Analytical pyrolysis of the bioplastic PBAT poly(butylene adipate-*co*-terephthalate)

Irene Coralli [a], Alessandro G. Rombolà [b], Daniele Fabbri [a],[*]

[a] *Department of Chemistry "Giacomo Ciamician" and CIRI FRAME, University of Bologna, Tecnopolo di Rimini, Via Dario Campana 71, Rimini 47922, Italy*
[b] *Department of Chemistry "Giacomo Ciamician", University of Bologna, Via Sant'Alberto 163, Ravenna, Italy*

ARTICLE INFO

ABSTRACT

PBAT (poly(butylene adipate-*co*-terephthalate)) is an important player in the field of bioplastics for its biode-gradability performance and good mechanical properties. Awareness of the forecasted increased use of PBAT has prompted researchers to develop methods for its analysis in a variety of samples. Py-GC-MS, conventional or with derivatising agents, is a technique of excellence for the analysis of polymers that relies on a detailed structural knowledge of the evolved products. This study presents a comprehensive investigation on the chemical composition of the pyrolysate of PBAT evolved at 600 °C alone and in the presence of various reagents (hex-amethyldisilazane, HMDS; acetic anhydride, Ac$_2$O, tetramethylammonium hydroxide, TMAH). Identification of relevant pyrolysis products was confirmed through the analysis of pure standards and associated reagents/byproducts. A GC-MS data set of about 50 compounds was compiled, including open chain fragments of the polymer and their derivatives as well as single and mixed subunit cyclic dimers. A compound distinctive of PBAT (but-3-en-1-yl (4-((6-(but-3-en-1-yloxy)-6-oxohexanoyl)oxy)butyl) terephthalate) containing the adipic, tereph-thalic and butylene units was tentatively identified by its mass spectrum. Pyrolysis products with active hy-drogens (alcoholic and carboxylic) were efficiently silylated by HMDS. Two pyrolysis products containing the hydroxybutyl moiety could be acetylated by pyrolysis with Ac$_2$O. Thermally assisted hydrolysis and methylation with TMAH caused important transmethylation of the ester groups of the polymer chain with the formation of dimethyl adipate and dimethyl terephthalate. The importance of the results for the analysis of PBAT in com-mercial bioplastics and environmental samples was discussed.

1. Introduction

Bioplastics are a heterogeneous family of materials that are emerging as persuasive and ecological solution to tackle the problem of pollution caused by conventional fossil-based plastics. An increase of global bio-plastics production capacity has been predicted from around 2 Mt (0.5 % of the 400 Mt annual production of plastics) in 2022 [1] to over 7 Mt in 2028 [2].

It is commonly thought that bioplastics are polymers produced from renewable feedstocks (bio-based) which can be degraded by microor-ganisms (biodegradable). Nevertheless, also fossil-based biodegradable plastics and bio-based non-biodegradable plastics are included in the family of bioplastics. Poly(butylene adipate-*co*-terephthalate), abbrevi-ated as PBAT, belongs to the former category and nowadays is among the most utilised bioplastics [3].

China is the principal worldwide producer of PBAT (about 370 ktons current capacity production) and the production capacity of PBAT ma-terials in China is expected to increase [4].

PBAT properties conjugate the biodegradability associated to the hydrolysable aliphatic adipate units with the good mechanical proper-ties brought by the aromatic terephthalate units, normally not exceeding 40 wt% [3]. Although PBAT exhibits some mechanical properties (elongation and flexibility) comparable to those of low density poly-ethylene, its higher costs and lower resistance are limiting its applica-tions and developments [5]. The field of applications of PBAT is expanded by blending with other polymers. Blends of PBAT with bio-based materials PLA (polylactate) and starch are very common especially for manufacturing shopping/refuse bags in everyday life and mulch films utilised in agriculture [3,6].

The expected increase of bioplastic production, the extent of biode-gradability under real conditions, the effective awareness of consumers for a correct way of disposal are factors raising concerns about the

---

environmental fate and impact of PBAT [7,8]. Consequently, researchers are testing analytical methods to reveal its presence in various samples representative of real world or indicative of artificial systems. Proton NMR was adopted to investigate the possible occurrence of PBAT in microplastics extracted from different types of composts [9]. Vibrational spectroscopy (FTIR, Raman), widely utilised for the polymer identification of microplastics, has shown its potential for the analysis of PBAT in complex matrices [9–11]. Sample pretreatments were also developed based on the particle-specific buoyant densities of polymers capable to separate PBAT fragments from microplastic mixtures [12].

Thermoanalytical techniques, such as Py-GC-MS, have acquired increasing importance for the determination of microplastics [13,14] and nanoplastics in environmental samples [15–17]. Recently, Py-GC-MS has been applied to the analysis of PBAT and other micro-bioplastics in wastewaters, biosolids and sediments [18]. Thermally assisted hydrolysis and methylation with tetramethyl ammonium hydroxide (THM-TMAH) was the procedure adopted by the authors that utilised dimethyl adipate as indicator (marker) for quantitation of PBAT. However, dimethyl adipate is not unique of PBAT being released by THM of polymers containing the adipate moiety, such as PBA (poly (butylene adipate) and PBSA (poly(butylene succinate and adipate)) [18]. Similarly, dimethyl terephthalate is a prominent THM product of PBAT, but not specific being characteristics of other polymers containing the terephthalate subunit, like PET (poly(ethylene terephthalate)) and PBT (poly(butylene terephthalate)).

The pyrolysate of PBAT in the absence of TMAH is more complex. Tetrahydrofuran, cyclopentanone, benzoic acid, 1,6-dioxacyclododecane-7,12-dione, 3-butenyl 4-hydroxybutyl adipate and but-3-enyl hydrogen terephthalate were the compounds reported upon Py-GC-MS of PBAT by Okoffo et al. [18]. In addition to these compounds, De Falco et al. reported the 3-butenyl esters of benzoic, pentanoic, adipic and terephthalic acids along with 1,3-butadiene, benzene, diphenyl, benzophenone [19]. The same pyrolysis products have been reported by Rizzarelli et al. in a study focused on PBAT blends [20].

Although Py-GC-MS is less sensitive for quantitation than THM due to the lower intensity of the multitude of peaks evolved upon pyrolysis, it is useful for the identification of PBAT in commercial items of unknown composition. Py-GC-MS enabled the identification of PBAT and PLA in a commercial compostable plastic bag used for leaching tests, even though the reported structures were not fully correct [21]. PBAT was found in blend with PLA in biodegradable mulching films by double shot Py-GC-MS and EGA-MS analysis [19]. Moreover, Py-GC-MS uncovered the presence of PBAT in shampoo bottles that were labelled PLA utilised to produce microparticles for toxicity studies [22].

Given the widespread occurrence of PBAT in biodegradable commercial items and the potential of thermoanalytical techniques for its identification, a detailed Py-GC-MS study has been undertaken to identify the products evolved from PBAT pyrolyzed at different reactive conditions. PBAT was pyrolyzed as such and in the presence of methylating, silylating and acetylating reagents. Structural attribution was performed based on literature data on similar polymers, mass spectral interpretation and by direct GC-MS and Py-GC-MS analysis of pure substances. One of the objectives was the identification of pyrolysis products specific of PBAT useful for its confirmation in polymer mixtures.

2. Experimental

2.1. Materials

PBAT beads were commercial products by BASF. Before the analysis, PBAT was minced with a blade and about 0.15 mg was transferred into the pyrolysis cup using tweezers. The same amount of polymer was weighted to carry both unreactive and reactive pyrolyses. Three commercial shopping bags were collected in different shops. They were accompanied by certified labels, indicating to be biodegradable in industrial composting, according to standard ISO 14855.

2.2. Standards

Standard compounds of 1,6-dioxacyclododecane-7,12-dione (cyclic butylene adipate abbreviated CBA, CAS: 777–95–7), 1,4-benzenedicarboxylic acid, di-3-butenyl ester (dibutylene terephthalate abbreviated DBT, CAS: 62680–75–5), but-3-enyl hydrogen adipate (abbreviated BHA, CAS: 64084–45–3) were purchased by CymitQuimica, Barcelona, Spain. Standards were dissolved in acetonitrile (Sigma Aldrich) to 1 mg mL^{-1}, then they were individually injected into pyrolysis cups (30 μL of BHA and 10 μL of CBA and DBT) and analysed after solvent evaporation at room temperature. Other standards (benzoic acid, adipic acid) were from Sigma-Aldrich.

2.3. Reagents

Three different derivatisation reagents were tested, tetramethyl ammonium hydroxide (TMAH 25 % wt. in methanol), hexamethyldisilazane (HMDS ≥ 99 %) and acetic anhydride (Ac$_2$O) from Sigma-Aldrich.

2.4. Py-GC-MS

Cups containing sample solutions (PBAT, standards or reagents) were analysed by Py-GC-MS using a multi-shot pyrolyzer (EGA/PY-3030D Frontier Lab) setting the furnace and the interface temperatures at 600 °C and 280 °C, respectively. The pyrolysis temperature of 600 °C was the same utilised in other studies [18,19] and is well above the peak temperature of 398 °C determined by EGA-MS [19]. Pyrolyzed samples were online transferred to a gas chromatograph (7890B Agilent Technologies) equipped with a capillary column (HP-5MS, stationary phase 5 %-phenyl, 95 %-methyl polysiloxane 30 m × 0.25 mm i.d. ×0.25 μm film thickness, Agilent Technology). Entering the GC inlet (280 °C, 1:50 split, constant helium flow 1.0 mL min^{-1}), pyrolysis products were separated through the column with an oven programmed temperature starting at 40 °C, held for 2 min, and then ramping up at 20 °C min^{-1} to 305 °C, where it was held for 12 min. Mass spectra were recorded by a quadrupole mass spectrometer (5977B Agilent Technologies) under 70 eV electron ionisation in the *m/z* 30–600 interval at 2.6 scan sec^{-1}. The temperature of the ion source and the quadrupole were 230 °C and 150 °C, respectively.

2.5. Reactive Py-GC-MS

Quartz wool (pre-treated in muffle at 400 °C for 4 h) was added to the cup to improve the contact between the sample and the derivatisation reagent (5 μL TMAH, HMDS or Ac$_2$O). Analyses started immediately after the injection of the reagent into the pyrolysis cup, to evaluate the in-situ derivatisation. The same instruments and operative conditions of conventional Py-GC-MS were used for the analysis, setting furnace and interface at 600 °C and 280 °C, respectively. The temperature of 600 °C was utilised in the literature in the analysis of bioplastics with TMAH [18] however, the same methylated products were obtained by conducting THM-TMAH at 400 °C. Different solvent delays were set in the analyses to avoid the detection of the reagent, 3.8 min, 5.1 min and 4.7 min for TMAH, HMDS and Ac$_2$O, respectively.

3. Results

3.1. Py-GC-MS

Pyrolysis of PBAT generated complex chromatographic traces as that shown in Fig. 1. Full identification of some relevant pyrolysis products was accomplished by the analysis of the standard compounds. Specifically, BHA (# 14), CBA (# 15) and DBT (# 20) were identified by direct
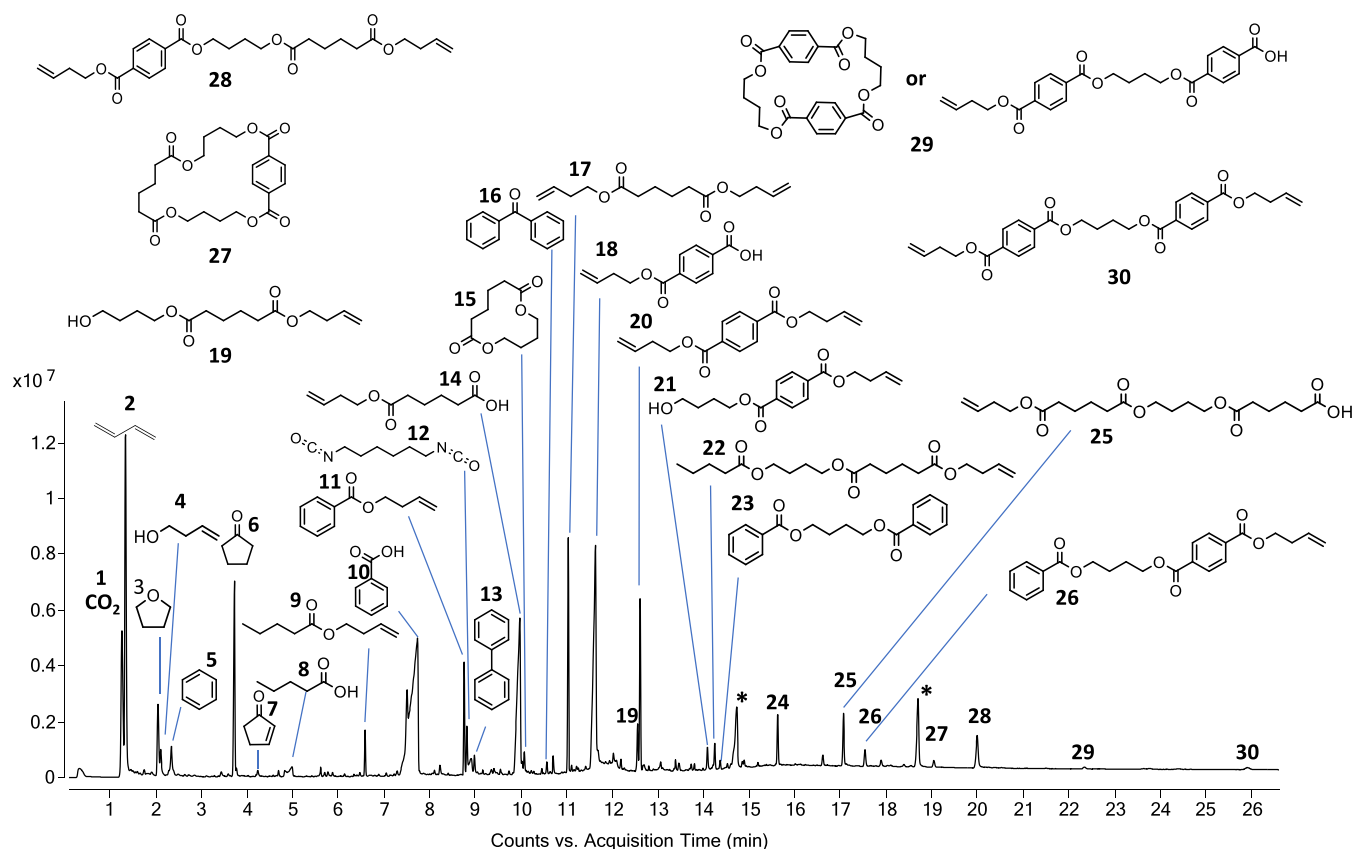
Fig. 1. MS-pyrogram of PBAT from Py-GC-MS at 600 °C. Peak numbers refer to Table 1. * Not identified m/z 77, 135, 149, 205, 370.

GC-MS injection, and confirmed by Py-GC-MS under the same conditions used for PBAT (data in Table 1). The co-occurrence of reagents or by-products from the synthesis of the standards enabled the identification of but-3-en-1-ol (# 4) and di(but-3-en-1-yl) adipate (# 17).

The main ion fragments in the mass spectra of the standard compounds, shown in Fig. 2, were useful for the peak assignment of other pyrolysis products of PBAT. The odd electron ion at m/z 54 ($C_4H_6^{+\bullet}$) is indicative of the butyl or butenyl radical in the esters of both adipic and terephthalic acid often accompanied by an intense $C_4H_7^+$ ion at m/z 55. The mass spectra of pyrolysis products arisen from the adipate sequence were characterised by the ions at m/z 111 (assigned to $^+O{\equiv}C\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH{=}C{=}O$), m/z 129 (assigned to $^+O{\equiv}C\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}COOH$). Instead, the mass spectra of terephthalate sequence were characterised by the ions at m/z 132 ($^+O{\equiv}C\text{-}Ph\text{-}CO^\bullet$), m/z 149 ($^+O{\equiv}C\text{-}Ph\text{-}COOH$) and m/z 105 ($^+O{\equiv}C\text{-}Ph$), while the butenyl terephthalate moiety was evidenced by the ion at m/z 203.

The importance of these ions for structural assignment is due to the high stability of the acylium ion formed from the homolytic dissociation (α-cleavage) of the molecular ion with charge retention on the carbonyl group ($^{+\bullet}O{=}CR\text{-}OR' \rightarrow {}^+O{\equiv}CR + {}^\bullet OR'$). The high stability of acylium ions in the mass fragmentation of pyrolysis products of polyesters was remarked in Py-MS analyses with a soft ionisation technique, where these ions were observed along with protonated molecules [25]. In particular, the acylium ions at m/z 129 and m/z 183 (and higher members at m/z 383, 583 etc.) were characteristics of poly(alkylene adipate) [25]. The acylium ion at m/z 183 was distinctive of the adipate butenyl ester and the acylium ion at m/z 203 of the butenyl ester of terephthalate.

On these grounds, several pyrolysis products were tentatively identified by attributing the structure of the acylium ion to an intense or high mass peak in the mass spectrum. For instance, peak # 21 was attributed to but-3-en-1-yl 4-hydroxybut-1-yl terephthalate for the intense ion at

m/z 221 (base peak) assigned to the terephthalic derived acylium ion containing the 4-hydroxybutyl ester.

Similarly, the structure of compound # 22 was based on attribution of acylium ions for the peaks at m/z 85, 183 and 285. The presence of the pentanoyl ion fragment (m/z 85 $^+O{\equiv}C\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$) is in agreement with the occurrence of pentanoic acid and its butenyl ester in the pyrolysate (compound # 8 and 9). The C5 unit can be virtually considered as the decarboxylated adipic acid. Similarly, the decarboxylated terephthalic acid derivatives benzoic acid (# 10) and its butenyl ester (# 11) were observed in the pyrolysate.

The structure of other pyrolysis products was attributed by comparing the pyrolysate of PBAT with those of PBT and PBSA [23]. On the contrary, pyrolysis products # 27 and # 28 were unique of PBAT as they exhibited mass spectra containing the ion peaks of both adipate (m/z 111, 129, 183) and terephthalate (m/z 149, 203) subunits (Table 1). Compound # 28 was identified by interpreting its mass spectrum (Fig. 2) as the but-3-en-1-yl (4-((6-(but-3-en-1-yloxy)-6-oxohexanoyl)oxy)butyl) terephthalate for its high mass ions at m/z 474 (molecular ion), m/z 403 (acylium ion from the loss of 71 u, $CH_2{=}CH\text{-}CH_2\text{-}CH_2\text{-}O^\bullet$) and the intense ion at m/z 275 ($C_{15}H_{15}O_5$). This compound, in short a butenyl terephthalate butylene adipate butenyl ester, is proposed as a pyrolysis product specific of PBAT. In order to evaluate the relevance of compound # 28 as a pyrolysis marker of PBAT in bioplastic items, commercial compostable bags from different sources were analysed by Py-GC-MS. The resulting pyrograms confirmed the occurrence of PBAT by the matching the peaks in Fig. 3 with those of Fig. 1, above all for the presence of specific compound # 28. The presence of PBAT in all the three samples (Fig. 4) is in agreement with the widespread use of PBAT in commercial compostable bags [8].

The products described so far are open-chain fragments of the polyester chain. Cyclic species are another important group of pyrolysis products of polyesters [26]. However, cyclic are isobaric with linear

Table 1

Structural attribution and GC-MS data of products evolved from pyrolysis of PBAT at 600 °C. RI: Kovats' retention indices. ID: identification based on pyrolysis products of PBT or PBSA [23]; (ii) NIST: library match; (iii) MS: interpretation of mass spectrum; (iv) Std: GC-MS and Py-GC-MS of standard compound.

#	Compounds	*m/z* (% abundance)	RT (min)	RI	ID
1	carbon dioxide	**44**	1.26	-	
2	1,3-butadiene	39 (82), 53 (69), *54 (100)*	1.34	-	PBT
3	tetrahydrofuran	**42 (100)**, 71 (55), *72 (59)*	2.05	-	PBSA
4	but-3-en-1-ol	**42 (100)**, 41 (38), 57 (11), *72 (12)*	2.11	-	Std BHA byproduct
5	benzene	52 (13), 77 (23), *78(100)*	2.35	-	NIST
6	cyclopentanone	41 (27), **55 (100)**, *84 (63)*	3.73	794	PBSA
7	2-cyclopentenone	39 (43), 53 (32), *82 (100)*	4.23	839	NIST
8	pentanoic acid	41 (11), **60 (100)**, 73 (43), *102 (nd)*	4.99	907	NIST
9	3-buten-1-yl pentanoate	54 (50), 57 (46), **85 (100)**, 115 (7), *156 (<1)*	6.59	1078	NIST
10	benzoic acid	77 (66), **105 (100)**, *122 (86)*	7.74	1222	Std
11	but-3-en-1-yl benzoate	54 (34), 77 (38), **105 (100)**, 122 (2), *176 (< 1)*	8.76	1366	PBT
12	hexane, 1,6-diisocyanate-	41 (67), **56 (100)**, 85 (58), *168 (< 1)*	8.82	1375	PBSA
13	biphenyl	76 (15), 153 (40) *154 (100)*	8.99	1399	PBT
14	but-3-en-1-yl hydrogen adipate (BHA)	**54 (100)**, 55 (84), 83 (36), 101(39), 111 (70), 129 (92), *200 (nd)*	9.98	1557	Std BHA
15	1,6-dioxacyclododecane-7,12-dione (CBA)	**55 (100)**, 54 (75), 71 (30), 84 (66), 100 (48), 111 (20), 129 (24), 172 (10), *200 (< 1)*	10.09	1573	Std CBA
16	benzophenone	77 (54), **105(100)**, 182 (49)	10.57	1657	NIST
17	di(but-3-en-1-yl) adipate	**55 (100)**, 54 (49), 83 (10), 111 (45), 129 (33), 183 (48), *254 (nd)*	11.04	1741	Std BHA byproduct
18	but-3-en-1-yl hydrogen terephthalate	54 (38), 65 (16), 121 (15), **149 (100)**, *220 (< 1)*	11.64	1854	PBT
19	but-3-en-1-yl (4-hydroxybut-1-yl) adipate	54 (53), **55 (100)**, 83 (17), 101 (23), 111 (56), 129 (83), 183 (32), *272 (nd)*	12.56	2040	PBSA
20	di(but-3-en-1-yl) terephthalate (DBT)	54 (39), 104 (14), 149 (46), **203 (100)**, *274 (< 1)*	12.61	2051	Std DBT
21	but-3-en-1-yl, 4-hydroxybut-1-yl terephthalate	54 (79), 71 (23), 104 (25), 149 (89), 203 (24), **221 (100)**, *292 (< 1)*	14.09	2386	MS
22	but-3-en-1-yl (4-(pentanoyloxy)butyl) adipate	54 (82), **55 (100)**, 85 (92), 111 (44), 129 (35), 157 (76), 183 (37), 285 (4), *356 (nd)*	14.25	2425	MS
23	butane-1,4-diyl dibenzoate	54 (21), 77 (31), **105 (100)**, 176 (9), 193 (8), *298 (nd)*	14.38	2454	PBT
24	Two overlapping products, not identified	105, 177 //149, 305	15.62// 15.63	2778	-
25	6-(4-((6-(but-3-en-1-yloxy)-6-oxohexanoyl)oxy)butoxy)-6-oxohexanoic acid	54 (50), **55 (100)**, 111 (54), 129 (57), 183 (66), 255 (26), 383 (7), *400 (nd)*	17.07	3085	MS
26	4-(benzoyloxy)butyl but-3-enyl terephthalate	54 (75), 77 (29), **105 (100)**, 149 (48), 203 (29), 325 (82), *396 (nd)*	17.54	3160	PBT
27	Cyclic dibutylene adipate terephthalate	54 (66), 55 (73), 71 (47), 104 (71), 132 (39), **149** (100), 221 (67), 289 (11), 420 (9)	19.0	3351	MS
28	but-3-en-1-yl (4-((6-(but-3-en-1-yloxy)-6-oxohexanoyl)oxy) butyl) terephthalate	54 (75), 55 (66), 111 (32), 129 (14), 149 (53), 183 (10), **203 (100)**, 221 (30), 275 (48), 403 (6), *474 (1)*	20.00	3452	MS
29	cyclic dibutyleneterephthalate (in alternative 4-((4-(4-((but-3-enyloxy)carbonyl)benzoyloxy)butoxy) carbonyl)benzoic acid)	**54 (100)**, 104 (56), 132 (96), 149 (75), 324 (12), 369 (65), *440 (17)*	22.36	3636	[24] or PBT
30	dibut-3-enyl'-butane-1,4-diyl diterephthalate	**54 (100)**, 149 (79), 203 (50), 369 (95), 423 (17), *494 (nd)*	25.91	-	PBT

oligomers with butenyl and carboxylic acids end group and their discrimination is not straightforward without the use of pure standards. The cyclic species of the butylene adipate (CBA # 15), already proposed in the literature [18–21] was confirmed by the analysis of the pure compound. Compound # 29 was tentatively attributed to the cyclic di (butenylterephthalate) by comparison with the MS spectrum reported in the literature [24], even though it could be questionable without the analysis of the pure oligomer (see Section 4). The mass spectrum of peak # 27 was tentatively assigned to the cyclic adipate-terephthalate dibutylene due to the presence of the ions of adipate (*m/z* 111, 129), terephthalate (*m/z* 104, 132, 149) and butyl chain (*m/z* 54, 55) and the molecular ion at *m/z* 420. Alternatively, the isobaric open chain fragment with the butenyl and carboxyl end groups could be proposed. Likewise compound # 28, pyrolysis product # 27 is a very minor peak, but fully distinctive of PBAT and detectable in the total ion pyrolysates of commercial products (Fig. 3).

Besides pyrolysis products generated from PBAT, the pyrograms of all the commercial bags presented the broad peak of levoglucosan indicative of starch-based materials, while lactides identified PLA in one commercial item. These results confirmed once more the validity of Py-GC-MS for the characterisation of bioplastics [19–21].

3.2. Silylation and acetylation

The structural attribution of pyrolysis products containing alcoholic and carboxy functionalities was further supported by pyrolysis silylation. An example of pyrogram obtained from Py-GC-MS of PBAT mixed with HMDS is reported in Fig. 4a. Firstly, the TMS ester of compound # 14 was confirmed by pyrolysis silylation of the standard BHA (# S-4 in Table 2). Typical ion fragments are generated by the loss of methyl (-15 u) and oxybutyl (- 71 u) radicals, in the last case forming an acylium ion useful for structural attribution of butenyl ester derivatives (Fig. 2). Silylated by-products of the standard compounds helped further in structural attribution (# S-5 and S-6). Other pyrolysis products containing the COOH group (# 8, 10, 14, 18 and 25 of Table 1) were all detected as TMS esters (# S-1, S-2, S-4, S-6 and S-9 of Table 2). The presence of the peak ion due to the acylium ion formed from the loss of 89 u (OTMS radical) and the *m/z* 183 ion of butylene adipate helped for the identification of # S-9. In the case of hydroxybutyl pyrolysis products, the detection of the acylium ion containing the TMSoxy moiety from the loss of 71 u butenyl radical aided structural assignments (*m/z* 273 for # S-7 and *m/z* 293 for # S-8). The TMS derivatives of mixed adipate terephthalate units were not revealed. The application of pyrolysis silylation of bioplastics was described in the literature, but not for PBAT [19].
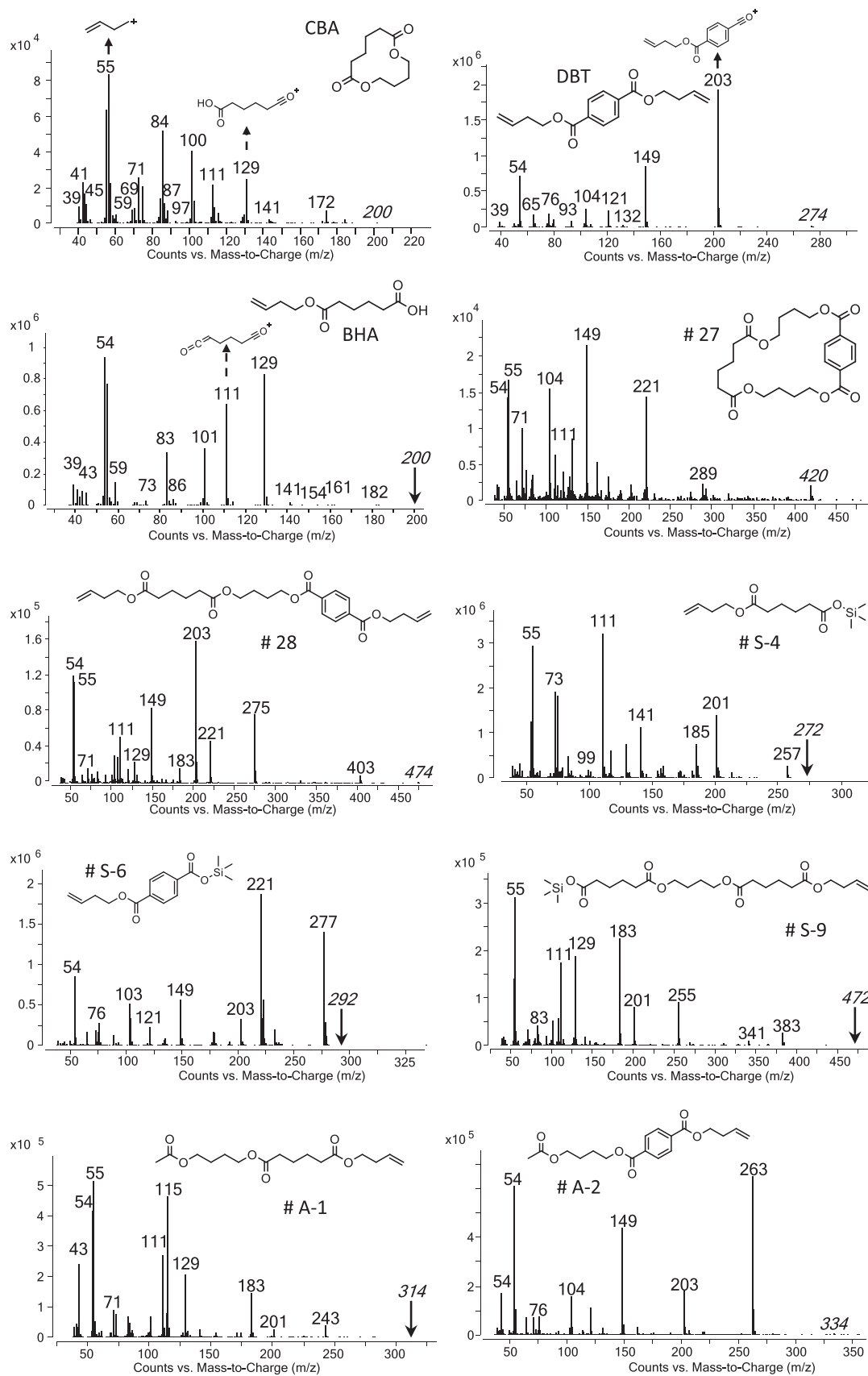
Fig. 2. Mass spectra of standard compounds (CBA, BHA, DBT) and some relevant products from Py-GC-MS, pyrolysis silylation and pyrolysis acetylation of PBAT. Molecular ion in italics (with arrow when not detected).
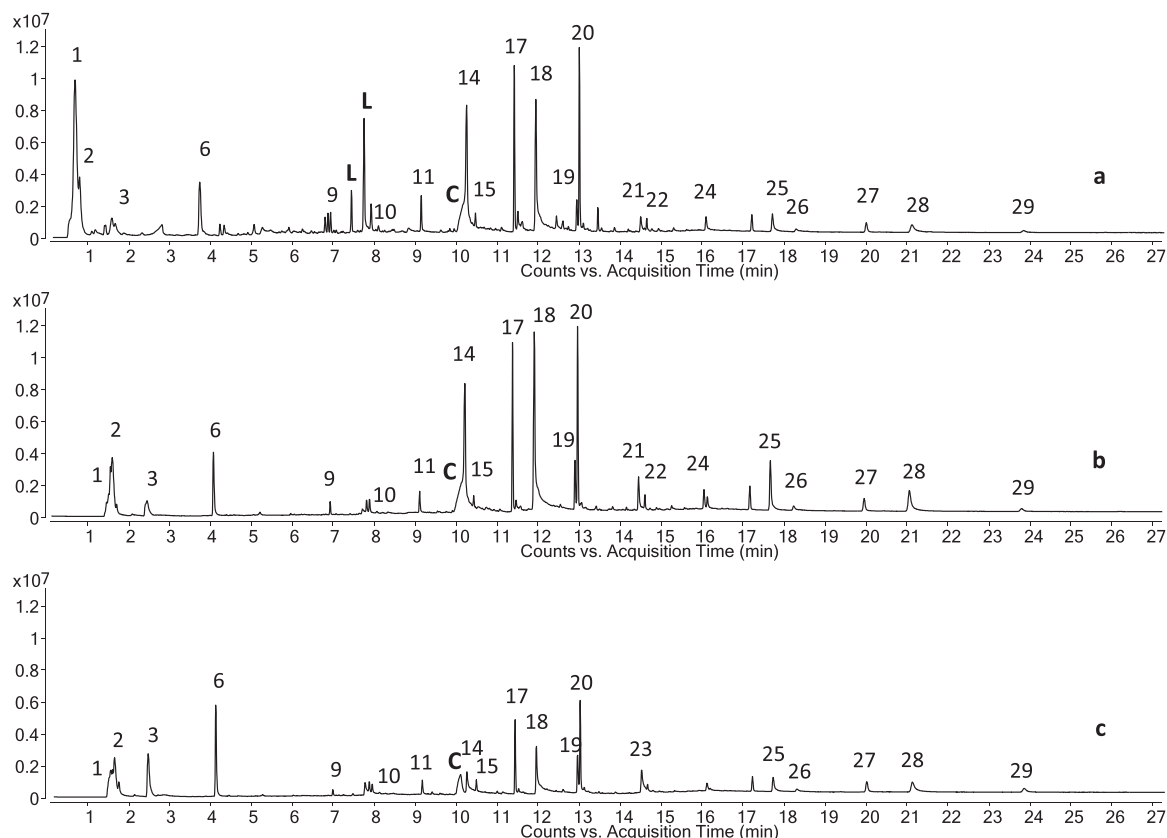
Fig. 3. Total ion chromatograms from Py-GC-MS of compostable plastic bags of different origin. Peak numbers refer to Table 1; L and C are markers from other biopolymers in the samples (L: lactide stereoisomers from PLA, C: levoglucosan from starch-based composites).

As far as acetylation is concerned, Ac$_2$O was described as a suitable reagent for online derivatisation of nitrogen containing polymers by Py-GC-MS [27], but polyesters have not been tested yet. Fig. 4b shows the GC-MS trace from pyrolysis acetylation of PBAT. The two pyrolysis products containing the hydroxybutyl end group # 19 and # 21 could be successfully converted into the acetyl derivatives # A-1 and # A-2 of Table 3, respectively. Again, the detection of distinctive peaks in the mass spectra attributed to the acylium formed from the loss of 71 u helped in structural assignment, namely at *m/z* 243 for # A-1 and at *m/z* 263 for A-2. Carboxylic acids could be potentially acetylated, but it is expected that the corresponding anhydrides, if formed, were unstable and rapidly reconverted to acids.

3.3. Methylation

THM of PBAT generated a simpler chromatogram in comparison to unreactive Py-GC-MS which was featured by the two intense peaks of adipic acid dimethyl ester # M-5 and terephthalic acid dimethyl ester # M-9 (Fig. 4c and Table 4). This finding indicates that transmethylation of the polyester chain was effective as confirmed by THM of the standard compounds CBA, BHA and DBT. Dimethyladipate was the unique product of THM of the cyclic ester CBA and the dominant peak of BHA, while dimethyl terephthalate was the principal TMH product of DBT. A second less intense peak attributed to the methyl ester of BHA (# M-8) was found in the chromatogram from THM of BHA. The methylated BHA was a very minor product in the THM of the polyester PBAT (Fig. 4c).

Interestingly, two peaks # M-6 and # M-7 were tentatively assigned to the dimethyl ester of adipic acid further methylated on the carbon atoms in alpha to the carbonyl group. Similarly, the carbon in alpha to the carbonyl group of cyclopentenone was observed (# M-1). Finally, the 1,4-dihydroxybutane was susceptible to methylation fully (# M-2) or partial (# M-3). However, C-methylation could not be confirmed by

THM-TMAH of standard adipic acid that produced exclusively the dimethyl ester derivative.

4. Discussion

The structure of the pyrolysis products of PBAT is coherent with the mechanism of degradation of polyesters presented in the literature where the chemical bonds more susceptible to cleavage are the C-O bond and C-C bond in beta to C=O (e.g. [26] for PET and PBT). The primary process at high temperatures is the concerted ester linkage cleavage with H-transfer favoured by the six-member transition state leading to vinyl and carboxylic acid terminal groups [25,26,28,29,30]. Alternatively, cyclic oligomers are primary pyrolysis products that decompose rapidly at pyrolysis temperatures into open chain oligomers [26]. Carboxylic acids at high temperatures undergo decarboxylation [31,28,30]. Decarboxylation of the carboxylic acids formed by pyrolysis has been observed for aromatic polyesters [30,32], including terephthalates [28, 31]. This reaction explains the occurrence of pentanoic acid (from adipate) and benzoic acid (from terephthalate) derivatives in the pyrolysates of PBAT along with the peak of CO$_2$. The cleavage of the C-O bond followed by H abstraction is responsible for the formation of hydoxy ester derivatives [25,31]. In the case of PBAT, this process is in agreement with the presence of 4-hydroxybuyl esters of adipate and terephthalate whose identity was supported by pyrolysis silylation and pyrolysis acetylation through the corresponding derivatives.

At low pyrolysis temperatures the formation of cyclic oligomers could be favoured over the open chain fragments from some polyesters [26,30]. The cyclic ester CBA is a minor, but common pyrolysis product of PBAT and more in general polymers containing butylene adipate subunits [18–21]. As far as the aromatic portion is concerned, cyclic butylene terephthalate oligomers were reported for PBT in the literature [24]. A small peak exhibiting the same mass spectrum reported in the
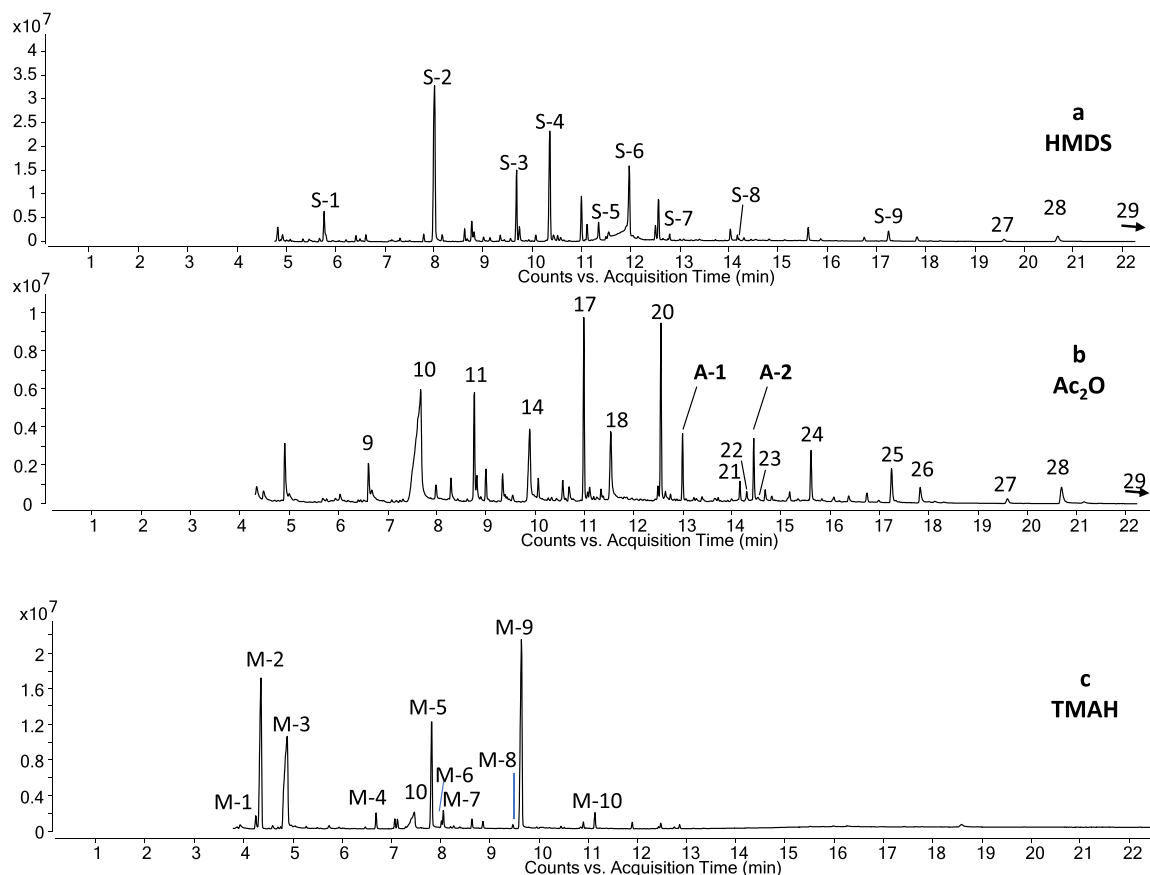
Fig. 4. Total ion chromatograms from (a) pyrolysis silylation (peak S-labels refer to Table 2); (b) pyrolysis acetylation (peak labels A-1 and A-2 refer to Table 3; (c) THM-TMAH (peak M-labels refer to Table 4); peak numbers refer to Table 1.

literature (at 100 eV) and attributed to the cyclic dimer di(butylene-terephthalate) [24] was revealed among the pyrolysis products of PBAT (# 29). However, a different attribution, the open chain oligomer with a carboxylic acid end group, was reported by Tsuge *et al.* [23]. The detection of this compound in the silylated pyrolysate of PBAT along with the absence of the TMS ester of the linear oligomer would support the hypothesis of the cyclic dimer, further supported by the relative high intensity of the molecular ion (m/z 440, 17 %). Its small intensity could be justified by the fact that the formation of terephthalate cyclic oligomers could be hampered by steric hindrance. In fact, cyclic oligomers are relevant thermal degradation products of aromatic polyesters containing the *meta* phthalic acid unit, and negligible products from polyesters with the *para* isomer [30]. Similarly for the mixed subunit oligomer, by assuming that silylation is quantitative the presence of peak # 27 in Fig. 4a would support the attribution of # 27 to the cyclic dimer rather than the butenyl-carboxylic acid open chain fragment. The technique of MALDI combined with high resolution MS, demonstrated to be a useful tool to investigate cyclic and linear oligomers from polyesters, could provide definite answer about the discrimination of cyclic and alkenyl terminated species [33].

It is worth underlining that cyclic oligomers could be evolved from vaporisation of impurities already present in the polyester. In fact, CBA was found among the products in the solvent leachate of bioplastic manufacts containing PBAT [21]. PBAT is synthesized by polycondensation [6] involving terephthalic acid together with adipic acid and 1,4-butanediol which may generate CBA.

Among pyrolysis products, 1,6-hexane diisocyanate was found (peak # 12 in Table 1). Although the presence of nitrogen does not fit with the structure of PBAT, it was reported in other studies possibly originated form a polymer additive [18,19].

The deep knowledge of the composition of pyrolysates is

fundamental for the selection of pyrolytic indicators for the determination of PBAT in commercial items utilised, for example, in toxicity studies or in environmental samples. Most of the pyrolysis products of PBAT described above were also common to the polymers containing the adipate or terephthalate units. Therefore, they cannot be used to distinguish PBAT from mixtures, for examples of PBT and PBA. By definition, bioplastics are not included in the polymer group of microplastics. However, when microplastics are analysed by thermoanalytical techniques, some bioplastic particles could be counted into this pollutant category when markers are common to different polymers. This is the case for example for benzoic acid or diphenyl (PET, PBT, PBAT) in unreactive Py-GC-MS or dimethylterephthalate in THM-TMAH (PET, PBT, PBAT).

Notably, compounds # 27 and # 28 are highly specific of PBAT containing both the adipate butylene terephthalate units. Although pyrolysis products containing two subunits could be also derived from intermolecular ester exchange reactions in the co-presence of the single homopolymers [25], the occurrence of blends is expected to be marginal in the environmental analysis of plastic pollution where concentrations are low. However, they could be formed in the case of commercial bioplastics as suspected in the literature for the co-pyrolysis of PBAT and PLA based mulching films [19]. Markers # 27 and # 28 can be confidentially used to confirm PBAT and distinguish it from similar polymers in commercial items. In this respect, Py-GC-MS is superior to FTIR where PBAT could not be distinguished from PET [8]. These pyrolysis markers are minor pyrolysis products not well suited for quantitation of PBAT in environmental samples containing trace levels of bioplastic particles, unless highly selective techniques are considered, such as tandem mass spectrometry [34].

To the best of our knowledge studies on pyrolysis silylation and acetylation of PBAT have not been published, and only one article on

Table 2

Structural attribution and GC-MS data of products evolved from pyrolysis silylation of PBAT at 600 °C. RI: Kovats' retention indices. ID identification: NIST: library match; MS: interpretation of mass spectrum; Std: pyrolysis silylation of the corresponding standard compound.

#	Compounds	m/z	RT (min)	RI	ID*
S-1	pentanoic acid TMS ester (# 8 silylated)	73 (85), **75** (100), 117 (23), 159 (75), 174 (nd)	5.75	984	NIST
S-2	benzoic acid TMS ester (# 10 silylated)	51 (11), 77 (50), 135 (59), **179** (100), 194 (10)	8.01	965	Std
S-3	adipic acid, bisTMS ester	**73** (100), 75 (85), 111 (88), 141 (39), 147 (69), 172 (32), 275 (33), 290 (< 1)	9.69	1510	Std BHA byproduct
S-4	but-3-en-1-yl adipic acid TMS ester (# 14 silylated)	55 (92), 73 (59), **111** (100), 141 (35), 185 (22), 201 (43), 257 (8), 272 (nd)-	10.38	1625	Std BHA
S-5	terephthalic acid, bisTMS ester	73 (14), 103 (23), 221 (26), 251 (13), **295** (100), 310 (6)	11.38	1804	Std DBT byproduct
S-6	but-3-en-1-yl terephthalic acid TMS ester (# 18 silylated)	54 (50), 149 (36), **221** (100), 277 (73), 292 (< 1)	12.00	1924	Std DBT byproduct
S-7	but-3-en-1-yl (4-TMSoxybut-1-yl) adipate (# 19 silylated)	55 (92), 73 (44), 111 (56), 129, **145** (100), 183 (49), 273 (6), 344 (nd)	12.83	2100	MS
S-8	but-3-en-1-yl (4-TMSoxybutyl) terephthalate (# 21 silylated)	54 (28), 73, 103 (31), 149 (17), **203** (100), 277 (39), 293 (15), 349 (7), 364 (nd)	14.26	2427	MS
S-9	but-3-en-1-yl (4-((6-oxo-6-(TMSoxy)hexanoyl)oxy)butyl) adipate (# 25 silylated)	**55** (100), 111 (56), 129 (62), 183 (71), 201 (26), 255 (29), 383 (8), 472 (nd)	17.32	3126	MS

THM-TMAH in the context of environmental analysis of micro-bioplastics [18]. Dimethyl terephthalate is the most intense thermo-chemolysis product of PBAT, but is common to other polymers containing terephthalate ester units, when analysed by THM-TMAH, for example PET, PBT, polyarylate, poly(1,4-cyclohexane dimethylene terephthalate), etc. [23]. Dibke et al. [35] introduced the notation C- which stands for cluster (e.g., C-PET with PET polymer used for calibration), to specify that plastic quantification included, not only the respective pure polymer (used for calibration), but also its copolymers, polymer-containing formulations and even related polymers that release corresponding, characteristic indicator ion(s) during pyrolysis. The second most intense peak was the adipate dimethyl ester used for quantification within micro-bioplastics in environmental samples [18]. Again, this marker is indicative of a class of polyesters containing the adipate units, supporting the relevance of the C-notation. In fact, PBAT specific methylated products are not produced by THM-TMAH because the transmethylation reaction is almost quantitative.

Instead, structurally informative adipate and terephthalate butenyl and TMS esters are generated by pyrolysis silylation of PBAT with HMDS. However, the most intense peak in the silylated pyrolysate of PBAT is produced by benzoic acid which is not distinctive of bioplastics. Although acetylation with Ac_2O is effective under pyrolysis conditions, only hydroxybutyl esters of adipate and terephthalate are derivatised which are rather small products to be of interest for quantitation.

5. Conclusions

The chemical composition of the pyrolysate of PBAT can be described as derived from pyrolysis of the single homopolymers PBT and PBA that share a common mechanism of degradation widely investigated in the literature for polyesters. Both the butylene adipate and butylene terephthalate units are fragmented through alpha cleavage and hydrogen transfer of the ester bond with formation of butenyl esters and carboxylic acids. The latter compounds are decarboxylated with loss of CO_2 and formation of pentanoic and benzoic acid derivatives. The O-CO scission brings about the formation of hydroxybutyl end groups. The evolution of cyclic oligomers was definitively confirmed for butylene adipate, and tentatively proposed for di(butylene terephthalate) and the mixed adipate-terephthalate dibutylene species. At the best of our knowledge, this latter species along with a pyrolysis product containing both the adipate and terephthalate butylene moieties were reported for the first time. These compounds are proposed as specific markers for the identification of PBAT in commercial items or environmental samples. They are not sufficiently abundant in the PBAT pyrolysate to be faithfully proposed for quantitation in environmental samples but could be used to estimate the amount of PBAT in compostable items. Intense products that can be used for quantitation can be generated by trans-methylation (adipate and terephthalate methyl esters) and silylation (TMS ester of butenyl adipate and butenyl terephthalate). Products from pyrolysis silylation are more specific than those from methylation as they contain the butylene moiety. Acetic anhydride resulted effective for the acetylation of hydroxybutylated pyrolysis products, but served essentially to support structural assignment and it is not expected to be appropriate for the analysis of real samples in monitoring studies.

Author statement

All persons who meet authorship criteria are listed as authors, and all authors certify that they have participated sufficiently in the work to take public responsibility for the content, including participation in the concept, design, analysis, writing, or revision of the manuscript. Furthermore, each author certifies that this material or similar material has not been and will not be submitted to or published in any other publication before its appearance in the **Journal of Analytical and Applied Pyrolysis**.

Table 3

Structural attribution and GC-MS data of products evolved from pyrolysis acetylation of PBAT. RI: Kovats' retention indices. Identification based on mass spectrum interpretation.

#	Compound	*m/z* (% abundance)	RT (min)	RI
A-1	but-3-en-1-yl (4-acetoxybut-1-yl) adipate (# 19 acetylated)	43 (47), **55** (100), 54 (81), 111 (52), 115 (90), 129 (40), 183 (28), 243 (7), *314* (nd)	13.05	2110
A-2	but-3-en-1-yl, 4-acetoxybut-1-yl terephthalate (# 21 acetylated)	43 (24), 54 (92), 104 (24), 149 (64), 203 (27), **263** (100), *334* (< 1)	14.51	2489

Table 4

Structural attribution and GC-MS data of products evolved from THM-TMAH of PBAT at 600 °C. RI: Kovats' retention indices. ID identification based on NIST: library match; MS: interpretation of mass spectrum; CBA, DHA, DBT: THM of standard compound.

#	Compounds	*m/z* (% abundance)	RT (min)	RI	ID
M-1	2-methyl cyclopentanone	**42** (100), 55 (75), 69 (50), 83 (18), *98* (73)	4.368	851	NIST
M-2	1,4-dimethoxy butane	45 (90), **58** (100), 71 (20), 86 (17), 103 (25), *118 (nd)*	4.471	860	NIST
M-3	4-methoxybutan-1-ol	**45** (100), 58 (63), 71 (17), *126* (nd)	5.01	909	NIST
M-4	methyl benzoate	51 (18), 77 (57), **105** (100), 136 (34)	6.813	1104	DBT
M-5	dimethyl adipate	55 (69), 59 (89), 74 (43), 83 (28), 101 (78), 111 (77), **114** (100), 143 (67), *174* (nd)	7.948	1251	CBA, DHA
M-6	2-methyl adipic acid dimethyl ester	59 (81), 69 (85), **88** (100), 97 (49), 115 (44), 128 (77), 157 (37), *188 (nd)*	8.185	1283	NIST
M-7	2,4-dimethyl adipic acid dimethyl ester	59 (48), **88** (100), 101 (14), 111 (18), 115 (37), 142 (25), *202 (nd)*	8.39	1321	MS
M-8	methyl, but-3-en-1-yl adipate	54 (87), **55** (100), 111 (91), 143 (71), 183 (9), *214 (nd)*	9.597	1494	BHA
M-9	dimethyl terephthalate	103 (13), 135 (23), **163** (100), *194 (28)*	9.764	1521	DBT
M-10	Terephthalate methyl but-3-en-1-yl ester	54 (41), 104 (9), 135 (13), **163** (100), 180 (9), 203 (6), *234 (< 1)*	11.265	1783	DBT

CRediT authorship contribution statement

Irene Coralli: Writing – review & editing, Methodology, Formal analysis. **Alessandro Girolamo Rombolà:** Data curation, Conceptualization. **Daniele Fabbri:** Writing – review & editing, Writing – original draft, Supervision, Resources, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

References

[1] Plastics – the fast Facts 2023 ● Plastics Europe, Plastics Europe (n.d.). https://plasticseurope.org/knowledge-hub/plastics-the-fast-facts-2023/ (accessed February 19, 2024).

[2] S. Ishimwe, Bioplastics market development update 2023, European Bioplastics e. V. (n.d.). https://www.european-bioplastics.org/bioplastics-market-development-update-2023-2/ (accessed February 19, 2024).

[3] L. Bartolucci, S. Cordiner, E. De Maina, G. Kumar, P. Mele, V. Mulone, B. Igliński, G. Piechota, Sustainable valorization of bioplastic waste: a review on effective recycling routes for the most widely used biopolymers, IJMS 24 (2023) 7696, https://doi.org/10.3390/ijms24097696.

[4] W. Xu, A study on the synthesis, modification and current market status of PBAT, E3S Web Conf. 385 (2023) 04007, https://doi.org/10.1051/e3sconf/202338504007.

[5] F.V. Ferreira, L.S. Cividanes, R.F. Gouveia, L.M.F. Lona, An overview on properties and applications of poly(butylene adipate-co-terephthalate) – PBAT based composites, Polym. Eng. Sci. 59 (2019) E7–E15, https://doi.org/10.1002/pen.24770.

[6] J. Jian, Z. Xiangbin, H. Xianbo, An overview on synthesis, properties and applications of poly(butylene-adipate-co-terephthalate) – PBAT, Adv. Ind. Eng. Polym. Res. 3 (2020) 19–26, https://doi.org/10.1016/j.aiepr.2020.01.001.

[7] M. Shen, B. Song, G. Zeng, Y. Zhang, W. Huang, X. Wen, W. Tang, Are biodegradable plastics a promising solution to solve the global plastic pollution? Environ. Pollut. 263 (2020) 114469 https://doi.org/10.1016/j.envpol.2020.114469.

[8] E. Binner, C. Zafiu, P. Beigl, B. Vay, M. Huber-Humer, Investigation on the formation of microplastics from compostable plastic bags during the rotting process in field tests, SSRN, 2023. https://doi.org/10.2139/ssrn.4411942.

[9] T. Steiner, L.-C. Leitner, Y. Zhang, J.N. Möller, M.G.J. Löder, A. Greiner, C. Laforsch, R. Freitag, Detection and specific chemical identification of submillimeter plastic fragments in complex matrices such as compost, Sci. Rep. 14 (2024) 2282, https://doi.org/10.1038/s41598-024-51185-6.

[10] T. Steiner, Y. Zhang, J.N. Möller, S. Agarwal, M.G.J. Löder, A. Greiner, C. Laforsch, R. Freitag, Municipal biowaste treatment plants contribute to the contamination of the environment with residues of biodegradable plastics with putative higher persistence potential, Sci. Rep. 12 (2022) 9021, https://doi.org/10.1038/s41598-022-12912-z.

[11] F. Li, D. Liu, X. Guo, Z. Zhang, F.L. Martin, A. Lu, L. Xu, Identification and visualization of environmental microplastics by Raman imaging based on hyperspectral unmixing coupled machine learning, J. Hazard. Mater. 465 (2024) 133336, https://doi.org/10.1016/j.jhazmat.2023.133336.

[12] A. Jakobs, E. Gürkal, J.N. Möller, M.G.J. Löder, C. Laforsch, T. Lueders, A novel approach to extract, purify, and fractionate microplastics from environmental matrices by isopycnic ultracentrifugation, Sci. Total Environ. 857 (2023) 159610, https://doi.org/10.1016/j.scitotenv.2022.159610.

[13] Y. Picó, D. Barceló, Pyrolysis gas chromatography-mass spectrometry in environmental analysis: focus on organic matter and microplastics, TrAC Trends Anal. Chem. 130 (2020) 115964, https://doi.org/10.1016/j.trac.2020.115964.

[14] J. La Nasa, G. Biale, D. Fabbri, F. Modugno, A review on challenges and developments of analytical pyrolysis and other thermoanalytical techniques for the quali-quantitative determination of microplastics, J. Anal. Appl. Pyrolysis 149 (2020) 104841, https://doi.org/10.1016/j.jaap.2020.104841.

[15] M.E. Seeley, J.M. Lynch, Previous successes and untapped potential of pyrolysis–GC/MS for the analysis of plastic pollution, Anal. Bioanal. Chem. (2023), https://doi.org/10.1007/s00216-023-04671-1.

[16] E.D. Okoffo, K.V. Thomas, Quantitative analysis of nanoplastics in environmental and potable waters by pyrolysis-gas chromatography–mass spectrometry, J. Hazard. Mater. 464 (2024) 133013, https://doi.org/10.1016/j.jhazmat.2023.133013.

[17] Y. Li, X. Lin, J. Wang, G. Xu, Y. Yu, Quantification of nanoplastics uptake and transport in lettuce by pyrolysis gas chromatography-mass spectrometry, Talanta 265 (2023) 124837, https://doi.org/10.1016/j.talanta.2023.124837.

[18] E.D. Okoffo, C.M. Chan, C. Rauert, S. Kaserzon, K.V. Thomas, Identification and quantification of micro-bioplastics in environmental samples by pyrolysis–gas chromatography–mass spectrometry, Environ. Sci. Technol. 56 (2022) 13774–13785, https://doi.org/10.1021/acs.est.2c04091.

[19] F. De Falco, T. Nacci, L. Durndell, R.C. Thompson, I. Degano, F. Modugno, A thermoanalytical insight into the composition of biodegradable polymers and commercial products by EGA-MS and Py-GC-MS, J. Anal. Appl. Pyrolysis 171 (2023) 105937, https://doi.org/10.1016/j.jaap.2023.105937.

[20] P. Rizzarelli, M. Rapisarda, S. Perna, E.F. Mirabella, S. La Carta, C. Puglisi, G. Valenti, Determination of polyethylene in biodegradable polymer blends and in compostable carrier bags by Py-GC/MS and TGA, J. Anal. Appl. Pyrolysis 117 (2016) 72–81, https://doi.org/10.1016/j.jaap.2015.12.014.

[21] M. Capolupo, A. Rafiq, I. Coralli, T. Alessandro, P. Valbonesi, D. Fabbri, E. Fabbri, Bioplastic leachates characterization and impacts on early larval stages and adult mussel cellular, biochemical and physiological responses, Environ. Pollut. 319 (2023) 120951, https://doi.org/10.1016/j.envpol.2022.120951.

[22] K. Klein, T. Piana, T. Lauschke, P. Schweyen, G. Dierkes, T. Ternes, U. Schulte-Oehlmann, J. Oehlmann, Chemicals associated with biodegradable microplastic

drive the toxicity to the freshwater oligochaete Lumbriculus variegatus, Aquat. Toxicol. 231 (2021) 105723, https://doi.org/10.1016/j.aquatox.2020.105723.

[23] S. Tsuge, H. Ohtani, C. Watanabe, Pyrolysis–GC/MS data book of synthetic polymers - Pyrograms, thermograms and MS of pyrolyzates, Elsevier, 2012.

[24] K. Burzin, P. Frenzel, Massenspektrometrischer nachweis cyclischer oligomerer in poly(butylenterephthalat) und isolierung des cyclischen di(butylenterephthalats), Angew. Makromol. Chem. 71 (1978) 61–66, https://doi.org/10.1002/apmc.1978.050710106.

[25] B. Plage, H.-R. Schulten, Pyrolysis-field ionization mass spectrometry of aliphatic polyesters and their thermal interactions in mixtures, J. Anal. Appl. Pyrolysis 15 (1989) 197–207, https://doi.org/10.1016/0165-2370(89)85033-8.

[26] G. Montaudo, C. Puglisi, F. Samperi, Primary thermal degradation mechanisms of PET and PBT, Polym. Degrad. Stab. 42 (1993) 13–28, https://doi.org/10.1016/0141-3910(93)90021-A.

[27] I. Coralli, D. Fabbri, Pyrolysis acetylation: a novel on-line Py-GC-MS derivatisation for the characterisation of nitrogen-containing polymers, J. Anal. Appl. Pyrolysis 175 (2023) 106178, https://doi.org/10.1016/j.jaap.2023.106178.

[28] R.M. Lum, Thermal decomposition of poly(butylene terephthalate), J. Polym. Sci. Polym. Chem. Ed. 17 (1979) 203–213, https://doi.org/10.1002/pol.1979.170170120.

[29] H. Ohtani, T. Kimura, S. Tsuge, Analysis of thermal degradation of terephthalate polyesters by high-resolution pyrolysis-gas chromatography, Anal. Sci. 2 (1986) 179–182, https://doi.org/10.2116/analsci.2.179.

[30] S. Foti, M. Giuffrida, P. Maravigna, G. Montaudo, Direct mass spectrometry of polymers. X. Primary thermal fragmentation processes in totally aromatic polyesters, J. Polym. Sci. Polym. Chem. Ed. 22 (1984) 1201–1216, https://doi.org/10.1002/pol.1984.170220601.

[31] I.C. McNeill, M. Bounekhel, Thermal degradation studies of terephthalate polyesters: 1. Poly(alkylene terephthalates), Polym. Degrad. Stab. 34 (1991) 187–204, https://doi.org/10.1016/0141-3910(91)90119-C.

[32] Y. Sugimura, S. Tsuge, Studies on thermal degradation of aromatic polyesters by pyrolysis-gas chromatography, J. Chromatogr. Sci. 17 (1979) 269–272, https://doi.org/10.1093/chromsci/17.5.269.

[33] K.M. Saller, I. Gnatiuk, D. Holzinger, C. Schwarzinger, Semiquantitative approach for polyester characterization using matrix-assisted laser desorption ionization/time-of-flight mass spectrometry approved by [1] H NMR, Anal. Chem. 92 (2020) 15221–15228, https://doi.org/10.1021/acs.analchem.0c03844.

[34] M. Albignac, T. De Oliveira, L. Landebrit, S. Miquel, B. Auguin, E. Leroy, E. Maria, A.F. Mingotaud, A. Ter Halle, Tandem mass spectrometry enhances the performances of pyrolysis-gas chromatography-mass spectrometry for microplastic quantification, J. Anal. Appl. Pyrolysis 172 (2023) 105993, https://doi.org/10.1016/j.jaap.2023.105993.

[35] C. Dibke, M. Fischer, B.M. Scholz-Böttcher, Microplastic mass concentrations and distribution in German bight waters by pyrolysis–gas chromatography–mass spectrometry/thermochemolysis reveal potential impact of marine coatings: do ships leave skid marks? Environ. Sci. Technol. 55 (2021) 2285–2295, https://doi.org/10.1021/acs.est.0c04522.