 μL of the mixture was dropped onto a stainless steel MALDI−TOF MS plate, and the solvent was evaporated.

Thin-Layer Chromatography (TLC). The TLC was performed on TLC aluminum sheets (silica gel 60 F_{254}, Merck, Darmstadt) using the same PET oligomer and polymer solution samples prepared for MALDI−TOF MS. The linear oligomers were separated using a solvent mixture of dichloromethane/chloroform/carbon tetrachloride/acetone 3/9/1/1 (v/v), and the cyclic oligomers were separated using a solvent mixture of chloroform/diethyl ether 9/1 (v/v).[14] After separation, the oligomer spots were detected using a 254 nm UV lamp.

Porous Silicon Preparation for DIOS—MS. Porous silicon surface was obtained by electrochemically etching low resistivity (0.005−0.02 Ω-cm) n-type Si (100) wafers (Silicon Quest Intl) in 25% v/v hydrofluoric acid (HF)/ethanol with white light illumination at a current density of 3 mA/cm^2 for 2 min. The hydride-terminated chip was then washed with methanol and dried with a stream of N_2 before oxidation by a stream of ozone. Following the initial etching and oxidation, chips were then reetched in a 5% v/v HF/water solution and immediately used for mass analysis.

MALDI−TOF MS and DIOS—MS Analysis. All MALDI−TOF MS and DIOS−MS spectra were recorded in linear mode using a Micromass M@LDI LR Instrument from Waters (U.K.) equipped with a pulsed (4 ns) nitrogen laser emitting at 337 nm. The detector was operated in positive ion mode. The pulse voltage was set to 1523V for MALDI−TOF MS and to 700−800V for DIOS−MS. To obtain best spectral resolution, the laser intensity was set at medium to high levels for MALDI−TOF MS and to high level for DIOS−MS. At least 10 spectra were collected and combined.

TOF−SIMS Analysis. TOF−SIMS analysis was performed on a Physical Electronics TRIFT II TOF−SIMS (model 2100) instrument working in high mass resolution mode with 15 keV Ga^+ ion beam at 600 pA current. Positive ions spectra of the virgin and degraded PET samples were recorded. This technique is very sensitive to contaminant presence therefore special precautions were taken for preparing the samples to avoid contamination. Thus, samples were ultrasonically cleaned with solvents prior to subjecting them to degradation and TOF−SIMS analysis.

Results and Discussion

TLC Study. Thin-layer chromatography was performed on virgin and degraded PET samples solutions and on the corre-

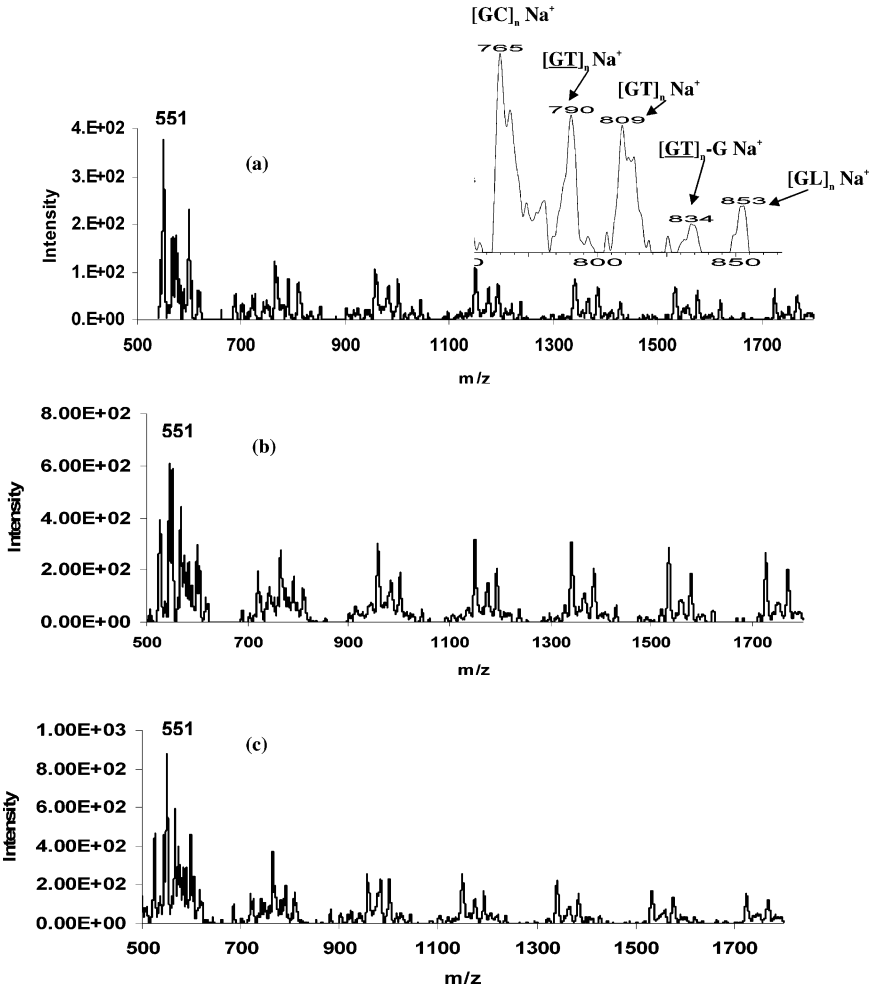


Figure 3. MALDI−TOF MS spectra of PET degraded for 30 (a), 60 (b), and 120 min (c).

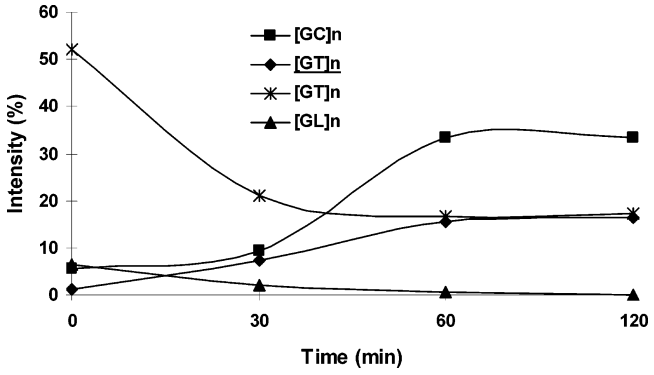
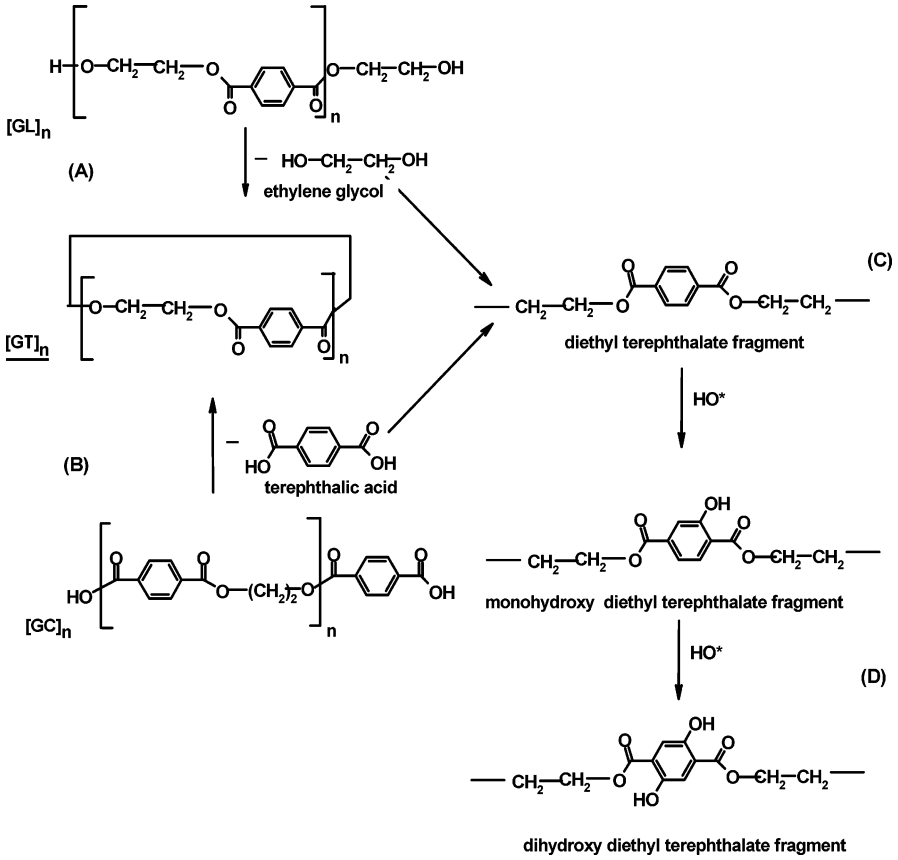


Figure 4. Intensities vs heating time of the MALDI−TOF MS peaks corresponding to various oligomeric species present in the degraded PET samples.

sponding oligomer extracts. By comparing the spot positions and calculating the retention factors (retention factor $R_f = 0.64$ for first spot for cyclic oligomers and 0.45 for first spot for linear oligomers), the TLC chromatograms of the polymer samples and of the oligomeric extract are found to be identical. Parts a and b of Figure 1 only show the distribution of the linear and cyclic oligomers extracted from the virgin and degraded polymer samples. It can be seen that linear oligomers (Figure 1a) are present in all virgin and degraded PET samples. A small amount of low molecular weight cyclic oligomers is present in the virgin PET sample (Figure 1b). In the degraded PET samples, however, the presence of higher molecular weight cyclic oligomers can be observed, suggesting that they are formed during thermooxidative degradation (Figure 1b). The TLC chromatograms show only the distribution of oligomers in the polymer samples without giving any information about their structure and molecular mass information. A detailed identification of such oligomers in virgin and degraded PET samples was possible using MALDI−TOF MS.

MALDI−TOF MS Study. The MALDI−TOF MS spectra of the virgin PET sample and of the extracted oligomers are reported in Figure 2, parts a and b. The main oligomeric species found in the untreated PET sample are listed in Tables 1 and 2 with their corresponding theoretical and experimental masses (*m*/*z*). It can be observed that the linear trimer $[GC]_n$ ($[M + H]^+$, *m*/*z* 551) (Figure 2a, Table 1) bearing two carboxyl end groups (elucidated structure) is the predominant species followed by the linear tetramer bearing two carboxyl −COOH end groups $[GC]_n$ ($[M + H]^+$, *m*/*z* 743) (Figure 2a, Table 1). The linear trimer can also be found in all degraded PET samples (Figure 3a−c). Other species present in the virgin PET samples are the glycol terminated linear oligomers (having two hydroxyl −OH end groups) $[GL]_n$ (*m*/*z* 831−1813) (Table 1) the heterotelechelic OH and COOH terminated linear oligomers $[GT]_n$ (*m*/*z* 787−1745) (Table 1) together with a low amount of cyclic oligomers $\underline{[GT]}_n$ (Figure 2a). The presence of linear oligomers with different structures can be more clearly seen in the MALDI−TOF MS spectrum of the oligomers extracted from virgin PET (Figure 2b). In this case, the predominant species is the heterotelechelic hydroxyl and carboxyl terminated linear oligomers $[GT]_n$ (Table 1), the other peaks being assigned to the

Scheme 1. Formation of Cyclic Oligomers and Colored Compounds



glycol terminated oligomers (Table 1) and to a small amount of oligomers bearing two carboxyl end groups.

Parts a−c of Figure 3 show the MALDI−TOF MS spectra of PET degraded in air for different time intervals. The inset picture shows the assignment of the major peaks found in the degraded polymer samples. The main oligomeric species present in degraded PET are listed in Table 2. Significant changes in the MALDI−TOF MS spectra of the degraded polymer can be observed compared to that of untreated polymer. In this case, the linear oligomers with two COOH end groups followed by the cyclic oligomers $[GT]_n$ are the main oligomer species present in all degraded PET samples. A small amount of cyclic oligomers with an ether linkage in the backbone as sodium adducts $[GT]_n$−G (Table 2) can also be observed (*m*/*z* 834, 1028 1220 1412) (Figure 3 inset, Table 2) in the PET sample degraded for 30 min. Both the $[GT]_n$ linear oligomers and a small amount of glycol terminated linear oligomers as sodium adduct ions can still be found in the polymer sample after 30 min of heating ($[GL]_n$ $[M + Na]^+$: *m*/*z* 852, 1044, 1236, 1428, 1620, 1812, Figure 3a inset, Table 1), their intensity decreasing with longer heating times. This change in oligomer distribution in the degraded polymer is represented in Figure 4 where the average intensities of the main oligomeric peaks found in the virgin and degraded PET samples are plotted against heating time. It can be seen that the intensity of both the heterotelechelic OH and COOH terminated linear oligomers $[GT]_n$ and glycol terminated linear oligomers $[GL]_n$ decrease rapidly during the first 30 min of heating with consequent evolution of additional cyclic $[GT]_n$ and linear oligomers bearing two carboxyl end groups $[GC]_n$. After 30 min, the intensity of the oligomers $[GT]_n$ and $[GC]_n$ increases faster, reaching a maximum after 60 min countered by the additional intensity fall of the $[GT]_n$ and $[GL]_n$ linear oligomers. These observations can give an insight into the mechanism of formation of the various oligomeric species observed in the degraded material.

The presence of both cyclic oligomer $[GT]_n$ and cyclic oligomer with an ether link in the backbone $[GT]_n$−G of the degraded PET implies two different mechanisms of formation. These are presented in Scheme 1, parts A and B. The $[GT]_n$ cyclic oligomer is formed from the glycol terminated linear oligomers by elimination of diethylene glycol (Scheme 1A). This is supported by the decrease in intensity of the peaks assigned to glycol terminated oligomers (Figure 4). A similar mechanism was also proposed by Weidner et al.[12] It is certainly also possible that some cyclic oligomers are formed from the linear precursor bearing two carboxyl end groups $[GC]_n$ (Table 1) after elimination of terephthalic acid (Scheme 1B). The formation of terephthalic acid was previously observed by Edge et al. while investigating the species responsible for yellowing of PET.[3]

The terephthalic acid thus formed can react with the diethylene glycol producing the diethylene terephthalate fragments (*m*/*z* 225) (Scheme 1C). This is also observed in the DIOS−MS spectrum of the Soxhlet degraded polymer extract. This fragment is believed participate in the formation of low molecular weight colored compounds such as dihydroxy terephthalate, which imparts a green color when the sample is heated in air for 30 min (Scheme 1D).

The cyclic oligomer with an ether linkage in the backbone $[GT]_n$−G (Table 2) is presumably formed from higher molecular weight ($n > 4$) glycol-terminated oligomers by elimination of water via an intramolecular backbiting mechanism. The amount of such oligomers is smaller compared to that of the cyclic oligomer $[GT]_n$ suggesting that the formation of $[GT]_n$ is the favored mechanism. As the heating time increases the

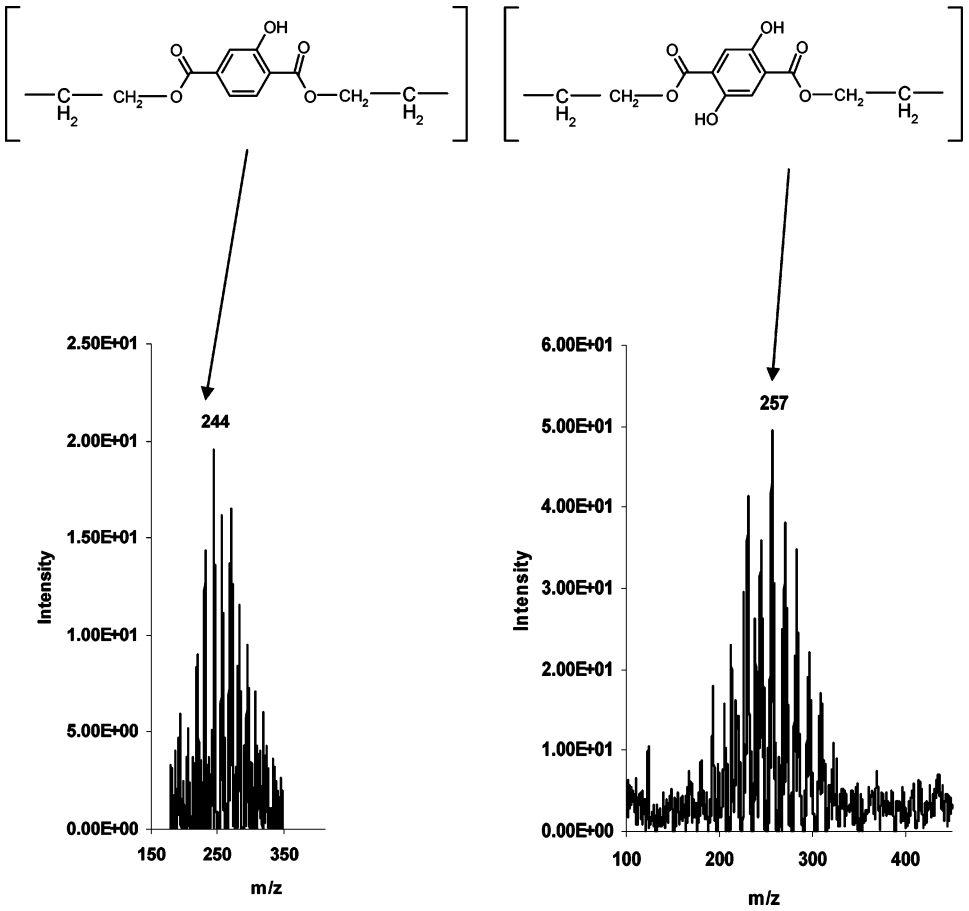


Figure 5. On-spot (TLC) MALDI−TOF MS spectra of extracts from degraded PET sample.

cyclic oligomers with an ether linkage in the backbone become unstable and their intensities decrease.[9,10]

As shown in Figure 3, parts a−c, and Figure 4, the oligomers with two carboxyl chain ends and the trimer at *m*/*z* 551 are the predominant oligomeric species in the spectra of all degraded PET samples. The increase in two carboxyl terminated species points to the fact that scission of the ester link has occurred during thermooxidative treatment.[1,2,10] While the heterotelechelic OH and COOH terminated linear oligomers $[GT]_n$ are still present in the degraded PET samples (Figures 3 and 4), their intensities are reduced compared to the oligomers with two COOH end groups and they are no longer the dominating species.

On heating in air, the formation of cyclic oligomers and especially of oligomers with two COOH end groups indicates that the formation of such species is the favored mechanism during thermal oxidation. The formation of cyclic oligomers has been previously observed by other authors studying thermal, chemical, hydrolytic, and photooxidative degradations of PET, using MALDI−TOF MS.[10,12,14] This suggests that irrespective of the degradation process, formation of cyclic oligomers (Table 2) represents the initial favored mechanism of degradation and subsequent discoloration. The low molecular weight compounds formed by the recombination of fragments generated during the evolution of the cyclic oligomers are involved, as shown in Scheme 1, parts A−D, in the color formation in the degraded polymer samples. The formation of COOH end group oligomers was also reported by Samperi et al. studying the thermal degradation of PET under inert atmosphere at elevated temperatures.[10] However, during thermooxidative degradation the evolution of acid groups takes place faster and at lower temperature than during thermal degradation alone, accelerating the color formation and degradation of the material.

TLC/MALDI−TOF MS and DIOS—MS Study. In regular MALDI−TOF MS, low molecular weight species presumably involved in the color formation could not be observed due to the matrix interference. To confirm the existence of such compounds, MALDI−TOF MS was performed directly on the spots of the TLC plate. For this, longer elution time was allowed for better spot separation and the TLC solvent mixture was evaporated in a vacuum. The MALDI−TOF MS spectra, thus obtained, reveal the presence of the low molecular weigh compounds in the degraded polymer. Parts a and b of Figure 5 show the MALDI−TOF MS spectra of two spots (from degraded PET) on the TLC plate. As the matrix is absent, in situ fragmentation may occur. Therefore, the peaks in both spectra represent ionic fragments present in the degraded PET. The main peaks at *m*/*z* 244 (Figure 5a) and at *m*/*z* 257 (Figure 5b) are attributed to monohydroxy diethyl terephthalate and dihydroxy diethyl terephthalate units respectively formed during cyclic oligomer evolution and subsequent reactions (Scheme 1D).

Parts a and b of Figure 6 show the DIOS−MS spectra of virgin PET (a) and of PET degraded for 60 min (b). It is possible that some in situ fragmentation may also occur due to the absence of a matrix. The mass peaks in the spectrum of PET degraded for 60 min are similar to that of virgin PET, the only difference being in various peak intensity. This difference can be attributed to the characteristic PET structures present in the virgin polymer that undergo degradation producing changes in the peak intensity as seen in the spectrum of degraded material. Noticeable changes are the formation of additional carboxyl end groups as suggested by the increase in peak intensity at *m*/*z* 121, *m*/*z* 152, and *m*/*z* 197 corresponding to various structures with a carboxyl end group (Figure 6b) and formation of

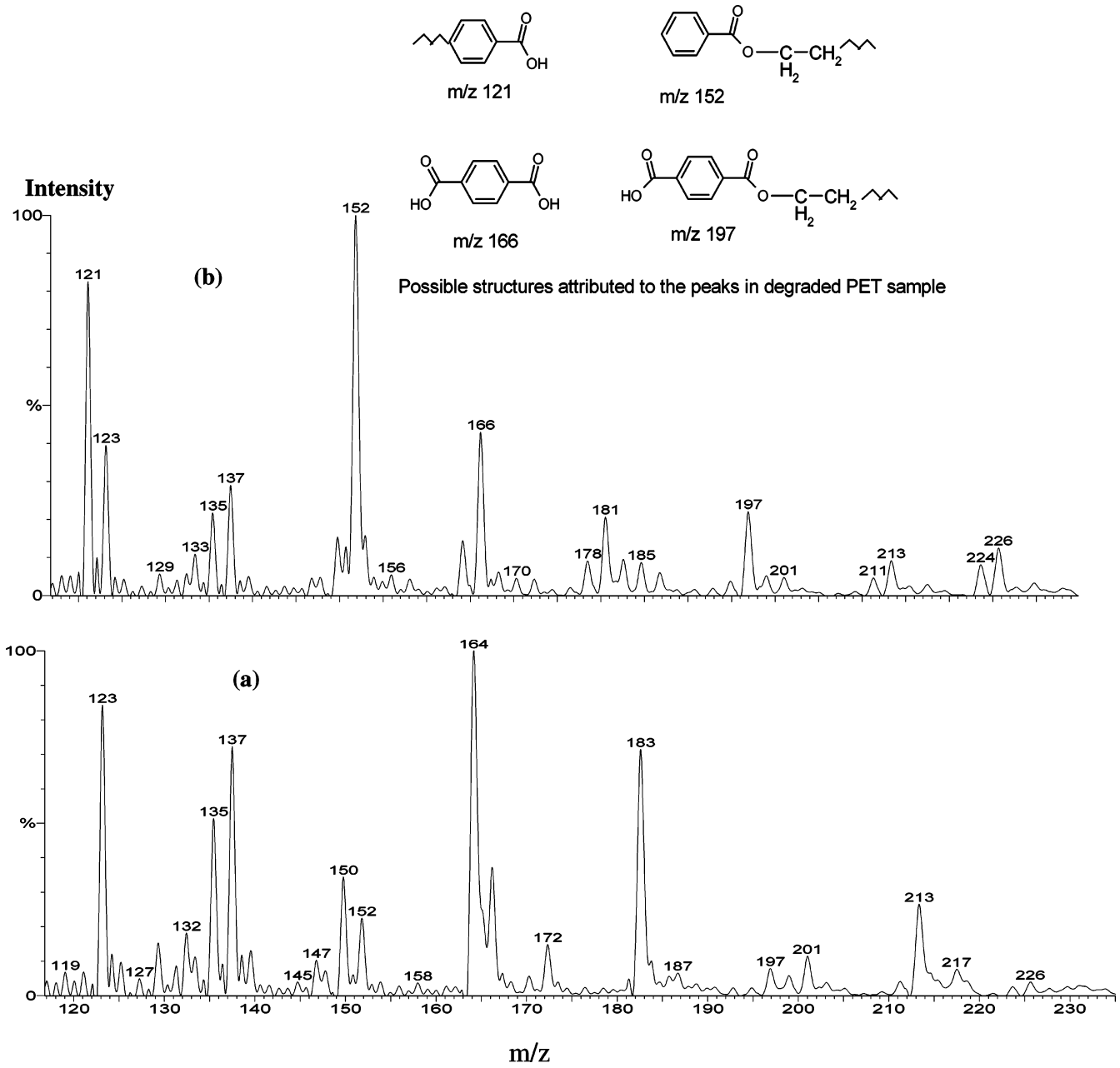


Figure 6. DIOS spectra of virgin PET (a) and PET degraded for 60 min (b). The major distributions are assigned with the possible structures present in degraded PET. Noticeable changes are the formation of additional carboxyl end groups as suggested by the increase in peak intensity at *m*/*z* 121, *m*/*z* 152, and *m*/*z* 197 corresponding to various structures with a carboxyl end group (part b) and formation of additional terephthalic acid suggested by the increase of the peak at *m*/*z* 166.

additional terephthalic acid suggested by the increase of the peak at *m*/*z* 166 (Figure 6b). The peaks at *m*/*z* 224−226 correspond to a small amount of diethyl terephthalate. These additional carboxyl groups (chromophores) formed during thermal oxidation together with the hydroxylated species that arise from the hydroxylation of the terephthalic ring account for the color formation in the material.[2]

Figure 7 shows the DIOS spectrum of the Soxhlet extract from PET degraded for 60 min. For the lower molecular weight part between *m*/*z* 121 and *m*/*z* 225, the spectrum is similar to that of PET sample degraded for 60 min (Figure 6b). The presence of terephthalate units (predominant) and various structures bearing carboxyl end groups is evidenced by the peaks at *m*/*z* 121, *m*/*z* 135, *m*/*z* 149, and *m*/*z* 225. The small peak at *m*/*z* 258 is attributed to the dihydroxy diethyl terephthalate compound, also observed in the MALDI−TOF MS analsysis performed on the TLC plate (Figure 5). Elsewhere in the spectrum, the formation of a small amount of linear oligomer containing biphenyl structures and terephthalate anhydride is suggested by the peaks at *m*/*z* 270, 348 and *m*/*z* 664, respectively. These results are in line with our earlier study regarding PET discoloration,[2] which demonstrates that more than one species are involved in color formation during melt processing.

TOF−SIMS Study. TOF−SIMS was also used to analyze the surface of virgin and degraded PET samples. Figure 8 shows a section of the positive ion TOF−SIMS of virgin PET and PET heated in air at 280 °C for 2 h. It is clear that the characteristic mass peaks that appear in the degraded PET sample are similar to that of virgin PET, the only difference being in the relative intensity of the peaks. In the degraded PET sample, the intensity ratio between the peak at *m*/*z* 149 and *m*/*z* 148 is noticeably higher than that for the virgin PET. This difference is attributed to a preexistent polymer end group that can give rise to the fragment at *m*/*z* 149 rather than at *m*/*z* 148

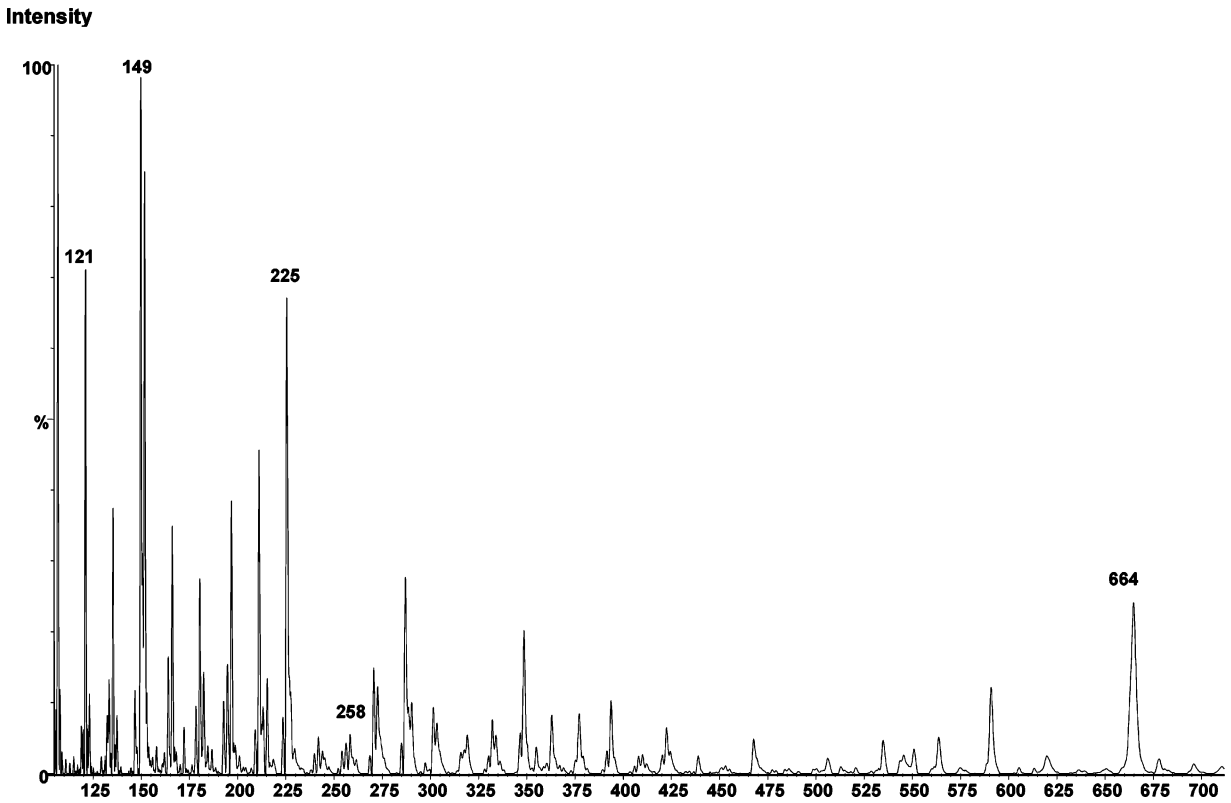


Figure 7. DIOS spectrum of Soxhlet extract from PET degraded for 60 min.

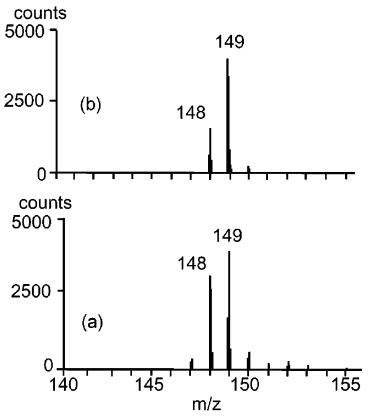


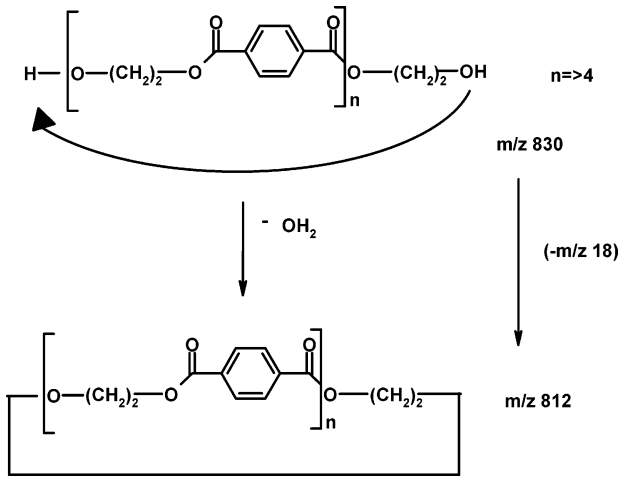
Figure 8. Enlarged section of positive ions TOF−SIMS of virgin PET (a) and PET degraded in air for 120 min (b). The intensity ratio between the peak at *m*/*z* 149 and *m*/*z* 148 is noticeably higher in degraded PET than that for the virgin PET due to a preexistent polymer end group that can give rise to the fragment at *m*/*z* 149 rather than at *m*/*z* 148.

(Scheme 3), and a similar observation was made by Zhu et al. while studying the effect of deep UV irradiation on PET.[26] Such a group can be the carboxyl end group or phenyl end group present in the virgin PET as also seen in the DIOS−MS spectrum of virgin PET (Figure 6a). Thus, TOF−SIMS results are in line with the MALDI observations for the virgin and degraded PET samples which support the mechanism of discoloration.

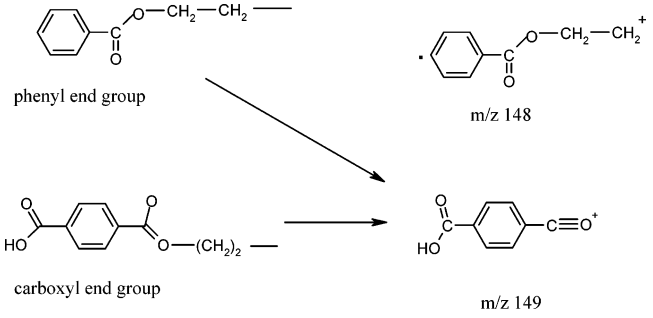
Conclusions

TLC, MALDI−TOF MS investigations enable us to establish the mechanism of discoloration with precise structure and molecular weight information. Both techniques show the presence of linear and cyclic oligomers with different structures in the PET samples. TOF−SIMS results are in line with DIOS−

Scheme 2. Formation of an Oligomer Bearing an Ether Group in the Backbone



Scheme 3. Formation of Ion Fragment at *m*/*z* 149



MS observation showing the presence of additional carboxyl end groups in the degraded polymer. Formation of additional COOH end group linear oligomers by scissions of the ester links during thermal oxidation was evident for degraded PET samples.

Additionally, cyclic oligomers (*m*/*z* 764 to 1532; Table 2) are also formed from the glycol terminated linear oligomers via elimination of diethylene glycol and also by elimination of terephthalic acid from the oligomers bearing two carboxyl chain ends. The terephthalic acid can react with the diethylene glycol producing diethyl terephthalate. The diethyl terephthalate can be hydroxyated by the OH radicals formed during thermal oxidation yielding the colored compound. The other types of cyclic oligomers (*m*/*z* 812 to 1576) observed in the MALDI−TOF MS spectra of the degraded PET samples can arise by elimination of water from the higher molecular weight glycol terminated linear oligomers. The TLC/MALDI−TOF MS and DIOS−MS complemented the MALDI−TOF MS and showed mainly the presence of low molecular weight compounds: terephthalic acid, diethyl terephthalate, and a small amount of mono- and dihydroxy diethyl terephthalate fragments responsible for color formation in PET.[2,4] This study demonstrates that a clever combination of mass spectrometry techniques can be a very powerful tool to investigate such degradation and discoloration.

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