



## Pyrolysis acetylation: A novel on-line Py-GC-MS derivatisation for the characterisation of nitrogen-containing polymers

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### ABSTRACT

Several on-line chemical reactions have been combined with Py-GC-MS to improve the chromatographic behaviour of polar pyrolysis products. Derivatisations, principally methylation and silylation, have been widely employed to the analysis of oxygenated pyrolysis products, while the conversion of nitrogen-containing compounds resulted more challenging. The present study shows that amines can be efficiently converted into the corresponding *N*-substituted amides (acetamides) by conducting pyrolysis in the presence of acetic anhydride (PyAc). PyAc was assessed on three common N-containing polymer families, polyethylenimine (PEI, linear and branched), polyurethane (PUR, based on the methylenediphenyl diisocyanate monomer) and nylons (polyamide PA6 and PA66). Upon PyAc, PEI produced a series of *N*-methyl, ethyl, ethenyl acetamides indicative of the formation of several alkylated monoamines that were more difficult to detect in the free form by conventional Py-GC-MS. Acetyl derivatives of linear acyclic polyamines and piperazines were also identified confirming previous investigations. In the case of PUR, the acetylated 4,4'-diaminodiphenylmethane was generated along with the diisocyanate monomer. PyAc of PA66 produced the acetyl derivative of 1,6-hexyldiamine, while the caprolactam of PA6 was only partially acetylated. The effectiveness of acetylation was confirmed by PyAc of calibration standards for microplastic analysis. Besides the acetylated amines distinctive of PUR and PA66, the acetylated forms of 1,4-butanediol from PUR and bisphenol A from polycarbonate were detected. The results showed the potential of extension of PyAc to other polymer families and highlighted some weaknesses to be solved.

### 1. Introduction

In analytical chemistry, pyrolysis can be considered a type of sample pre-treatment that allows the characterisation of polymers by means of gas chromatography-mass spectrometry (GC-MS). At high temperatures, polymers are fragmented into compounds that are volatile enough to be separated by GC. Pyrolysis can be conducted on-line (Py-GC-MS) for direct analysis of the evolved products or off-line when pyrolysis products are first trapped and successively analysed by GC-MS. With both configurations, pyrolysis products with polar functionalities could exhibit poor chromatographic behaviour with commonly used non-polar stationary phases. Therefore, derivatisation procedures have been developed in combination with pyrolysis. Pyrolysis with tetramethylammonium hydroxide (TMAH), also named as TMAH-thermochemolysis trans-methylation or thermally assisted hydrolysis and methylation (THM), has become widely popular to obtain characteristic methyl ester/methyl ether derivatives [1,2]. Undesired side reactions, such as double bond

isomerisation and migration, reported with TMAH could be mitigated by trifluoromethylphenyl-trimethylammonium hydroxide [3] and trimethylsulfonium hydroxide (TMSH) [4]. Other derivatising agents have been investigated, such as tetramethylammonium acetate for the methylation of free acids [5], dimethyl carbonate for the methylation of bound fatty acids in triacylglycerols [6] and *N,N*-dimethylformamide dimethylacetal (DMF-DMA) for the enantiomeric analysis of cometary organic matter [7].

Beyond methylation, silylation was developed as a mild pre-treatment capable to derivatise polar pyrolysis products from the thermal breakdown of several polymers, such as polysaccharides [8], proteins [9], lignocellulose [10], acrylic resins [11]. One of the limits of pyrolysis silylation is the insufficient derivatisation with the formation of partially silylated products for sterically hindered OH groups [12,13]. The efficiency of persilylation can be improved by increasing the reagent-sample contact time with appropriate instrument configurations [14].

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Although pyrolysis products belonging to several chemical families containing oxygen polar functional groups have been successfully converted into derivatives suitable to GC analysis, nitrogen-containing compounds, in particular amines, resulted problematic to derivatise. For instance, THM-TMAH is widely used for the analysis of microplastics for its ability to generate fully methylated esters of terephthalic acid and methylated ether of *p*-hydroxy-*tert*-butylbenzene as pyrolytic markers of poly(ethyleneterephthalate) and polycarbonate, respectively [15]. However, the pyrolytic marker of nylon 6,  $\epsilon$ -caprolactam, was only partially methylated to *N*-methylcaprolactam [15].

In the case of polyurethanes, 4,4'-diaminodiphenylmethane could be quantitatively methylated, while the 2,5-toluenediamine was only partially methylated probably due to the *ortho* effect [16].

On-line silylation of nitrogen-containing pyrolysis products resulted challenging and especially complex for the characterisation of polypeptides [17]. Even in the simple case of amino acids, the monosilylated ester was dominant over the disilylated species containing the silylated amino group [18].

In general, free amines could be degraded over GC columns and tend to give broad peaks. Thus, derivatisation methods have been developed for the analysis of primary and secondary amines. Acylation is among the most widely utilised methods and acylated species tend to be more stable than silylated ones [19].

Acid anhydrides have been used in on-line derivatisation in the hot GC injection port [20], hence acylation should be fitted for Py-GC as well. In particular, acetic anhydride was demonstrated to be a suitable reagent for on-line acetylation [21–23]. Besides, the presence of water it is not an issue with acetic anhydride and preliminary sample drying is not necessary [24].

The objective of this study was to evaluate the potential of acetic anhydride as an on-line reagent in Py-GC-MS for the derivatisation of pyrolysis products bearing reactive nitrogenous groups. Pyrolysis acetylation (PyAc) was assessed to three categories of N-containing synthetic polymers: polyethylenimine (PEI) branched and linear, polyurethane (PUR) and polyamides (PA). The attention was focused on PEI due to its importance as sorbent in CO<sub>2</sub> capture technology [25]. Besides, a recent study has reported the occurrence of PEI in influents and effluents of wastewater treatment plants [26]. PyAc of PA and PUR was considered with special attention to the analysis of microplastics.

## 2. Materials and methods

### 2.1. Samples and reagents

Linear polyethyleneimine L-PEI (Mn 2100 Da, white solid) was purchased from Sigma-Aldrich. Branched PEI (B-PEI 5000 Da, 50% w/w water solution, Lupasol G100), standard pellet of PUR (Desmopan 2590 A), PA66 (DuPont Zytel® E53) were from BASF and PA6 from CDS analytical.

Acetic anhydride (pure reagent), ethylamine, piperazine, ethylenediamine, diethylenetriamine (N'-(2-aminoethyl)ethane-1,2-diamine), N-aminoethylpiperazine (1-piperazine ethanamine), hexamethylenediamine (hexane-1,6-diamine) were purchased from Sigma-Aldrich. Two microplastic calibration standards in SiO<sub>2</sub> and CaCO<sub>3</sub> were purchased from Frontier Lab. The standards contained known quantity of polyethylene (PE), polypropylene (PP), polystyrene (PS), poly(vinyl chloride) (PVC), acrylonitrile-styrene-butadiene copolymer (ABS), styrene-butadiene rubber (SBR), poly(methyl methacrylate) (PMMA), polycarbonate (PC), poly(ethylene terephthalate) (PET) poly(hexamethylene adipamide) (PA66), polycaprolactam (PA6), thermoplastic polyurethane of 4,4'-diphenylmethane diisocyanate (PUR) (not present in SiO<sub>2</sub> standard).

Liquid B-PEI and solid L-PEI were analysed as methanolic solutions in order to have the samples in a similar form prior to pyrolysis. Specifically, each sample was dissolved in methanol to obtain a polymer concentration of 50 mg mL<sup>-1</sup>; 5  $\mu$ L of the solution was introduced in cup

and analysed by Py-GC-MS after solvent evaporation. Conversely, plastic particles were analysed in solid form to evaluate a potential application of acetylation in microplastic investigation. Particles of commercial PUR and PA were obtained by cutting standard pellet with a scalpel (about 0.1 mg exactly weighted). Microplastic calibration standards were weighed prior to Py-GC-MS (about 4.3 mg, exactly weighted).

### 2.2. Py-GC-MS

Py-GC-MS experiments were performed using a multi-shot pyrolyzer (EGA/PY-3030D Frontier Lab) connected to a gas chromatograph (7890B Agilent Technologies) interfaced to a quadrupole mass spectrometer (5977B Agilent Technologies).

The samples were transferred or injected at the bottom of pyrolysis cups and methanol was evaporated for PEI solutions. Quartz wool was placed at the top of the cup, then it was embedded with 10  $\mu$ L of pure acetic anhydride right before the Py-GC-MS analysis. In this way acetic anhydride was physically separated from the sample in order to avoid or reduce its acetylation prior to pyrolysis. Actually, pyrolysis of acetylated samples has already been described in the literature, for example [27], while our objective was to evaluate on-line acetylation of pyrolysis products evolved from the original (untreated) sample. Although a systematic study of reagent/sample ratio was not performed, the selected amount of acetic anhydride (10  $\mu$ L) was in excess with respect to the sample and resulted adequate for efficient derivatisation without separation interferences [20]. For comparison, Py-GC-MS was also performed on a mixture of B-PEI (after elimination of methanol) and acetic anhydride under similar conditions. A preliminary set of Py-GC-MS analyses were conducted with B-PEI at different pyrolysis temperatures (300, 400, 500 and 600 °C). At 300 °C and 400 °C the signals were weak, while at 500 °C and 600 °C acetylated products could be clearly revealed. The final temperature was selected at 500 °C as a balance between formation and degradation at high temperature of the derivatives.

The pyrolysate was introduced (Py-GC interface 300 °C, 1:50 split conditions) into the GC column fused silica capillary column (HP-5MS, stationary phase 5%-diphenyl, 95%-dimethylpolysiloxane 30 m  $\times$  0.25 mm i.d.  $\times$  0.25  $\mu$ m film thickness). The gas chromatograph was operated in a constant helium flow of 1.0 mL min<sup>-1</sup>. The oven programmed temperature started at 40 °C, held for 5 min, and then it was ramped at 5 °C min<sup>-1</sup> to 300 °C, where it was held for 30 min. Mass spectra were recorded under 70 eV electron ionisation in the *m/z* 30–600 interval at 2.6 scan sec<sup>-1</sup>. The temperature of the ion source and the quadrupole were 230 °C and 150 °C, respectively. Pure standard analytes were analysed under the same PyAc conditions. L-PEI was also analysed by Py-GC-MS at 500 °C without the addition of acetic anhydride. Analyses were run at least in duplicate in order to confirm the formation of a given pyrolysis product, but quantitation was not performed to evaluate precision in this study. Compound identification was based on acetylation of pure compounds, NIST 14 library match and comparison with literature.

## 3. Results and discussion

### 3.1. Polyethylenimines

Although on-line and off-line analytical pyrolysis studies on branched PEI (B-PEI) have been recently published in the current literature [25,26], at the best of our knowledge Py-GC-MS of linear PEI (L-PEI) was not reported. Hence, an exemplar pyrogram of L-PEI is reported in Fig. 1.

The molecular structure of peaks that could be attributed by comparison with the injection of pure compounds or matched with published mass spectra were reported on the top of the peaks. Essentially, the main compound families were the same identified in the pyrograms of B-PEI [25], that is linear aliphatic polyamines, piperazines and

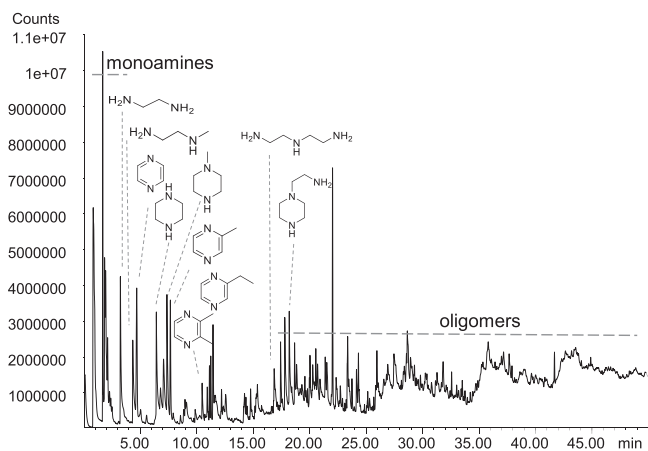


Fig. 1. Py-GC-MS of linear PEI at 500 °C (250 µg).

pyrazines Structural differences between L-PEI and B-PEI, in particular the presence of tertiary amino groups in the branched polymer, were not revealed by Py-GC-MS. Monoamines eluted at the beginning of the chromatograms with overlapping peaks, while oligomers produced very broad peaks, thus their identification resulted challenging. Pyrolysis in the presence of acetic anhydride (PyAc) generated the acetyl derivatives (acetamides) of primary and secondary amines that improved the comprehension of the chemical composition of PEI pyrolysates. The PyAc GC traces of L-PEI and B-PEI are presented in Fig. 2, while Fig. 3 shows in more detail the first elution region. In agreement with

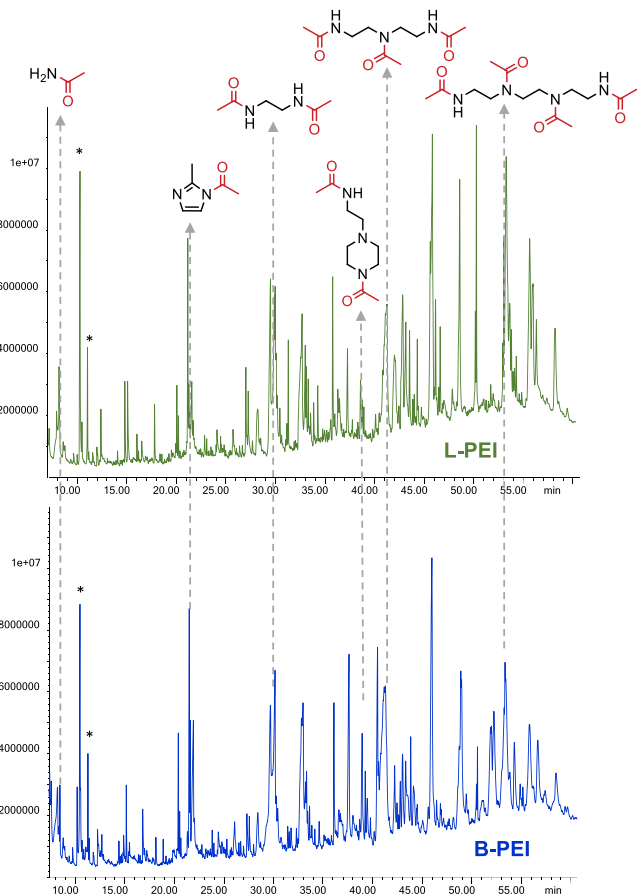


Fig. 2. TIC from pyrolysis in the presence of acetic anhydride of linear PEI (250 µg, top) and branched PEI (250 µg, bottom). Compounds identified by analysis of pure standards are reported in Table 1. (\*) peaks from the reagent.

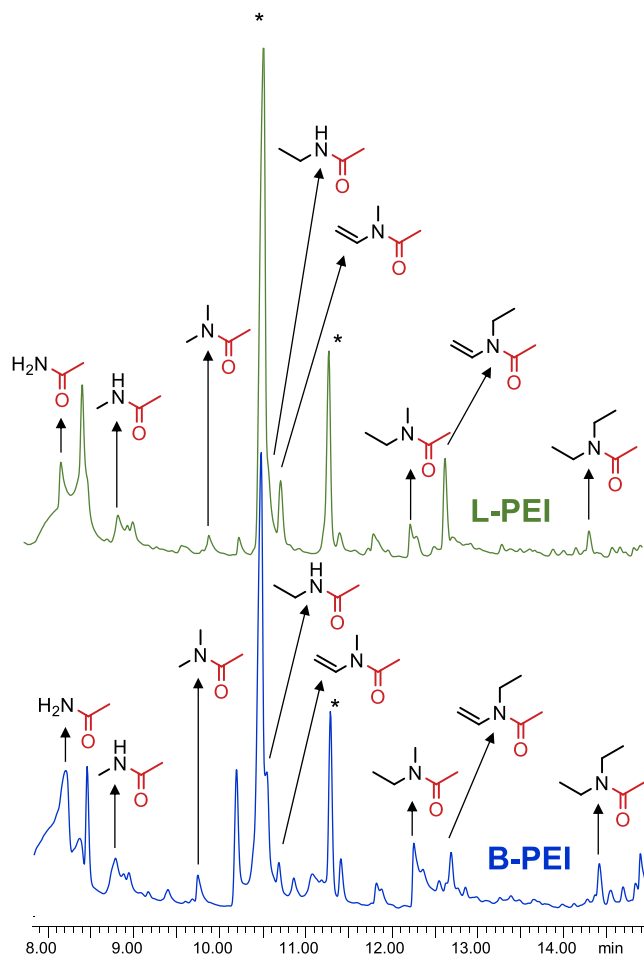


Fig. 3. TIC chromatogram of Fig. 2 expanded in the elution region of acetylated monoamines. (\*) peaks from the reagent.


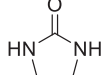
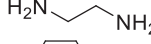
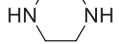
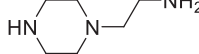
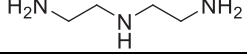
unreactive pyrolysis, no striking differences could be observed in the chromatograms capable to differentiate L-PEI from B-PEI. Acetylated monoamines (*N*-alkyl and *N,N*-dialkyl acetamides) produced GC peaks well separated by GC, even though rather broad with the common non-polar stationary phase used in this study (Fig. 3).

They were tentatively identified by the corresponding mass spectra, aided by the fact that amides can give detectable molecular ion peaks [28]. Acetamide (indicative of ammonia) and acetamides with one or two methyl, ethyl and ethenyl *N*-substituents indicative of primary and secondary monoamines were identified (Table 1). Acetic anhydride was physically separated from the polymer prior to pyrolysis, therefore we presumed that monoamines were first produced upon pyrolysis and thereafter acetylated. Nonetheless, in the case of B-PEI the same acetylated products were obtained by pyrolysis of the polymer already mixed with acetic anhydride. The presence of *N,N*-dimethyl and *N,N*-diethyl acetamides indicates that both C-C and C-N bonds, respectively, were cleaved upon pyrolysis. The rather intense *N*-ethyl-*N*-ethenyl acetamide is in accordance with the mechanism outlined by Vidović et al. [26]. The C-N bond is broken, with hydrogen transfer from a methylene unit to the nitrogen atom followed by fragmentation with formation of a terminal vinyl group.

The efficacy of derivatisation with acetic anhydride of primary and secondary amines was confirmed by the identification of acetylated ethylenediamine, diethylenetriamine, 1-ethylaminepiperazine (Table 1). The structural attribution was confirmed by the analysis of pure compounds under the same conditions. Notably, PyAc of pure ethylenediamine generated not only the *N,N*-acetyl derivative (Fig. 4), but also the *N,N,N'*-triacetyethylenediamine (*m/z* 30 (41%), 43 (100),

**Table 1**

GC-MS data and structural attribution of the pyrolysis products from pyrolysis acetylation of PEIs. RI: Kovats' retention indices;  $m/z$ : mass to charge ratio of relevant ions, base peaks are in bold, molecular ions in italics (in parenthesis when undetected). ID identification based on L library match, T tentative (not found in library), S PyAc of pure amine.

Compound	RI	$m/z$	Original amine	ID
acetamide	n.d.	43, 44, <b>59</b>	NH <sub>3</sub>	L
<i>N</i> -methylacetamide	n.d.	30, 43, 58, <b>73</b>	CH <sub>3</sub> -NH <sub>2</sub>	L
<i>N,N</i> -dimethylacetamide	822	<b>43</b> , 44, 72, <b>87</b>	CH <sub>3</sub> -NH-CH <sub>3</sub>	L
<i>N</i> -ethylacetamide	885	30, 43, 72, <b>87</b>	CH <sub>3</sub> -CH <sub>2</sub> -NH <sub>2</sub>	L
<i>N</i> -vinyl- <i>N</i> -methyl acetamide	895	30, 43, 56, <b>57</b> , 99	CH <sub>3</sub> -NH-CH=CH <sub>2</sub>	L
<i>N</i> -( <i>n</i> -propylacetamide) or <i>N</i> -ethyl- <i>N</i> -methyl acetamide	942	<b>44</b> , 58, 86, <b>101</b>	CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -NH <sub>2</sub> CH <sub>3</sub> -CH <sub>2</sub> -NH-CH <sub>3</sub>	L
<i>N</i> -ethyl- <i>N</i> -vinyl acetamide	954	<b>43</b> , 56, 71, <b>113</b>	CH <sub>3</sub> -CH <sub>2</sub> -NH-CH=CH <sub>2</sub>	T
<i>N,N</i> -diethylacetamide	1002	44, <b>58</b> , 72, 100, <b>115</b>	(CH <sub>3</sub> -CH <sub>2</sub> ) <sub>2</sub> -NH	L
<i>N</i> -acetyl methylimidazole	1117	43, 54, 81, <b>82</b> , <b>124</b>		T
1,3-diacetyl-2-imidazolidinone	1448	<b>43</b> , 86, 128, 142, <b>170</b>		L
<i>N,N'</i> -diacetyl ethylenediamine	1564	30, 43, 73, <b>85</b> , ( <b>144</b> )		S
1,4-diacetyl piperazine	1705	43, 56, 69, <b>85</b> , 111, <b>170</b>		S
<i>N</i> -ethylacetamide-1- piperazine-4-acetyl	2067	43, 99, 112, <b>141</b> , 154 ( <b>213</b> )		S
<i>N,N,N'</i> -triacetyldiethylenetriamine	2103	43, <b>86</b> , 115, 145, 157, 170 ( <b>229</b> )		S

73 (98), 85 (84), 123 (23), 186 M<sup>+</sup> (not detected) and *N,N,N',N'*-tetraacetyl ethylenediamine ( $m/z$  30 (24), 43 (100), 72 (59), 73 (62), 85 (52), 127 (49), 228 M<sup>+</sup> (not detected) indicating that amides can react with acetic anhydride under pyrolytic conditions. However, in the acetylated pyrolysates of PEI the *N,N'*-diacetylated form was prevalent in accordance to the fact that primary amines are more reactive than amides. The absence of peaks of the original free standard amines indicated that acetylation was quantitative.

Differing from the behaviour of monoamines, the mass spectra of polyamines did not exhibit the molecular ion, thus an important tool for identification was lacking. Nevertheless, an intense ion formed by the loss of a neutral fragment of 59 u (the ion peak (M-CH<sub>3</sub>CONH<sub>2</sub>)<sup>+</sup> was reported for acetamides of complex molecules [28]) could be employed for structural attribution. For example, analysing under PyAc conditions the standard compound diethylenetriamine, the resulting GC peak gave a mass spectrum with an intense ion at  $m/z$  170 (Fig. 4). The formation of this ion was explained by the loss of a neutral fragment of 59 u from the molecular ion (229 u) of the diethylenetriacetamide. Similarly, the mass spectrum obtained from PyAc of 1-ethylaminepiperazine showed a rather intense ion at  $m/z$  154 produced from the diacetylated derivative (molecular ion at  $m/z$  213) upon elimination of 59 u fragment (Fig. 4). The mass spectrum of fully cyclic piperazine presented an intense molecular ion at  $m/z$  170, and an intense ion at  $m/z$  111, again due to the loss of 59 u. Elimination of ketene (CH<sub>2</sub>=C=O 42 u) and alkyl loss are other important ionic fragmentation of amides [28]. The intense ion at  $m/z$  86 tentatively attributed to [CH<sub>3</sub>(C=O)NHCH<sub>2</sub>CH<sub>2</sub>]<sup>+</sup> featuring the mass spectra of several peaks at high retention times could be considered distinctive of acetylated aliphatic polyethyleneamines (see for example the mass spectrum of *N,N,N'*-triacetyldiethylenetriamine in Fig. 4).

Regarding aromatic amines identified in the pyrolysate of PEI [25, 26], pyrazines and pyridine cannot be acetylated, while pyrroles and imidazoles have reactive nitrogen atoms, but their acetyl derivatives could not be revealed.

### 3.2. Polyurethanes

Polyurethanes (PURs) are a widely utilised and heterogeneous class of polymers obtained by condensation reaction of diisocyanate and di (poly)ol monomers. The sample analysed in this study contained an urethane moiety from methylenediphenyl diisocyanate which is among the most abundant in the PUR family [16]. The GC trace (Fig. 5) obtained by PyAc showed the peak associated to 4,4'-methylene diphenyl diisocyanate, a typical pyrolysis product of this category of PUR [29].

In addition, the diacetylated 4,4'-methylene diphenyldiamine was tentatively identified (Fig. 4  $m/z$  282: M<sup>+</sup>;  $m/z$  240: M<sup>+</sup>- 42 u CH<sub>2</sub>=C=O;  $m/z$  198: 240-42 u (CH<sub>2</sub>=C=O);  $m/z$  197: 240-43 u;  $m/z$  106: H<sub>2</sub>N-Ph-CH<sub>2</sub><sup>+</sup>;  $m/z$  43: CH<sub>3</sub>-C=O<sup>+</sup>). The underivatized diamine was not detected, while a broad peak was tentatively identified as the monoacetyl derivative ( $m/z$  240: M<sup>+</sup>;  $m/z$  198: M<sup>+</sup>- 42 u CH<sub>2</sub>=C=O;  $m/z$  197: M<sup>+</sup>- 43 u CH<sub>3</sub>-C=O<sup>+</sup>;  $m/z$  106: [H<sub>2</sub>N-Ph-CH<sub>2</sub>]<sup>+</sup>), the peak had a low intensity indicating the acetylation was almost quantitative. The formation of 4,4'-methylene diphenyl diamine was reported in the literature [16,30,31]. It was attributed to pyrolysis conditions (e.g. hydrolysis of the corresponding diisocyanate with some matrices [30]) or the characteristics of domains in PUR chains (hard segments would favour the formation of amine with the elimination of CO<sub>2</sub>) [31,32].

Interestingly, the acetamide of the partially hydrolysed diisocyanate could be tentatively identified by interpretation of the mass spectrum ( $m/z$  266: M<sup>+</sup>;  $m/z$  240: M<sup>+</sup>- 26 u CN?;  $m/z$  224: M<sup>+</sup>- 42 u CH<sub>2</sub>=C=O;  $m/z$  182: [HNPh-CH<sub>2</sub>-Ph]<sup>+</sup>;  $m/z$  106: [H<sub>2</sub>N-Ph-CH<sub>2</sub>]<sup>+</sup>;  $m/z$  43: CH<sub>3</sub>-C=O<sup>+</sup>).

PyAc can provide information also on the alcohol units of the PUR. In fact, the diacetate 1,4-butandiol (4-acetyloxybutyl acetate) was tentatively identified by mass spectral matching with the library; it was derived by the acetylation of 1,4-butandiol a common chain extender of PUR or ester polyols. Finally, the occurrence of peaks with  $m/z$  55, 111, 115, 129, 183, 201 in the mass spectra suggested the probable occurrence of an adipate butanediol ester moiety [29].

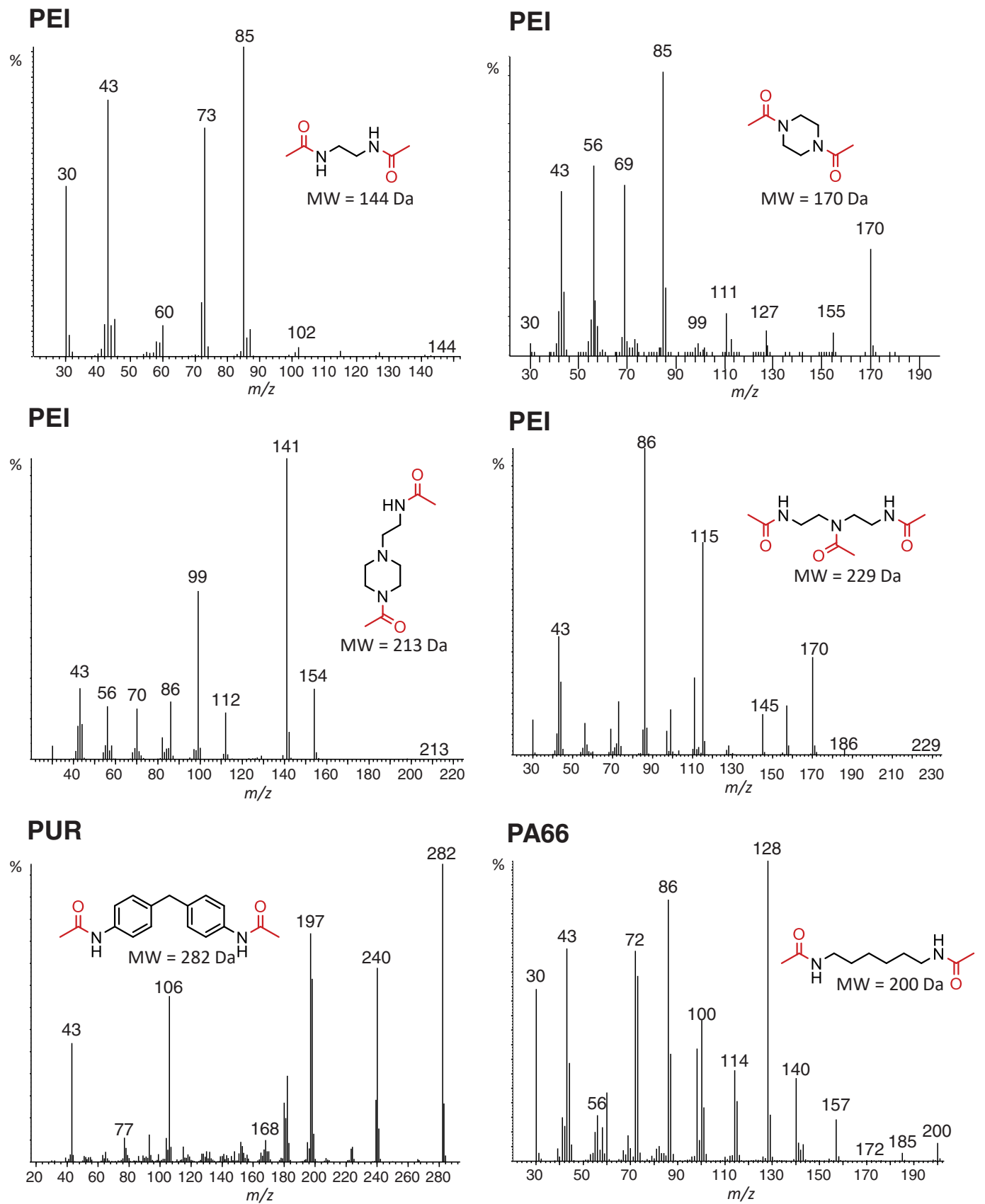


Fig. 4. Mass spectra of some acetylated pyrolysis products of PEI, PUR and PA66.

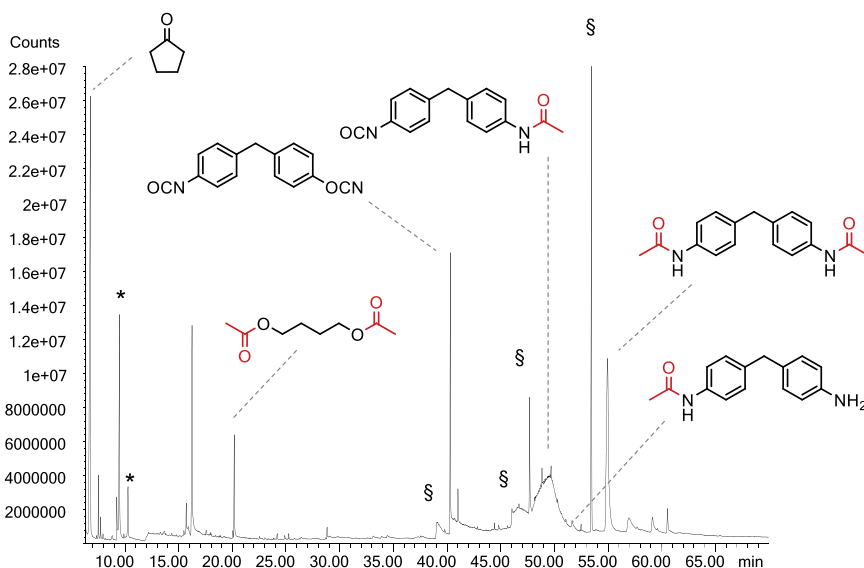


Fig. 5. TIC from pyrolysis in the presence of acetic anhydride of polyurethane. (\*) peaks from the reagent. (§) peaks probably due to adipate esters.

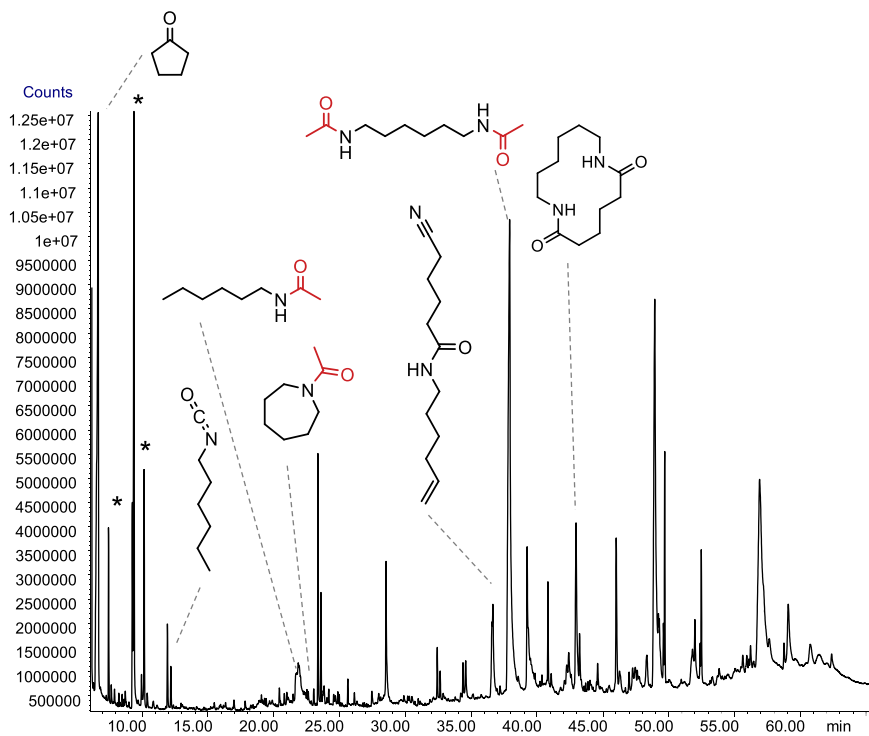


Fig. 6. TIC from pyrolysis in the presence of acetic anhydride of PA66. The structural formula of acetylated pyrolysis products is shown. (\*) peaks from the reagent.

### 3.3. Polyamides

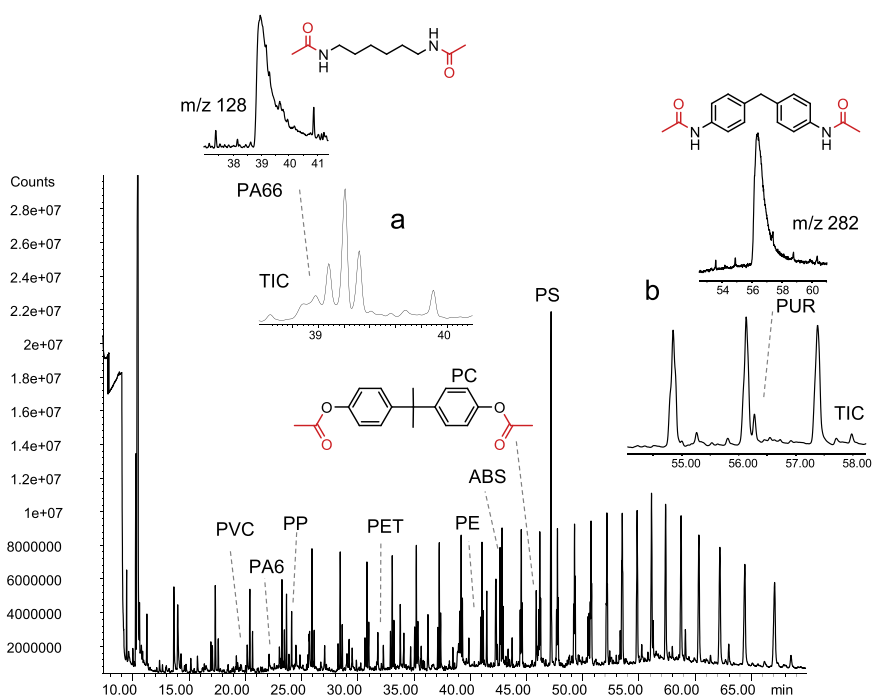
PA66 (poly(hexamethylene adipamide)) and PA6 (polycaprolactam) were analysed by PyAc. An exemplar pyrogram of PA66 under acetylation conditions is shown in Fig. 6. Hexamethylene diamine, a prominent pyrolysis product of PA66 [29], was converted by acetic anhydride into the corresponding bisacetamide. The acetylated hexan-1-amine was also identified by spectral match with library. Several pyrolysis products of PA66 that do not contain reactive amino groups could be detected in agreement with conventional Py-GC-MS, as for instance 1,8-diazacyclotetradecane-2,7-dione, and 5-cyano-N-(hex-5-enyl)pentanamide [29].

In the case of PA6, the pyrogram from PyAc (not shown) was featured by an intense GC peak of caprolactam, and only occasionally a minor peak due to the acetylated caprolactam could be detected. As observed above in the case of PEI, amides could be acetylated, but apparently the reaction is dependent on experimental conditions.

### 3.4. Standard polymer mixtures

Besides pure polymers, the potential of PyAc was confirmed by analysing inorganic matrices containing a mixture of different polymers including PUR, PA6 or PA66. The chromatogram obtained under PyAc





**Fig. 7.** TIC from pyrolysis in the presence of acetic anhydride of microplastic standard mixture in  $\text{CaCO}_3$ . The pyrolytic markers indicative of each polymer (with the exception of PMMA) are indicated. The insets (a) and (b) show the expanded elution region in TIC and extracted ion chromatogram of the acetylated pyrolytic marker of PA66 and PUR, respectively.

conditions of a standard polymer mixture diluted with  $\text{CaCO}_3$  is reported in Fig. 7. The pyrolytic markers reported by Ishimura et al. [33] were revealed in the chromatogram for PS (styrene trimer), PE (1,20-heneicosadiene), PVC (naphthalene), ABS (2-phenethyl-4-phenylpent-4-enitrile), PA6 (caprolactam). The marker of PP (2,4-dimethyl-2-heptene) and PMMA (methyl methacrylate) could not be evidenced because they eluted under the peak of acetic anhydride. However, in alternative, the three stereoisomers of 2,4,6,8-tetramethyl-1-undecene were revealed as potential PP markers. In the case of condensation polymers, acetylated derivatives could be successfully detected for PUR and PA66. The inset of Fig. 7 shows the peak of 4,4'-methylenediphenyl diacetamide in the extracted mass chromatogram at  $m/z$  282 that confirmed the presence of PUR.

The GC peak of the diacetylated hexamethylenamine characteristics of PA66 could be clearly revealed in the mass chromatogram at  $m/z$  128 (inset of Fig. 7).

Noteworthy, bisphenol A which is a marker of polycarbonate, was revealed as the diacetylated derivative with mass spectrum  $m/z$  213 (100%), 228 (30%), 270 (20%), 312 (7%) at 45.9 min

A similar behaviour was observed with the standard plastic mixture diluted in  $\text{SiO}_2$  (data not shown). In the case of PET, the peak of benzoic acid was revealed with the  $\text{SiO}_2$  diluent and benzophenone with the  $\text{CaCO}_3$  diluent [33]. Interestingly, the acetylated marker of PA6 (*N*-acetylcaprolactam) was tentatively identified ( $m/z$  43, 85, 112, 127, 155  $\text{M}^{+\bullet}$ ) in the chromatogram of the  $\text{SiO}_2$  based standard confirming that amides could be acetylated under PyAc conditions.

In summary, PyAc does not interfere significantly with the detection of polyolefins and produces acetylated pyrolysis products for PUR, PA6, PA66, PC that could be considered alternative pyrolytic markers of these polymers. On a qualitative base, the N-containing polymers PU, PA6 and PA66 were also detected in the plastic standard mixtures analysed without derivatisation or by THM-TMAH, utilising the typical markers ([15,30]). However, the performance of PyAc for quantitative analysis of microplastic was not evaluated in this study.

#### 4. Conclusions

This study highlighted potential and limitations of acetic anhydride for the on-line derivatisation of pyrolysis products of some relevant N-containing synthetic polymers. Acetylation resulted efficient for primary and secondary amines evolved from the pyrolysis of polyethylenimine, polyurethane and polyamide. In the case of polyethylenimines, the identification of the acetyl derivatives (acetamides) of low molecular weight monoamines was facilitated in comparison to the original free amines for the better chromatographic separation and relatively intense molecular ions in the mass spectra. The identification of polyamines was more challenging due to the absence of molecular ions in the mass spectra, but specific fragment ions could aid in the attribution of compound class. Some acetamides gave broad chromatographic peaks with non-polar stationary phase utilised in this study, improving peak shape and resolution with proper stationary phases could be the subject of future investigations.

The efficacy of pyrolysis acetylation was demonstrated for polyurethane and nylon-66 that generated the corresponding acetamides of aromatic and aliphatic diamines, respectively. Acetylated pyrolysis products from these polymers and others preliminary found in this work (acetylated bisphenol A from polycarbonate) could find application as new markers in the analysis of microplastics.

Besides amines, amides can react with acetic anhydride which could be a downside because multiple derivatisation may occur for primary amine complicating the pyrolytic pattern. However, the acetylation of amides resulted less effective and dependent on experimental conditions. The peaks generated by the reagent are another drawback because they may cover pyrolysis products eluting at low retention times.

Expanding the potential of pyrolysis acetylation for the characterisation of other polymers evolving polar pyrolysis products and its potential for quantitative analysis are topics worth of considerations for future studies.

## CRedit authorship contribution statement

**D.Fabbri:** Funding acquisition, Resources. **I.Coralli** Investigation, Validation, Visualization and Editing. **D.Fabbri:** Drafting the manuscript. Approval of the version of the manuscript to be published: **Irene Coralli, Daniele Fabbri.**

## 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.

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