

Towards quantitative microplastic analysis using pyrolysis-gas chromatography coupled with mass spectrometry

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ABSTRACT

Microplastic pollution from everyday plastic items has increased tremendously worldwide. Pyrolysis gas chromatography coupled to mass spectrometry (Py-GC/MS) has been widely investigated for the qualitative and quantitative analysis of microplastics in environmental samples. However, there are several pitfalls to consider when developing an appropriate protocol for their analysis. This study aimed at the development of an in-house database of primary (single) polymers, binary (two) polymers and tertiary (three) polymer mixtures. In this context the potential occurrence of gas phase reactions during pyrolysis of binary and tertiary polymers were investigated. Further, different diluters were tested for the accurate preparation of calibration standards for quantification purposes.

Seven different polymers were included in this study, which were chosen due to their prevalence in daily plastic appliances. For each single polymer specific peaks could be identified and recommendation for quantifier analytes given. The analysis of binary polymer mixtures revealed gas phase reactions for PET with PVC, PVC with MDI-PU and PE with PVC. For these binary polymers, several different novel pyrolysis products, specific for the according binary polymer mixture, could be identified. These results confirmed that especially PVC exhibits strong interactions during co-pyrolysis with ester- and ether-based polymers. Similar results were obtained for tertiary polymers.

For accurate preparation of calibration standards different diluters (silica, deactivated silica, calcium carbonate, THF and HFIP) were tested. It was observed that deactivated silica had only an influence on the pyrolysis of PET. Whereas, dilution with silica affected PA-6/66, PE, PET and MDI-PU. Only PVC was not influenced by dilution with silica.

In conclusion, our results highlight the necessity of an international standard of reference material as well as a standardized analytical protocol for the analysis and quantification of polymers in environmental samples. It is crucial to use diluters suitable for the specific polymer, to exclude potential interactions of diluters with the polymer. The present work has to be seen as a foundation, but future work is needed to adequately address the quantification of polymers in environmental samples.

1. Introduction

1.1. Microplastics

Synthetic polymers, often also referred to as plastics, are globally a growing problem due to plastic pollution. These materials are long

chains of polymeric molecules from organic and inorganic crude materials derived from oil, coal and natural gasses [1,2]. Due to plastics robustness, corrosion-resistances and relative cheap price, is it a very attractive material for various kinds of applications [3]. Additionally, plastics are lightweight, can be shaped in various different forms and can be transported easily. The polymers included in this study are depicted

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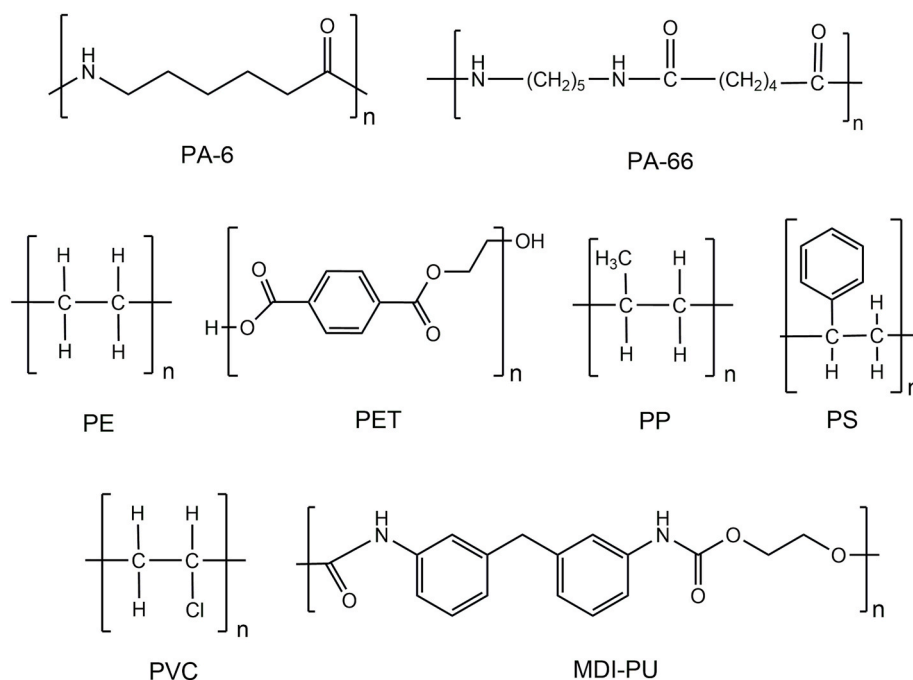


Fig. 1. Chemical structures of the most abundant polymers; PA-6 and PA-66 are caproamidehexamethylene adipamide copolymers [6]. MDI-PU is a result of the condensation polymerisation of methylene diphenyl diisocyanate and a polyol (e.g. polyester, polyether or polylactone).

in Fig. 1. These polymers can be commonly found in various types of daily-use plastic products [4,5].

In the environment, plastic breaks down into plastic fragments, which have been found in the atmosphere, aquatic and terrestrial environment [3], but their presence was even confirmed in humans [7]. The term microplastics refers to small particles of plastic, with dimensions between 1 and 1000 μm [8]. Further, nanoparticles are considered particles smaller than 1 μm . Microplastics can be differentiated into primary microplastics, which are in personal care products (e.g. facial cleansers with “micro-beads”) and secondary plastics which are products of larger plastics fragmentation and decomposition [9]. Secondary plastics can be a result of long sunlight exposure, since ultraviolet radiation causes oxidation of the polymer, which is a chemical change that reduces the average molecular weight of polymers. They can also be formed from abrasion (tires on the road) or wave-action (fishing nets, marine vessels) [10].

Traditional methods for microplastic detection include microscopy [11], spectroscopy [12] and flow cytometry [13], which each come with their own advantages and disadvantages. Including, that the continuous aging and disintegration into smaller fragments of microplastics can negatively influence the results [9]. Recently, different groups have investigated the application of pyrolysis gas chromatography coupled to mass spectrometry (Py-GC/MS) for the qualitative and quantitative analysis of microplastics [9,14–16].

1.2. Py-GC-MS

Py-GC/MS can be used to provide qualitative information on even complex polymer mixtures [17].

The high temperatures (500–1000 $^{\circ}\text{C}$) applied in Py-GC-MS, induce chemical changes in the sample, via bond breakage starting from the weakest to the strongest bond depending on the temperature. The main reactions occurring are depolymerisation (decomposition to the basic unit—a monomer, or oligomers), random excision (randomly smaller fragments) and the elimination of side groups forming double bonds. Additionally, char formation, cross-linking, cyclization, hydrogenation, isomerization and oxidation are possible reactions [18]. Fig. 2 illustrates the difference between combustion (presence of oxygen) and pyrolysis

(absence of oxygen). Pyrolysis of polymers can result into different peak types: specific peaks for a certain polymer (green), ambiguous for a certain polymer (blue) and non-specific for a certain polymer (red) that originate from the corresponding database used for data evaluation. For qualitative as well as quantitative analysis of polymers using Py-GC-MS it is crucial to identify polymer specific peaks (analytes) and hence to provide specific databases that enable specific and accurate matching. Further, these specific peaks can be used as markers (Lour et al. refers to these as indicators) for quantification [9].

Recently, Matsui et al. developed an automated algorithm for the characterization of a sample which contained a mixture of eleven polymers using markers for each polymer.

Efforts are being made to develop a standardised analytical protocol for the characterisation of microplastics in any given environmental sample using Py-GC-MS, but there is not yet a generally accepted strategy by the scientific community. Further, the quantification of polymers in these samples renders even more difficult because often environmental samples contain more than one polymer, which can result in gas phase interaction of polymer fragments, like recombination reactions or acid-base reactions, during Py-GC-MS analysis. As a result, this can alter the pyrolytic yields and hence lead to errors in quantification. The identification and detection of pyrolysis products from gas phase reactions of mixed polymer samples, can serve as indicator compounds for the simultaneous presence of different polymers and hence, be used to confirm specific polymer mixtures. For example, it is known that the co-pyrolysis of PET and PVC particles results in the formation of gas phase reaction products such as chlorinated benzoic acid derivatives and terephthalic acid. These are formed, since PET degrades at higher temperatures than PVC, which allows HCl to react with PET before its degradation. In this sense, 2-chloroethyl benzoate, 1,4-benzenedicarboxylic and di-2-chloroethyl ester are found to be compound indicators for the confirmation of the polymer mixture of PET and PVC [19].

Additionally, often the concentrations of polymers in environmental samples are very low, hence the need for calibration curves in very low concentration ranges (down to ng/L) [20]. However, this is limited by the sensitivity of available scales as well as in the abilities of their operators. Usually, an analyte would be weighed-in in a higher weight

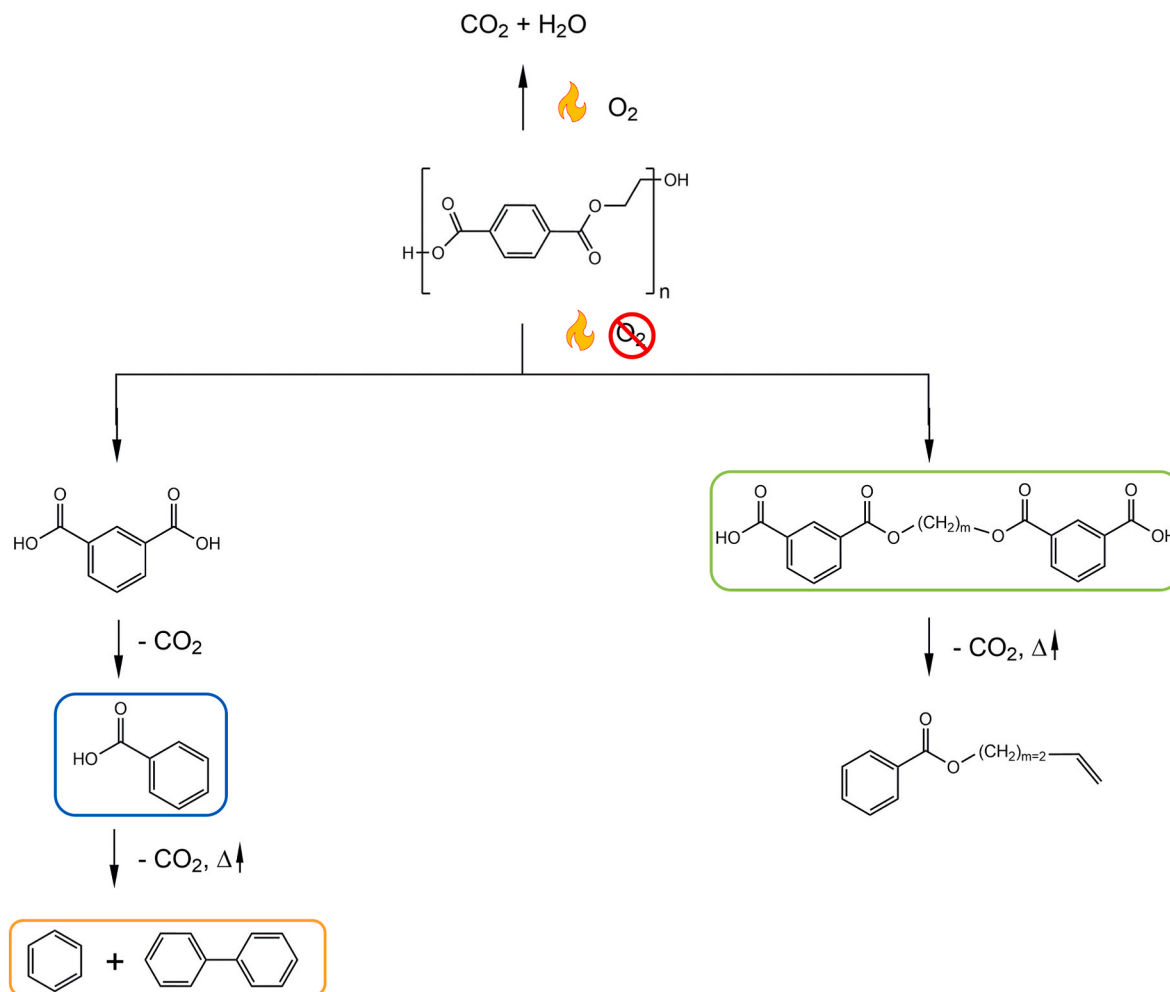


Fig. 2. Comparison of the combustion (with the presence of oxygen) and pyrolysis (absence of oxygen) of PET. Combustion in the presence of oxygen results in carbon dioxide and water. Pyrolysis leads to different peak types: green: marker peaks that are specific for a certain polymer, blue: ambiguous for a certain polymer and red: non-specific for a certain polymer. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

range and then diluted with a solvent to the needed range. In this sense two different approaches can be taken, either with liquid dilution (using organic solvents e.g.: hexfluoror-2-propanol, dichloromethane or tetrahydrofuran) or by solid dilution (using an inert material such as silicium dioxide, calcium carbonat, aluminium oxide, titan dioxide) [21]. But when it comes to Py-GC-MS it is not clear if these diluters could potentially influence the analysis in any way.

This work is aimed to establish the foundation for future quantification of binary polymer mixtures using Py-GC/MS. For this purpose, an in-house polymer database applicable for the detection and identification of microplastic in environmental samples was developed, including the identification of marker peaks for each mono-polymer. In this context we explored the potential occurrence of gas phase reactions of binary polymer mixtures and further identified characteristic marker peaks which can be used in future work for calibration curves and hence quantification of distinct polymers. Further, we investigated the influence of different diluters on the Py-GC-MS analysis, which is the basis of preparing accurate and adequate calibration curves for the quantification of polymers and polymer mixtures.

2. Materials and methods

2.1. Chemicals and reagents

Following polymers and chemicals were purchased from Merck (Zug, Switzerland): polyamide 6/66 (granules), polyethylene (powder), polyethylene terephthalate (granules), polypropylene (granules), polystyrene (powder and granules), polyvinyl chloride (powder), dichloromethane (99.8 %) tetrahydrofuran (99.0 %), heptane (99.0 %), toluene (99.8 %), hexamethyldisilazane (98+%), tetramethylammonium hydroxide (25 wt% in methanol) and trimethylchlorosilane (99 %). Polyurethane was taken from a filament for 3D printers.

Hexafluoro-2-propanol and xylene (mixture of isomers, 99.5 %) were obtained from Avantor (Dietikon, Switzerland), silica (SiO_2 , 40–63 μm), calcium carbonate (CaCO_3 , 99.0 %) and glass microfiber filters (without binder, grade MN 85/90 BF) were purchased from Macherey Nagel (Oensingen, Switzerland).

2.2. Reference standard and sample preparation

The reference standards in form of granules (PA-6/66, PET, PS, PP and MDI-PU) were first manually degraded on a steel block into smaller particles. This was followed by cryo-milling with liquid nitrogen in cooled-down cryo-mill grinding bowls and 5 mm stainless steel balls.

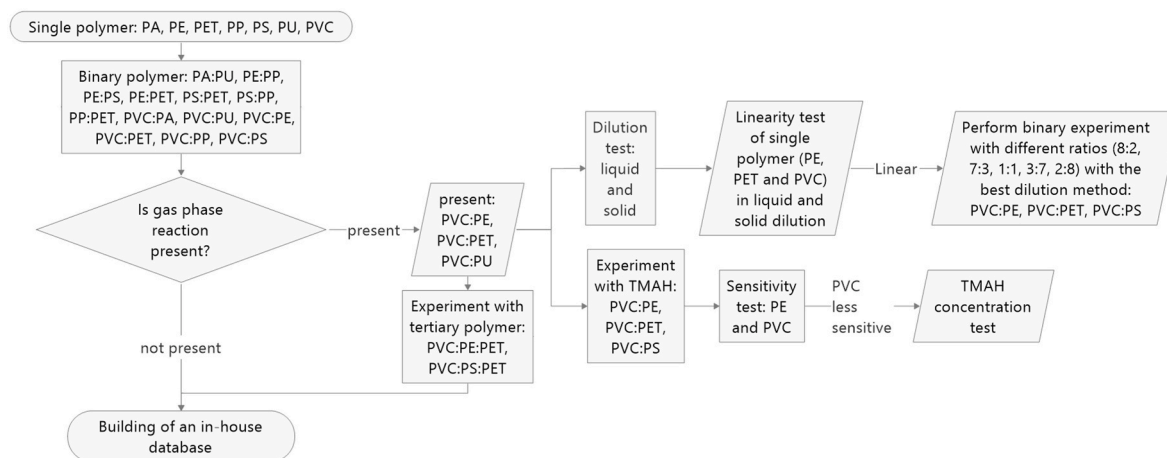


Fig. 3. Systematic approach for the development of the in-house database.

Pellets were cryo-milled for 10 min in two 5 min intervals and cooling in between. 20 min cryo-milling for PP, 30 min for PET and 70 min for PA-6/66 and MDI-PU were performed. Samples were directly weighed into the GERSTEL pyrolysis vials (standard closed bottom without slid) without any further pre-treatment.

2.3. Data evaluation using an in-house database

An in-house microplastic database was developed and used for the identification of microplastics with Py-GC-MS. This database includes single, binary and tertiary microplastic mixtures. First, single polymers (PA-6/66, PE, PET, PP, PVC, PS and MDI-PU) were measured, and their characteristic pyrolysis products identified. Following this, a mixture of two polymers (binary polymers) in a 1:1 ratio (PA-6/66:MDI-PU, PE:PP, PE:PS, PE:PET, PS:PET, PS:PP, PP:PET, PVC:PA-6/66, PVC:PE, PVC:PET, PVC:PP, PVC:PS, PVC:MDI-PU) were tested to identify any potential gas phase reactions. Furthermore, different dilution methods such as liquid (organic solvents) and solid (deactivated silica and calcium carbonate) were evaluated: PE (xylol and toluene), PET (THF and HFIP), PVC (in DCM:THF 1:1 v,v and in THF), PA-6/66 (HFIP) and MDI-PU (THF) in liquid dilutions (10 mg/mL); PE, PET, PVC, PA-6/66 and MDI-PU (deactivated silica and calcium carbonate) solid dilutions (3:17, m:m). Each spectrum was evaluated manually, and conspicuous peaks were analysed using the “GC/MS Data Book of Synthetic Polymers” by S. Tsuge et al.. Furthermore, the selected peaks were confirmed with the NIST database (version 14). All substance names listed in the spectra are molecular ions.

Further, the linearity of the single polymers of PET and PVC in liquid dilutions (70 μ L, 90 μ L, 110 μ L, 130 μ L, 150 μ L) and for PE, PET and PVC in solid dilutions (0.47 mg, 0.60 mg, 0.73 mg, 0.87 mg, 1 mg) were evaluated. Following this, binary experiments with different polymer ratios (8:2, 7:3, 1:1, 3:7 and 2:8), using the most suitable dilution method, were conducted for PVC:PET, PVC:PS and PVC:PE. Finally, tertiary polymer reaction of PE, PET and PVC in a 1:1:1 ratio were tested. All reference standards were at least measured in triplicates.

2.4. Analysis of microplastics using Py-GC-MS

Sample analysis was conducted using a GERSTEL pyrolyzer (GERSTEL, Mühlheim an der Ruhr, Germany), a thermal desorption unit (TDU), a cooled injection system (CIS), a multiple-purpose sampler (MPS) and an Agilent 8890 gas chromatograph coupled to an Agilent 5977B single quadrupole mass spectrometer (Agilent, Basel Switzerland) equipped with an electron impact (EI) source. Separation was conducted on an Agilent standard polysiloxane J&W DB-5 capillary column, which was operated in backflush mode (HP-5ms Ultra Inert (2

Table 1

Identified characteristic single polymer peaks; * peaks for quantification.

Polymer	Characteristic compound	Number of carbons	
PE	propane	C3	
	1-octene	C8	
	1-nonene	C9	
	dec-1-ene	C10	
	1-undecene	C11	
	1-dodecene	C12	
	1-tridecene	C13	
	1-tetradecene	C14	
	1-pentadecene	C15	
	cetene	C16	
	1-heptadecene	C17	
	1-octadecene	C18	
	1-nonadecene	C19	
	PET	benzene	C6
		vinyl benzoate	C16
		benzoic acid	C9
		1,1'-biphenyl	C14
		terephthalic acid, di(but-3-enyl)ester	C12
		1,2-ethanediol,dibenzoate	C16
PP	propene (propylene)	C3	
	2,4-dimethyl-1-heptene	C9	
	1-nonene,4,6,8-trimethyl	C12	
PVC	hydrogen chloride	-	
	benzene	C6	
	toluene	C7	
	naphthalene	C10	
	2-methylnaphthalene	C11	
	1-methylnaphthalene	C11	
PS	styrene	C8	
	styrene dimer	C16	
	styrene trimer	C24	
PA-6/66	cylopentanone	C5	
	5-cyano-1-pentene	C5	
	hexanenitrile	C6	
	caprolactam	C6	
MDI-PU	tetrahydrofuran	C4	
	1,4-butanediol	C4	
	phenol	C6	
	p-isopropenylphenol	C9	
	benzene, 1,1'-methylenebis(4-isocyanato)	C15	

$\times 15 \text{ m} \times 250 \mu\text{m} \times 0.25 \mu\text{m}$). The pyrolysis system was operated with the GERSTEL MAESTRO software (GERSTEL, Mühlheim an der Ruhr, Germany, version 1.4.27.7) and for the GC-MS system MassHunter Qualitative Analysis (Agilent, Basel, Switzerland, version 10.0) was

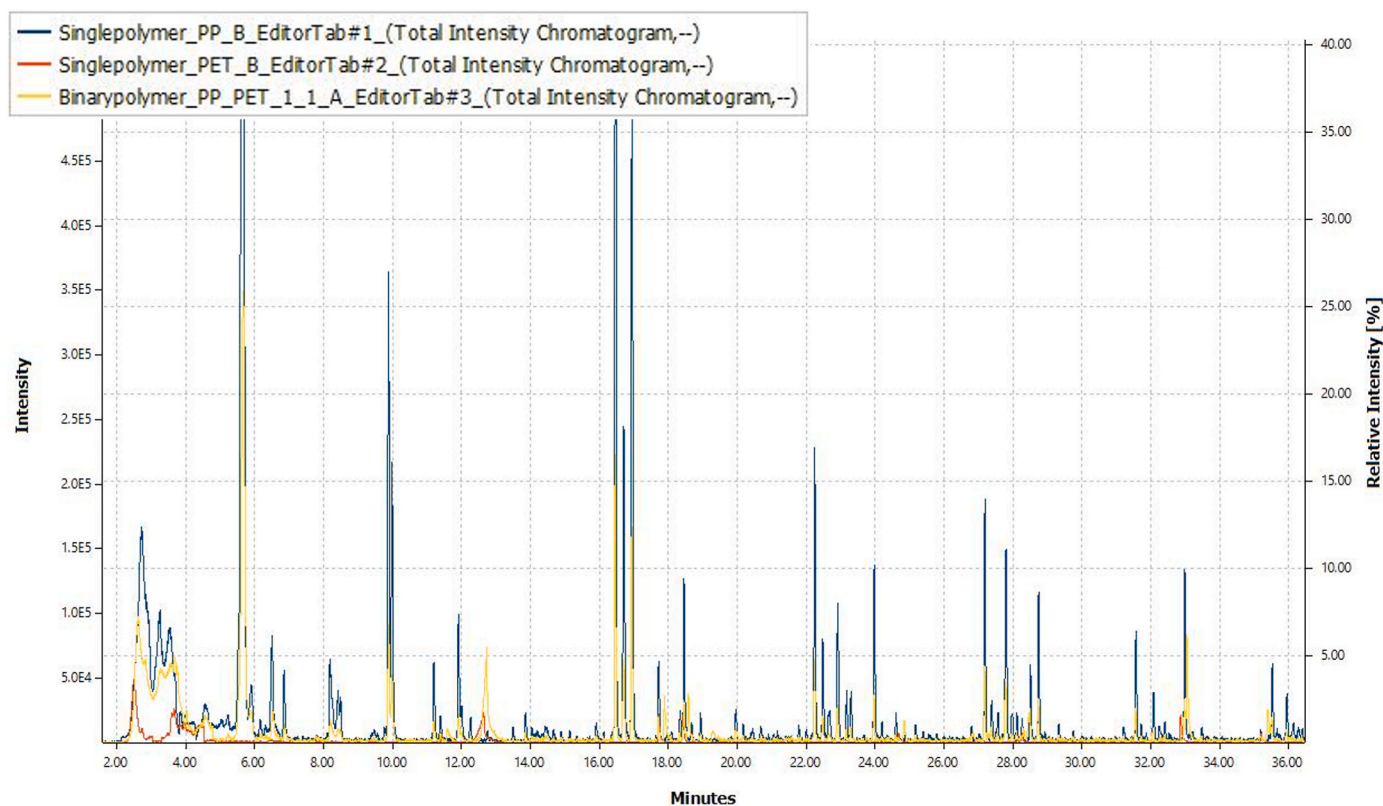


Fig. 4. Overlay chromatogram of single polymers PET (red) and PP (blue) as well as the binary polymer PET and PP (1:1) (yellow). No gas phase reactions could be identified. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

used. Helium was used as a carrier gas for separation at 1 mL/min. Helium was also used to transfer pyrolysis products to the column during pyrolysis at a split ratio of 1:200, with the gas saver activated to 20 mL/min after 2.5 min. The pyrolysis temperature was ramped from 300 °C to 800 °C (held for 0.5 min) at a rate of 5 °C/s. The TDU temperature was ramped from 290 °C to 350 °C (held for 1.47 min) at a rate of 300 °C/min. From 350 °C, the temperature was set to 320 °C (held for 1.43 min) at a rate of 0 °C/min. The GC oven gradient consisted of three steps: from 50 °C (held for 3 min) to 100 °C (held for 3 min) at a heating rate of 10 °C/min, from 100 °C to 285 °C with a heating rate of 5 °C/min and finally from 285 °C to 320 °C (held for 8 min) at a heating rate of 10 °C/min. Following MS parameters were applied: electron impact source, the ionization energy 70 eV, the ion source temperature 230 °C, the scan rate 4.9 Hz, and scan range m/z 29–600.

3. Results and discussion

3.1. In-house database

3.1.1. Single polymers

A systematic approach for developing the in-house database was followed (see Fig. 3). First the single polymers were analysed, and their specific peaks identified and categorized according to their chain length (see Table 1).

For PA-6/66, caprolactam had the highest intensity and could be used for quantification purposes (see Supplement Fig. 1 and Supplement Table 1). However, caprolactam is not only specific for PA-6/66 but also for PA-6. Cyclopentanone, which had the second highest intensity in PA-6/66 has also been found in PA-4,6, PA-6,6 and PA-12,6⁶. In comparison with literature data only hexanenitrile, with the lowest intensity, deemed to be specific for PA-6/66⁶.

The chromatogram of PE depicted various long-chain alkanes and alkenes, the latter having higher intensities (see Supplement Fig. 2 and

Supplement Table 2). While none of them were specific, and other substances containing hydrocarbon chains, such as surfactants, natural fats, lipids, and oils can also produce the same pyrolysis products, dec-1-ene depicted the highest intensity and is therefore proposed as a PE marker for quantification purposes.

The single polymer analysis of PET displayed bis(but-3-enyl) benzene-1,4-dicarboxylate to be the most abundant peak. However, this analyte is not specific for PET since it has been observed in other terephthalic polymers (e.g.: in polybutylene adipate terephthalate (PBAT)) [22]. For the chromatogram and detailed identified pyrolysis products see Supplement Fig. 3 and Supplement Table 3. Benzoic acid or vinyl benzoate could be taken as quantification peak for future experiments that includes PBAT.

For PP, alkenes with alkyl side chains were mainly observed and 2,4-dimethylhept-1-ene was chosen as the quantification peak (marker for PP) due to its high abundance. For the chromatogram and detailed identified pyrolysis products see Supplement Fig. 4 and Supplement Table 4.

The pyrolysis of PS produced three main products: styrene, its dimer and its trimer (see Supplement Fig. 5 and Supplement Table 5). Although styrene had the highest abundance and hence would be an ideal marker for quantification, it may not be suitable in matrixes containing natural products such as albumin, chitin, fish protein and wood (lignin), which can release or generate styrene monomers during pyrolysis [23].

The pyrolysis of PVC resulted in a HCl peak, however, HCl also interacts with other polymers during pyrolysis. Therefore, 2-methylnaphthalene is suggested as a marker for PVC for quantification. For the chromatogram and detailed identified pyrolysis products see Supplement Fig. 6 and Supplement Table 6.

For MDI-PU, MDI was formed, which can be used as quantification peak (marker) due to its specificity. However, it's worth noting that the here used MDI-PU was not reference standard quality but taken from 3D-

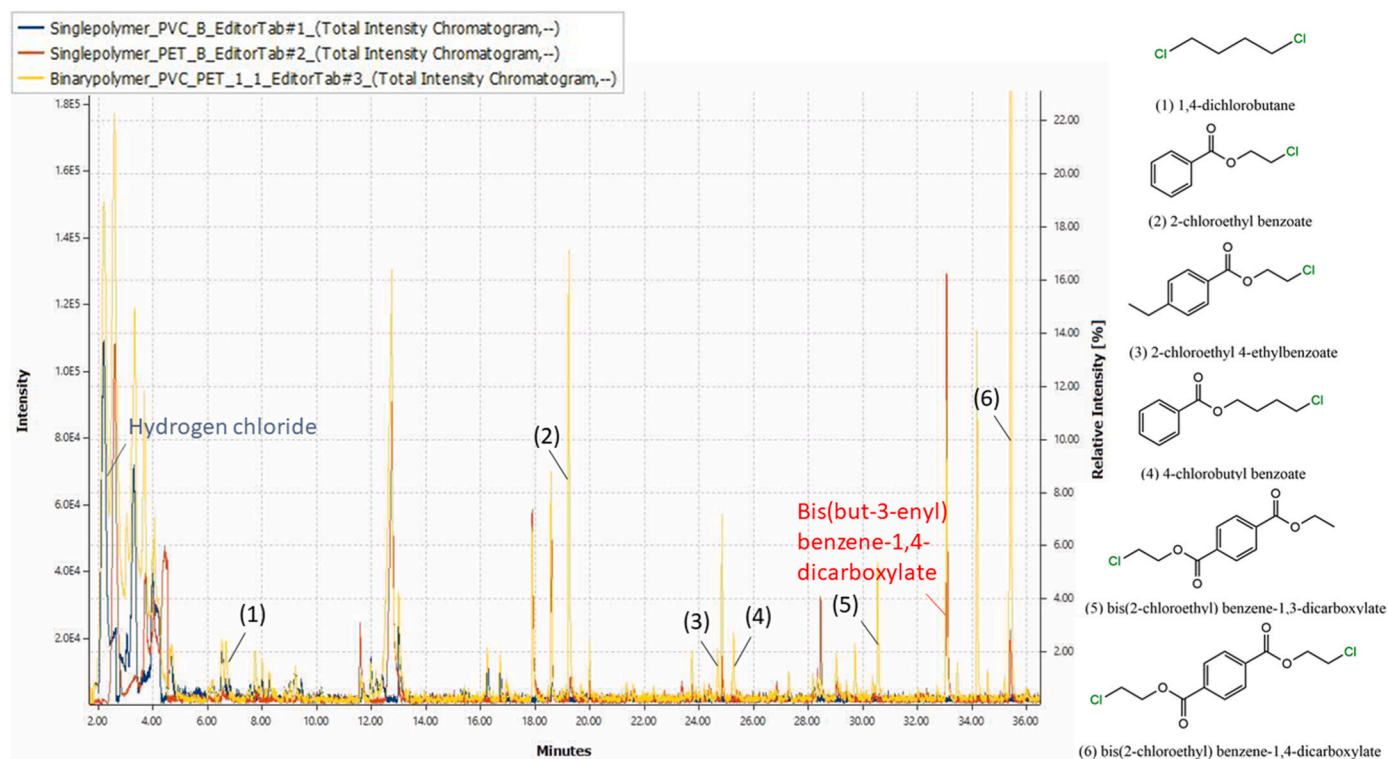


Fig. 5. Overlay chromatogram of single polymers PET (red) and PVC (blue) as well as the binary polymer PET and PVC (1:1) (yellow). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 2

Measured binary polymer mixtures (1:1) with their gas phase reactions, pyrolysis products and the number of carbons.

Polymers	Gas phase reaction	Pyrolysis products	Number of carbons
PE:PET	not present	–	–
PE:PP	not present	–	–
PE:PS	not present	–	–
PET:PP	not present	–	–
PET:PS	not present	–	–
PP:PS	not present	–	–
PE:PVC	present	hexane, 2-chloro	C6
PET:PVC	present	1,4-dichlorobutane	C4
		2-chloroethyl benzoate	C9
		2-chloroethyl 4-ethylbenzoate	C13
		4-chlorobutyl benzoate	C11
		bis(2-chloroethyl) benzene-1,3-dicarboxylate	C12
		bis(2-chloroethyl) benzene-1,4-dicarboxylate	C12
PP:PVC	not present	–	–
PVC:PS	not present	–	–
PVC:PA-66	not present	–	–
PVC:MDI-PU	present	4-Chlorobutan-1-ol	C4
		isocyanatobenzene	C7
		aniline	C6
		2-[2-(2-Chloroethoxy)ethoxy]-1-methyl-4-propan-2-ylbenzene	C10
PA-6/66:MDI-PU	not present	–	–

printer material. Due to the results, it is suspected that the used MDI-PU standard condensed with a polyester (tetrahydrofuran and butane-1,4-diol were confirmed) (see Supplement Fig. 7 and Supplement Table 7).

With these experiments, specific marker for PE, PET, PP, PS, MDI-PU, and PA-6/66 could be determined. However, for PVC no specific peaks could be identified.

In a next step to build an in-house library, different combinations of binary polymers were investigated for the potential occurrence of gas phase reactions.

3.1.2. Binary and tertiary polymers and gas phase reactions

A potential problem in Py-GC-MS analysis of polymer mixtures, can be gas phase reactions resulting from high temperatures or by the loss of the reactive group, resulting in co-pyrolysis products.

In order to identify gas phase reactions, the single polymer chromatograms were overlaid with the respective binary polymer chromatograms (see Figs. 4 and 5). Gas phase reactions could only be identified for the binary mixtures of PET:PVC, MDI-PU:PVC and PE:PVC (see Table 2). For those, several different novel pyrolysis products specific for the binary polymers could be identified for the respective binary polymer mixture. This confirmed that PVC exhibit strong interactions during co-pyrolysis with ester- and ether-based polymers.

The pyrolysis of binary polymer of PE and PVC produced no HCl, however a novel peak, 2-chlorohexane was identified. The Cl[•] radicals in the pyrolysis were inclined to the chain free radicals of PE rather than binding HCl with hydrogen.

For the pyrolysis of the binary polymer of PET and PVC, it was observed that HCl (peak could still be observed) accelerated the PET degradation rate, which resulted in the formation of a series of chloro-organic compounds, such as chloro-esters of benzoic acid derivatives. The PET specific peak bis(but-3-enyl) benzene-1,4-dicarboxylate was still formed during pyrolysis but two new compounds bis(2-chloroethyl) benzene-1,3-dicarboxylate and bis(2-chloroethyl) benzene-1,4-dicarboxylate were identified. In total six novel chlorinated pyrolysis products could be identified for the binary polymer mixture of PET and PVC (see Fig. 6).

The binary polymer of PVC and MDI-PU depicted no HCl peak and further chlorinated derivatives showed very low abundance. The most abundant peaks were isocyanatobenzene and aniline.

Analogue to the binary polymer experiments, were tertiary polymer

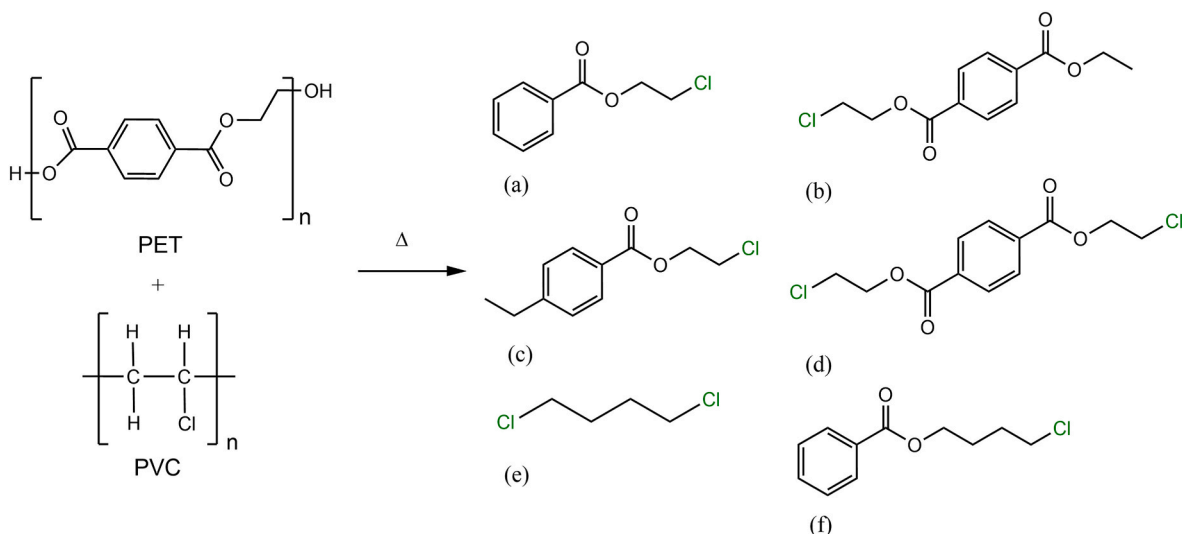


Fig. 6. Gas phase reactions of PET with PVC resulting in following chlorinated pyrolysis products: a) 2-chloroethyl benzoate, b) bis(2-chloroethyl) benzene-1,3-dicarboxylate, c) 2-chloroethyl 4-ethylbenzoate, d) bis(2-chloroethyl) benzene-1,4-dicarboxylate, e) 1,4-dichlorobutane and f) 4-chlorobutyl benzoate.

Table 3

Influence of diluters on the Py-GC-MS analysis and if tested on the linearity of the marker (quantification) peak; n/a: not applicable.

Polymer	Dilution type	Diluter	Diluter influence	Quantification peak	R [2] with outliers	R [2] without outliers
PA-6/66	Liquid	HFIP	None	n/a	n/a	n/a
PA-6/66	Solid	Silica	New peaks	n/a	n/a	n/a
PA-6/66	Solid	Deactivated silica	New peaks	n/a	n/a	n/a
PA-6/66	Solid	Calcium carbonate	None	n/a	n/a	n/a
PE	Liquid	Xylene and toluene	Not soluble	n/a	n/a	n/a
PE	Solid	Silica	New peaks	n/a	n/a	n/a
PE	Solid	Deactivated silica	None	1-decene		0.901
PE	Solid	Calcium carbonate	None	n/a	n/a	n/a
PET	Liquid	THF	Not soluble	n/a	n/a	n/a
PET	Liquid	HFIP	None	terephthalic acid, di(but-2-enyl) ester	0.867	0.973
PET	Solid	Silica	New peaks	n/a	n/a	n/a
PET	Solid	Deactivated silica	New peaks	n/a	n/a	n/a
PET	Solid	Calcium carbonate	New peaks	n/a	n/a	n/a
MDI-PU	Liquid	THF	No reaction but a characteristic THF peak	n/a	n/a	n/a
MDI-PU	Solid	Silica	New peaks	n/a	n/a	n/a
MDI-PU	Solid	Deactivated silica	New peaks	n/a	n/a	n/a
MDI-PU	Solid	Calcium carbonate	New peaks	n/a	n/a	n/a
PVC	Liquid	DCM:THF (1:1)	No reaction but a characteristic peak	HCl	0.409	0.903
PVC	Liquid	THF	No reaction but a characteristic peak	HCl	0.780	0.995
PVC	Solid	Silica	None	n/a	n/a	n/a
PVC	Solid	Deactivated silica	none	HCl		0.989
PVC	Solid	Calcium carbonate	None	n/a	n/a	n/a

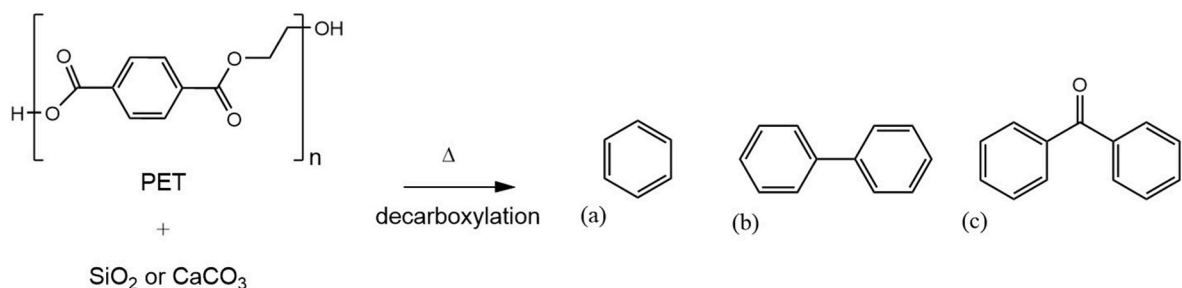


Fig. 7. The pyrolysis of PET and silica or calcium carbonate results in a) benzene, b) 1,1'-biphenyl and c) diphenylmethanone via decarboxylation.

Table 4
Diluted binary polymer mixtures, their characteristic pyrolysis products and linearity.

Mixture	Pyrolysis products	Number of carbons	R [2] of PVC with outliers (marker peak)	R [2] second polymer with/without outliers (marker peak)
PVC:PE	2-chloro-hexane	C6	0.996 (2-methylnaphthalene)	With: 0.856 (1-decene) Without: 0.508 (1-decene) Without: 0.910 (1-tetradecene)
PVC: PET	2-chloroethyl benzoate isophthalic acid 2-chloroethyl ethyl ester terephthalic acid Di(2-chloroethyl) ester	C9 C12 C12	0.843 (2-methylnaphthalene)	With: 0.477 (terephthalic acid, di(but-2-enyl) ester) Without: 0.544 (terephthalic acid, di(but-2-enyl) ester)
PVC:PS	No new peaks	n/a	0.9842 (2-methylnaphthalene)	With: 0.889 (styrene trimer) Without: 0.967 (styrene dimer)

samples analysed for gas phase reactions by overlaying their chromatograms with the respective single polymer chromatograms. Gas phase reactions could only be identified for the tertiary mixtures of PE: PET:PVC and PET:PS:PVC. For the combination of PE:PET:PVC less peaks were observed in comparison to their single polymer chromatograms, which was especially high for PE. We suspect that the combination of these three polymers resulted in a suppression of PE pyrolysis analytes. For PET:PS:PVC the observed peaks were comparable to the binary polymer mixture of PET:PVC.

3.1.3. Influence of diluters on the Py-GC-MS analysis

In order to conduct an accurate quantification of single polymers, a precise preparation of calibration standards is needed in the adequate concentration range. Therefore, potential diluters used in the preparation of calibration standards were tested. Each polymer was tested with at least one liquid and three solid diluters. The results are depicted in Table 3, which also includes the used specific marker peaks for the compounds for which the linearity was evaluated (PE, PET and PVC).

PET diluted in silica or calcium carbonate led to decarboxylation, resulting in an increase of benzene, diphenylmethanone and 1,1'-biphenyl peaks (see Fig. 7). But when diluting PET with HFIP a linear regression R^2 of 0.973 could be observed.

Analog to PET, a carbon monoxide loss was observed for MDI-PU diluted with silica. Further, when MDI-PU was diluted with calcium carbonate phosphonic acid was formed. However, no problems were observed when diluting MDI-PU with THF.

PE, PVC and PA-6-66 could be diluted in deactivated silica and calcium carbonate without the occurrence of novel peaks. Further, for PVC diluted in THF a linear regression R^2 of 0.995 could be obtained. PE was not soluble in any liquid diluter and was therefore diluted in deactivated silica with a linearity of 0.901. The silica must be deactivated with methylation prior usage.

PA-6/66 diluted in HFIP did not result in any novel peaks, hence it is a suitable diluter for it.

Dilution with deactivated silica had no influence on the pyrolysis of seven polymers. Only PET dilution resulted in novel peaks such as benzoic acid, TMS derivate.

3.1.4. Investigation of the dilution of binary polymers

The influence on diluters was investigated for PVC in combination with PE, PET and PS, respectively. The results are depicted in Table 4. For the evaluation of the linearity of PVC 2-methyl naphthalene was used as a specific marker. Following specific marker were used for the second polymer respectively: PE: 1-decene, PET: 1-terephthalic acid, di(but-2-enyl) ester and for PS: styrene dimer.

Binary polymer mixtures with observed gas phase reactions resulted into bad linearity: for PVC:PE a linearity of 0.508 without outliers was observed (with outliers: 0.856) and PVC:PET 0.544 without outlier (with outliers: 0.477). On the other hand, binary polymer mixture without any gas phase reactions observed resulted into good linearity: PVC:PS for example had a linearity of 0.967 without outlier and 0.8891 with outliers.

The linearity of PE increased to 0.910 with outliers, when the quantification peak was calculated with a longer carbon chain 1-tetradecene. This indicated that it would be recommended to verify the PE's linearity with another peak which has a longer carbon chain.

The linearity of PVC in different binary polymers confirmed these results, because PVC mixed with PET had the worst linearity of 0.843 with outlier, compared to PS 0.984 and PE 0.996.

The chlorinated pyrolysis product for the diluted binary polymer mixture of PVC:PE hexane, 2-chloro- was only present in ratios of 2:8 and 3:7. This concluded that a low concentration of PE did not result in gas phase reactions. This also explained the good linearity of PVC in mixture with PE. HCl was present in every ratio.

Additionally, the more PET there were in the mixture, the higher was the intensity of chlorinated pyrolysis products.

3.1.5. Influence of derivatisation agent TMAH

In order to eliminate observed gas phase reactions for PA-6/66, PE, PET, PVC and MDI-PU, TMAH was tested as a derivatisation agent.

Derivatisation with TMAH had advantageous effects on PET, PA-6/

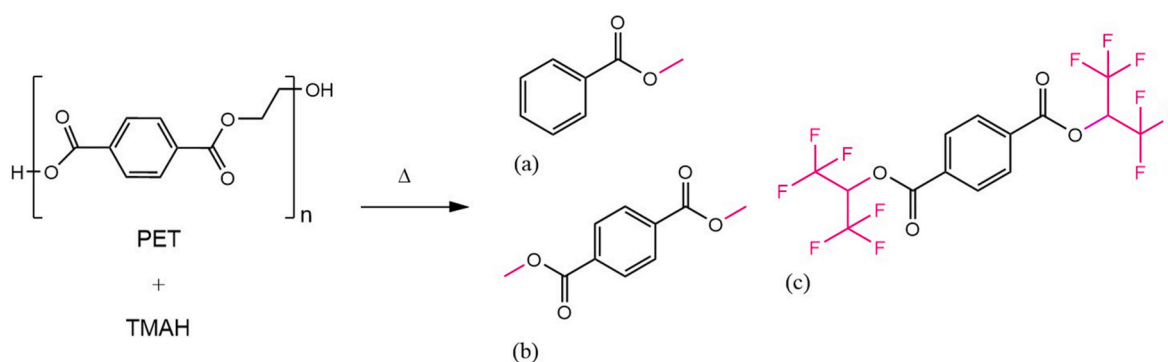


Fig. 8. Methylation of PET due to reactive pyrolysis with TMAH resulted in methylated pyrolysis products such as a) methyl benzoate, b) bis(1,1,1,3,3,3-hexafluoroisopropyl)terephthalate and c) HFIP solvent adducts such as dimethyl benzene-1,4-dicarboxylate.

66 and MDI-PU, since novel specific peaks, due to their OH and NH groups being methylated, were identified (compare Fig. 8). Because of this, binary polymer mixtures of PET in combination with PVC and derivatised with TMAH did not depict any chlorinated pyrolysis products. Since PE and PVC do not have any OH or NH groups, they were unaffected by derivatisation with TMAH. For PET, PA-6/66 and MDI-PU an increase in detection sensitivity was observed after derivatisation with TMAH. Additionally, TMAH derivatisation suppressed gas phase reactions for the binary polymer mixture of PET and PE and could minimize matrix interferences by the protection of active groups from matrixes and polymers.

Furthermore, had TMAH derivatisation a negative influence on the detection sensitivity by 40 %–50 % of PVC. This was also dependant on volume of TMAH (25 wt% in methanol, 11–15 μ L with 100 μ g polymer tested). Hence, PVC should not be derivatised with TMAH.

4. Conclusion

It was shown that new gas phase products are formed for specific polymer mixtures. However, those products are specific and hence can be used as confirmatory markers as well as for quantification purposes and were added to the in-house database for single polymers and binary mixtures. For tertiary mixtures, the spectra are more complex and therefore a unique identification of markers was difficult. To circumvent this problem, the authors suggest sample-preparation by separating them into less complex mixtures by density separation before Py-GC/MS analysis.

The developed and established database can be seen as a starting point in addressing the quantification of polymers in environmental samples. Especially considering, that a wider variety of polymers should be investigated and added to it, as well as references standards of the same polymer from different sources [14].

The results are particularly meaningful since different diluters for the respective polymer were identified to prepare adequate calibration curves in future studies.

Further, our results highlight the necessity of an international standard of reference material as well as a standardized analytical protocol for the analysis and quantification of polymers in environmental samples.

CRedit authorship contribution statement

Katharina Elisabeth Grafinger: Writing – original draft, Methodology, Conceptualization. **Celandin Ochiai:** Visualization, Investigation, Formal analysis, Data curation, Writing – review & editing. **Huan-Xiao Zhou:** Writing – review & editing, Resources. **Timm Hettich:** Writing – review & editing, Supervision, Methodology, Conceptualization. **Andre Büttler:** Supervision, Formal analysis, Data curation. **Romina Álvarez Troncoso:** Writing – review & editing. **Armin Zenker:** Writing – review & editing, Resources. **Stefan Gaugler:** Writing – review & editing, Supervision, Resources, Methodology, Funding acquisition, Conceptualization.

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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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.polymertesting.2024.108620>.

Data availability

Data is available upon request from the authors.

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