

Quantitation of polystyrene by pyrolysis-GC-MS: The impact of polymer standards on micro and nanoplastic analysis

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ABSTRACT

The analytical method for detecting and quantifying micro and nanoplastics (MNPs) using Pyrolysis-Gas Chromatography-Mass Spectrometry (Py-GC-MS) is evolving and continuously refined. The requirement for accurate analytical methods faces challenges during method validation due to the scarcity of relevant reference materials. Additionally, the wide array of polymer types and their diverse characteristics further complicate this validation process. This study evaluated the impact of using diverse polystyrene (PS) standards with different molecular weights, polydispersity indexes, tacticity, endcapping, and chain branching, on quantifying the mass concentration of PS in various products. The results for the PS-based products showed inconsistencies across different standards, indicating that the measurements for a single product varied substantially when different polystyrene (PS) standards were applied. The influence of sample quantity on pyrolysis revealed differences in the ratios of pyrolysis products among various PS standards and different sample amounts. This research emphasizes the complexities involved in the precise quantification of polymers using Py-GC-MS. It provides valuable insights crucial for quantitative MNP analysis, highlighting the need for refined calibration strategies and standardised reference materials to improve the reliability of the MNP analysis method.

1. Introduction

The prevalence of micro and nanoplastics (MNPs) in various environmental and human compartments has highlighted the need for analytical methods to accurately detect and quantify these contaminants. The study of plastic particles in environmental and biological samples is still an emerging research area, where various methods based on optical, spectroscopy or thermo-analytical approaches are used. Pyrolysis-gas chromatography coupled with mass spectrometry (Py-GC-MS), one of the thermo-analytical methods, is evolving as an analytical technique to quantify MNPs in complex matrices [1–5]. This method is valuable for studying synthetic plastics and has proven to be particularly effective in identifying polymers and quantifying the mass of polymer particles (MNPs) in samples [6]. For quantitative analysis, the mass concentrations of polymers in samples are calculated using calibration protocols based on known standards of the same polymers at various concentrations. A principal assumption in this analysis is that the

specific pyrolysis products used as polymer marker remains the same for different grades of that particular polymer type. This assumption simplifies the quantification process, as it permits the use of a consistent marker compound to estimate the specific polymer mass quantity across diverse samples. The analysis of PS using Py-GC-MS result in the formation of monomers, dimers, and trimers due to the repeating styrene units [7]. It has been shown that the properties and molecular characteristics of polystyrene influence the overall kinetic pyrolysis behaviour and yield of pyrolysis products [8,9]. The formation of styrene monomers predominantly follows end-chain β -scission, while dimers and trimers form via mid-chain β -scission, although other reaction families are also kinetically important [10,11]. The three major products are monomer, dimer, and trimer. Previous studies have shown that high pyrolysis temperatures promote the formation of the styrene monomer but suppress the formation of styrene trimer during polystyrene pyrolysis [12,13]. At relatively low pyrolysis temperatures (450 °C), the yield of tetramers increases, whereas at higher temperatures, only minute

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amounts (about 0.05 %) of tetramers are formed [10]. However, styrene monomers can also be formed from the pyrolysis of other polymers like PVC, and styrene-copolymers [7,14]. For quantification of PS, both the major dimer and trimer can improve the accuracy. The major styrene trimer (5-hexene-1, 3, 5-triyltribenzene) has been shown to be a reliable quantitative marker for PS, even in the presence of matrix [15].

The use of Py-GC-MS for the quantitative analysis of MNPs remains in an early developmental phase. Although substantial efforts have been made to improve the method validation process, the absence of reference materials presents challenges in achieving complete method validation [16]. These challenges are particularly evident in the field of polymer analysis due to the wide range of polymer types and their characteristics. The same type of polymer, such as polystyrene (PS), can exhibit differences in physical appearances like molecular weight, polydispersity index (PDI), tacticity, endcapping, and chain branching, leading to variations in characteristics such as mechanical properties, thermal stability, and crystallinity [17]. The styrene dimer was recently used for the quantitation of PS in human arteries [18]. However, in this study no PS was detected in any of the samples. In contrast, our group previously utilized styrene monomer as quantitation compound, a pyrolysis product of several polymerized styrenes (not exclusively PS), for the analysis of PS in human blood [5]. In this study, polymeric styrene was detected in 36 % of the samples, with concentrations reaching up to 4.8 µg/mL.

In this study, we applied a method previously developed for the analysis of MNPs using Py-GC-MS [5] to assess the impact of employing various PS standards on quantifying the mass concentration of PS in nine products. These PS-based products have the potential, through degradation, to transform into MNPs in the environment. Samples include: PS coffee lids, various PS foams, PS printing filaments, and recycled PS resin. Additionally, we analysed the PS content in a commonly used cell culture plate. The quantification of the PS content was conducted using two polymer mixtures and ten individual PS standards with varying tacticity, endcapping, molecular weight, and dispersity.

2. Material and methods

2.1. Polystyrene standards and products

Sample handling and preparation were conducted in a dedicated laboratory equipped with a laminar flow cabinet to minimize external contamination, complemented by controlled ventilation. Cotton

laboratory coats and mandatory nitrile gloves were used. The PS standards used are listed in Table 1, and consist of isotactic, atactic, and syndiotactic standards, each characterised by different levels of cross-linking, dispersity, endcapping, and average molecular weight. The PS plastic products analysed in this study are listed in Table 2 and include expanded PS (EPS) foam boards intended for insulation, foam packaging materials, and ordinary coffee cup lids obtained in the Netherlands. Additionally, unprinted 3D high impact PS (HIPS) filament and a sample of the same filament after the 3D printing process were used. Furthermore, a cell culture plate used for biochemical and molecular biology assays, and recycled PS resin were also included in the study.

2.2. Polymer calibration and product sample preparation

The polymer mixture, containing approximately 3 mg of each standard for poly(methyl methacrylate) (PMMA), polyethylene (PE), PS (Cospheric, Santa Barbara, California, USA), polypropylene (PP), polyvinyl chloride (PVC) (Sigma- Aldrich, Schnelldorf, Germany), and polyethylene terephthalate (PET) (Goodfellow Cambridge Ltd., United Kingdom) was accurately weighed on a micro-balance (Sartorius, Göttingen, Germany, SD = 1 µg) and transferred to a precleaned 22 mL stainless steel accelerated solvent extraction (ASE) cell containing a deactivated glass filter (Thermo Scientific, Waltham, MA, USA). The cell was filled with sea sand, which had been deactivated by heating at 600 °C for 1 h in a muffle oven, purged with nitrogen. The polymer mixture was extracted (dissolved/dispersed) with DCM (Biosolve, Valkenswaard, the Netherlands) at 180 °C using an accelerated solvent extractor (ASE) (350 Accelerator Solvent Extractor, Thermo Scientific, Waltham, MA, USA) as previously described by Okoffo et al. [19]. The solution was collected in a precleaned 60 mL ASE vial. The PS products and individual standards were prepared in a manner similar to the polymer calibration mixture, with approximately 3 mg added to the ASE cell. Six calibration levels were prepared by accurately transferring volumes of the polymer mixture using gastight glass syringes to pyrolysis cups fitted with an 8 mm glass microfiber filters (grade GF/F). The mass quantities for the calibration levels were 0.1, 0.25, 0.5, 1.0, 3.0, and 6.0 µg. For the analysis of the PS products a final amount of approximately 1.0 µg was added to the cups. The pyrolysis cups (Eco-cup LF, Frontier Laboratories, Saikon, Japan) were placed in a precleaned aluminium cupholder and placed in an oven, purged with nitrogen, at 50 °C to dry overnight. Prior to analysis 240 ng poly(4-fluoro) styrene (Polymer Source, Quebec, Canada) was added to the sample cups as an

Table 1

The names, product codes, description, and supplier of the polystyrene standards.

Name	Properties	Supplier
PS-Cospheric	Density 1.07 g/cm ³ , 85–105 µm microspheres fully crosslinked with divinylbenzene (DVB) crosslinking agent	Cospheric, Santa Barbara, California, USA
PS-MERCK	90 % isotactic, average Mw = 400 × 10 ³ g/mol,	Sigma- Aldrich, Schnelldorf, Germany
PS-P4279	Atactic; narrow dispersity (Mw/Mn < 1.2), Mn = 24 × 10 ³ g/mol, Mw = 26 × 10 ³ g/mol, PDI = 1.07, <i>tert</i> -butyl endcapped	Polymer Source Inc., Montreal, Quebec, Canada
PS-P42569	Atactic; narrow dispersity (Mw/Mn < 1.2) Mn = 85 × 10 ³ g/mol, Mw = 85 × 10 ³ g/mol, PDI = 1.01, <i>iso</i> -butyl endcapped	Polymer Source Inc., Montreal, Quebec, Canada
PS-P4288A	Atactic; narrow dispersity (Mw/Mn < 1.2) Mn = 77 × 10 ³ g/mol, Mw = 79 × 10 ³ g/mol, PDI = 1.03, <i>n</i> -butyl endcapped	Polymer Source Inc., Montreal, Quebec, Canada
PS-P5138	Atactic; broad dispersity (Mw/Mn > 1.2), Mn = 1.5 × 10 ³ g/mol, Mw = 1.9 × 10 ³ g/mol, PDI = 1.25, <i>tert</i> -butyl endcapped	Polymer Source Inc., Montreal, Quebec, Canada
PS-P1099H	Atactic; broad dispersity (Mw/Mn > 1.2), Mn = 3002 × 10 ³ g/mol, Mw = 3620 × 10 ³ g/mol, PDI = 1.21	Polymer Source Inc., Montreal, Quebec, Canada
PS-P2270	Syndiotactic, Mv 250 × 10 ³ g/mol, Syndiotactic ≥ 90 %	Polymer Source Inc., Montreal, Quebec, Canada
PS-P938-SBdT	Ω-butadiene-terminated, Mn = 1796.7 × 10 ³ g/mol, PDI = 1.21	Polymer Source Inc., Montreal, Quebec, Canada
PS-P40567	α,ω-bis-hydrogen-terminated, Mn = 561 × 10 ³ g/mol, Mw = 592 × 10 ³ g/mol, PDI = 1.05	Polymer Source Inc., Montreal, Quebec, Canada

Mv (Viscosity Average Molecular Weight).

Mn (Number Average Molecular Weight).

Mw (Weight Average Molecular Weight).

PDI (The ratio Mw/Mn, known as the polydispersity index).

Table 2

The PS content (%) and standard deviation (SD) in the PS products calculated using 5-hexene-1,3,5-triyltribenzene (C₂₄H₂₄), the styrene trimer, with 2 polymer mixtures (PP, PE, PVC, PMMA, PET and PS-Cospheric, and PS-MERCK) and 10 individual PS standards. The PS content was expressed as a percentage of the product mass analysed.

Standard	EPS-1 ^a		EPS-2 ^b		EPS-3 ^c		HIPS-F ^d		HIPS-PF ^e		EPS BL-1 ^f		EPS WL-1 ^g		PS-CCP ^h		PS-Recycled ⁱ	
	PS content (%)	SD (n = 3)	PS content (%)	SD (n = 3)	PS content (%)	SD (n = 3)	PS content (%)	SD (n = 3)	PS content (%)	SD (n = 3)	PS content (%)	SD (n = 3)	PS content (%)	SD (n = 3)	PS content (%)	SD (n = 3)	PS content (%)	SD (n = 3)
Polymix A	1800	100	1600	130	2600	370	2000	50	2100	180	1800	80	2400	550	2200	320	1300	180
Polymix B	78	4	70	5	108	15	85	2	90	7	77	3	99	23	95	14	59	7
PS-Cospheric	1200	70	1000	80	1600	230	1300	30	1400	110	1100	50	1500	350	1400	200	900	110
PS-MERCK	99	6	89	7	143	20	108	2	119	10	97	4	132	30	123	18	74	10
PS-P4279	92	6	80	8	154	22	102	3	128	11	90	5	141	33	122	20	64	11
PS-P42569	97	6	86	8	154	22	107	3	128	11	95	5	141	33	126	20	70	11
PS-P4288A	88	5	79	6	122	17	96	2	102	8	87	4	112	26	107	15	67	8
PS-P5138	111	7	98	9	176	25	123	3	146	12	109	6	161	38	144	22	80	12
PS-P1099H	214	13	190	16	322	46	235	5	267	22	210	10	295	68	270	41	157	22
PS-P2270	119	7	107	8	162	23	129	3	135	11	117	5	149	34	144	20	90	11
PS-P938-SBdT	132	9	116	11	214	31	146	4	178	15	129	7	196	46	173	27	94	15
PS-P40567	116	8	102	9	183	26	128	3	152	13	113	6	168	39	150	23	83	13
Min	78		70		108		85		90		77		99		95		59	
Max	1800		1600		2600		2000		2100		1800		2400		2200		1300	

^a EPS-1: EPS foam packaging for a television box (2022).

^b EPS-2: EPS insulation foam from a house built in 2007.

^c EPS-3: EPS foam packing "peanuts" obtained from the laboratory used for packaging laboratory equipment (2022).

^d HIPS-F: Unprinted 3D HIPS filament was obtained from 123-3D.nl (Filament, neutral, 1.75 mm, HIPS 1 kg, Jupiter series) (2022).

^e HIPS-PF: Printed 3D HIPS filament (same as HIPS-F, printed using a Creality CR 10S 3D Printer with Micro Swiss All Metal Hotend Kit, nozzle temperature of 245 °C, and bed temperature of 75 °C).

^f EPS BL-1: EPS black, non-branded coffee lid from the coffee corner at VU Amsterdam (2022).

^g EPS WL-1: EPS white, non-branded coffee lid from the coffee bar in Amsterdam (2022).

^h PS-CCP: HIPS cell culture plate used for biochemical and molecular biology assays (Sarstedt, Germany).

ⁱ PS-Recycled: PS resin pellets from Galloo (Menen, Belgium).

internal standard (IS) to compensate for variations in instrument response.

2.3. Py-GC-MS analysis

Quantitative pyrolysis was performed using the Multi-Shot pyrolyzer fitted with an Auto-Shot Sampler (EGA/PY-3030D and AS-1020E, Frontier Laboratories, Saikon, Japan), according to the method previously described by Leslie et al. [5], with minor modifications. To briefly explain, double-shot analysis was performed through initial thermal desorption from 100 to 300 °C (at a heating rate of 50 °C/min) to remove volatile constituents, followed by pyrolysis for (18 s) at 600 °C. The pyrolysis products were transferred into a GC-MS (Agilent 6890 GC and 5975C MS, Santa Clara CA, USA); the inlet was set at 300 °C operated in split mode (1:10) with helium as carrier gas at a flow rate of 3 mL/min. Compound separation was performed on a 30 m DB-5HT column (0.25 mm I.D. × 0.25 µm df; Agilent Technologies, the Netherlands). The column oven program started at 40 °C and held for 2 min, and increased to 360 °C at a heating rate of 20 °C/min, where it was held for 1 min. The transfer line was kept at 300 °C. The MS was equipped with electron impact (EI) ionisation and data was collected in full scan mode from m/z 29 to 350. The data acquired through Chemstation software was converted and processed using MassHunter software. The internal standard was employed to normalise the instrument response, and used in the quantitation of the polymer content in the samples.

2.4. Quality control

For the quantitative analysis, we applied a systematic methodology for the identification of volatile pyrolysis products. Identification of the volatile pyrolysis products was confirmed when three distinct criteria were met: firstly, the analyte peaks profile ($S/N \geq 3$) from the quantifier ion fully overlap with the profile from the qualifier ions. Secondly, the ion ratios of 3 ions are within $\pm 30\%$ (relative). Lastly, the retention times do not differ by more than 0.1 min from the average of the calibration standards. 5-Hexene-1,3,5-triyltribenzene (trimer) was selected as quantitation analyte for PS. The retention times, and quantifier and qualifier ions for the major pyrolysis products are provided in Table S1. The limit of detection (LOD) was calculated as 3 times the standard deviation of the solvent blank ($n = 6$) and the limit of quantitation (LOQ) as 3.3 times the LOD. These were 30 and 99 ng, respectively. The PS content for the products was determined by dividing the calculated mass of PS by the total mass of the product analysed, expressed as a percentage. It is important to acknowledge that the PS content for each product was unknown. The accuracy of the PS standards was calculated by dividing the measured concentration by the theoretical concentration, expressed as a percentage.

3. Results and discussion

The initial calibration mixture was prepared by adding PP, PE, PVC, PET, PMMA, and the PS-Cospheric standard as PS reference material (Polymix A) as previously employed by Leslie et al. [5]. As indicated in Table 2, we noted a substantial overestimation in the PS content, ranging from 1300 % to 2600 %, when this polymer calibration mixture was used for sample analysis. Given the absence of any matrix in this evaluation, the expected PS content should not exceed 100 %. This implies that this calibration standard is not suitable to reliably quantify the PS content in the products analysed. This discrepancy might be due to differences in the type of PS standard used for quantitation compared to the types of PS that could be found in the products and consequently as MNPs. Based on the information of the supplier, the PS-Cospheric standard consists of microspheres fully crosslinked with divinylbenzene (DVB), and designed to be resistant to organic solvents and to withstand higher temperatures. We conclude that the standard might not be soluble in DCM, even under high pressure and temperature. While

polymer solubility was not within the scope of our investigation, we observed, through visual inspection that the standard did not dissolve in solvents like DCM, THF, toluene, chloroform, etc. All samples and standards were therefore prepared using the ASE method to ensure consistency in results.

Following this observation, a new calibration mixture was prepared by adding PP, PE, PVC, PET, PMMA, and the PS-MERCK standard (Table 1) as PS reference material (Polymix B). The PS-MERCK standard is 90 % isotactic ($M_w = 400 \times 10^3$ g/mol), and readily dissolves in dichloromethane (DCM). Using this calibration mixture, the estimated PS content for the nine products may be considered more realistic, with values ranging from 59 to 108 %. As these products might contain additives or fillers (not analysed in this study) and the purity is probably not 100 %, a slight underestimation of the quantification would be expected.

To further explore the impact of different individual PS standards, we acquired eight additional commercially available standards with different tacticity, polydispersity indices (PDI), endcapping, and molecular weights for quantifying the PS content in the products (Table 1). Calibration curves were prepared for each individual standard at five mass levels (0, 0.1, 0.5, 1.0, and 2.0 µg) and the PS content in the products was calculated for the nine products. As shown in Table 2, the calculated PS content for the PS products ranged from 64 to 322 %, depending on the PS standard used for quantitation. The quantitation of PS using PS-P4288 as the standard yields the lowest PS content for all the products, ranging from 67 % to 122 %. With the exception of the PS-Cospheric standard, the PS-P1099H standard showed a substantial overestimation of PS content for all the products, ranging between 157 and 322 %. As depicted in Table 1, both standards are atactic and n-butyl endcapped. From the supplier information, PS-P4288 exhibits a narrow dispersity (PDI = 1.03) and a weight-average molecular weight of 79×10^3 g/mol, while PS-P1099H demonstrates broader dispersity (PDI = 1.21) and a weight-average molecular weight of 3620×10^3 g/mol. A review of polymer dissolution previously reported that polymers with a broad molecular weight distribution (broad dispersity) will dissolve more rapidly compared to polymers with narrow molecular weight distribution (narrow dispersity) [20]. It was also previously shown that for broad dispersity PS, there can be selective dissolution, with lower molecular weight polymers tending to be more soluble than their high molecular weight analogues [21].

In an effort to assess how closely the measured values align with the expected or theoretical values and to provide an indication of accuracy, we quantified each calibration level of the ten individual PS standards using the polymer mixture containing PS-MERCK (Polymix B) as a reference. As shown in Table S2, the standard deviations for the individual standards across the mass range (0.1–2 µg) varied from 4 to 36 %. For most polystyrene (PS) standards, we observed a decline in the agreement between measured and expected values as the polymer amount of standard increased. This was also observed when the individual PS-MERCK standard was quantified using the polymer mixture. The largest effect was observed for PS-P1099H, the same standard that gave an overestimation for the PS-content in the nine PS-products. We also observed that PS-P4288A, the standard that gave the lowest PS content for the nine products, showed a consistent accuracy across the amount of sample analysed ($SD = 4\%$).

To evaluate the effect of sample quantity on the pyrolysis process of various PS standards, we corrected the areas obtained for each marker by the mass of the PS standard, from which we calculated the relative ratios of pyrolysis products. This was done for styrene (monomer), α -methylstyrene, 1,2-diphenylethane, propane-1,2-diyldibenzene, 3-butene-1,3-diyldibenzene (styrene dimer), 1-pentene-2,4-diyldibenzen, and 5-hexene-1,3,5-triyltribenzene (styrene trimer). As shown in Fig. S1, we not only observe a difference in the pyrolysis product ratios between the different standards, but also between the different sample amounts. The styrene monomer/dimer ratio and the monomer/trimer ratios are shown in Fig. S2. It has been reported that both sample size

and molecular characteristics influence the overall kinetic pyrolysis behaviour of polystyrene [9]. In a prior study using Py-GC-MS, Hancox et al. [22] examined the influence of sample size (amount) on monomer/dimer and monomer/trimer ratios. Although the type of PS was not specified, they similarly observed a substantial decrease in the monomer/dimer ratio with increasing sample size, accompanied by a modest reduction in the monomer/trimer ratio. They concluded that, under the specified conditions, dimers primarily originate from secondary reactions, and trimers, at least to some extent, also result from these conditions. It was recently proposed that the primary reaction pathway in the formation of styrene monomer involves end-chain β -scission, while mid-chain β -scission primarily contributes to the formation of the styrene dimer and trimer [11]. As depicted in Fig. S2, similar ratio profiles were observed for the high molecular weight standards (PS-MERCK and PS-P1099H), with higher monomer/dimer ratios. In a previous study by Kaal et al. [23] the influence of molecular weight on the pyrolysis process of narrow dispersity PS was assessed. Their findings demonstrated that molecular weight does not affect the pyrolysis process of narrow dispersity PS. A recent study, however, noted an increase in monomer-dimer formation in high molecular weight PS and found no significant difference in monomer-trimer formation compared to low molecular weight PS [8]. The narrow dispersity standards (PS-P4279, PS-P42569, and PS-P4288A) analysed in this study showed good similarity compared to the theoretical amounts added, regardless of the presence of end capping. The effect of sample amount on the monomer/dimer ratio and monomer/trimer ratio from polystyrene standard PS-MERCK as individual compound and in a polymer mixture with PMMA, PVC, PE, PP, and PET (Polymix B) are shown in Fig. 1. From this result it can be suggested that the polymer mixture may affect the pyrolysis of PS, potentially resulting in a reduced formation of the monomer (compared to the individual standard) and an increased formation of the dimer and trimer. Bate & Lehrle [14], previously found that by analysing a mixture of PS and PMMA (at 500 °C and amounts more than 2.5 μg), the thermal degradation behaviour of the corresponding polymers was modified, resulting in less formation of the monomers compared to the individual standards. In this study, pyrolysis was employed at a temperature of 600 °C, as done earlier by Leslie et al. [5]. It could be that this temperature is not the optimal temperature to produce the dimer and trimer, and as such the higher temperature affects lower amounts of PS resulting in increased monomer/dimer and monomer/trimer ratios. These findings highlight the critical importance of selecting a suitable polystyrene (PS) reference material as a calibrant, along with choosing an appropriate quantity of the sample. Both factors significantly influence the accuracy and outcomes of analytical

measurements using Py-GC-MS.

4. Conclusions

The over- or underestimation of the true amounts may occur when there is insufficient similarity between the polymer characteristics of the standard used for calibration and the polymer particles in the sample. Due to the lack of a priori knowledge on these polymer characteristics of particles present in the sample, data should be interpreted with some caution. In our previous work on human blood, it is possible that the PS levels were overestimated, although this is not certain as we have no information on the characteristics of the polystyrene particles in the blood samples.

These considerations on the choice of the appropriate reference material and the suitable quantity is equally relevant for other polymers, such as PE, which encompasses various grades like low-density PE (LDPE), high-density PE (HDPE), linear low-density PE (LLDPE), and ultra-high-molecular-weight PE (UHMWPE) (Dyneema PE). In addition, PE might also contain varying percentages of fillers and additives. Similarly, for polypropylene (PP), the tacticity is a crucial factor, and in the case of impact-PP used in applications like car bumpers, the material contains additional rubbery domains.

Our findings emphasize that for the future of quantitative analysis of MNPs in various matrices using Py-GC-MS, the selection of appropriate reference materials as standards is crucial to provide coherent data while, at the same time, allowing for the comparison of results between methods and laboratories.

CRediT authorship contribution statement

M. Brits: Writing – original draft, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **B. van Poelgeest:** Writing – review & editing, Validation, Investigation, Formal analysis, Data curation. **W. Nijenhuis:** Writing – review & editing, Validation, Investigation, Data curation. **M.J.M. van Velzen:** Writing – review & editing, Methodology. **F.M. Béen:** Writing – review & editing, Conceptualization. **G.J.M. Gruter:** Writing – review & editing, Supervision, Conceptualization. **S.H. Brandsma:** Conceptualization, writing – review & editing. **M.H. Lamoree:** Writing – review & editing, Supervision, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial

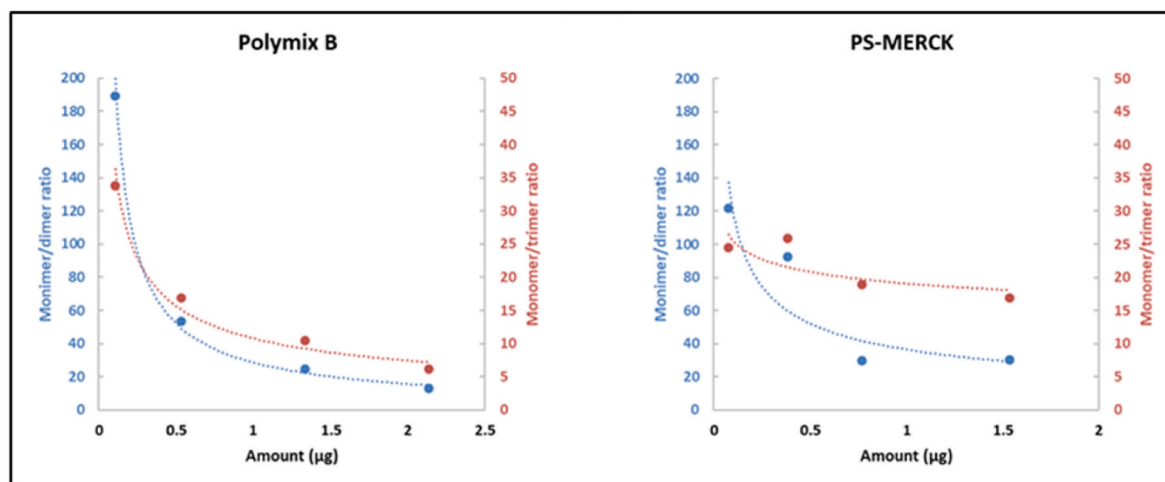


Fig. 1. Sample amount dependence of the monomer/dimer ratio (blue) and monomer/trimer ratio (red) from polystyrene (PS-MERCK) in a mixture and individual. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

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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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.polymertesting.2024.108511>.

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