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Journal of Chromatography A, 976 (2002) 145–154

JOURNAL OF CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Characterization of poly(butylene terephthalate) by size-exclusion chromatography and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry

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Abstract

Poly(butylene terephthalate) (PBT) samples have been analyzed with size-exclusion chromatography (SEC) using a mixed solvent of 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) and chloroform as the mobile phase. Several matrices and different sample deposition methods have been investigated to analyze PBT with matrix-assisted laser desorption/ionization (MALDI) time-of-flight (TOF) mass spectrometry (MS). Optimum results have been acquired by depositing PBT on top of a 2,4,6-trihydroxyacetophenone matrix. The found MALDI-TOF-MS method can be used to analyze the end group functionalities of PBT, as demonstrated with the samples at hand. By combining SEC (off-line) with MALDI-TOF-MS, absolute molecular masses of PBT can be measured, and these have been found to be considerably lower than those determined with SEC using polystyrene standards.

Keywords: Poly(butylene terephthalate)

1. Introduction

Poly(butylene terephthalate) (PBT) is a polymer that is produced on a large industrial scale. It is synthesized by numerous firms worldwide and is sold at a rate of hundreds of thousands of tons per year. Its outstanding properties are reflected by its wide use in fibers, films and extruded and injection molded applications [1–3]. Unfortunately, the molecular characterization of PBT is seriously hindered by its poor solubility in commonly used organic solvents, such as toluene, chloroform, tetrahydrofuran (THF), alcohols, etc.

Size-exclusion chromatography (SEC) is a fast and widely accepted method for determining the molecular mass (distribution) of polymeric samples. Only limited uses of this method for the analysis of PBT can be found in the literature [4,5]. Comparatively more SEC data have been reported on a similar aromatic-aliphatic polyester, poly(ethylene terephthalate) (PET) [6–12], and these may be of value with respect to the analysis of PBT. *m*-Cresol is frequently applied in the SEC of PET [6,7], but the use of this eluent implies that the column must be operated at elevated temperatures, as *m*-cresol has a

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0021-9673/02/$ – see front matter
PII: S0021-9673(02)01149-4

too high viscosity at room temperature (high column temperatures are unwanted as these may result in polymer degradation). Several mixed solvent systems including nitrobenzene–tetrachloroethane [8], phenol–tetrachlororethane [11], and *o*-chlorophenol–chloroform [12], have been reported in the room temperature SEC of PET, but extended heating is still required to dissolve the polymer. Another essential disadvantage associated with the mentioned eluents is their UV absorption, prohibiting the use of sensitive UV detectors. 1,1,1,3,3,3-Hexafluoroisopropanol (HFIP) can dissolve PBT and PET at room temperature and has been used for their SEC analysis [13,14], but unfortunately the routine application of HFIP as eluent is significantly restricted by its high cost, toxicity, and partial incompatibility with normal SEC packings [6,15,16]. Weisskopf [17] has described that diluting HFIP in chloroform at low HFIP levels (2%) is a good and reliable alternative mobile phase for PET. Using this mixed solvent, the SEC separation of PET can be performed at room temperature, the SEC column is stable over a long time, and a sensitive UV detector can be employed. So far, no application of the HFIP–chloroform mixed solvent in the SEC of PBT has yet been reported.

In SEC, molecular mass calibration is usually a tedious and/or error prone process. When standards of one polymer—typically polystyrene (PS)—are used to characterize polymers of a different type, large errors in the estimated (relative) molecular mass can be the result. Absolute calibration methods are therefore in demand. This can be carried out by combining a concentration-sensitive detector (e.g. refractive index or UV–Vis) with molecular-mass-sensitive detector(s) (e.g. light scattering (LS) and/or viscometer) on the condition that dn/dc values (for LS) and Mark–Houwink constants (for viscometer) of the given polymer system are known. Unfortunately, the sources of these data are scarce, and both LS and viscometer are only sensitive to high-molecular-mass molecules.

First developed by Karas and Hillenkamp [18], matrix-assisted laser desorption/ionization (MALDI) time-of-flight (TOF) mass spectrometry (MS) is an established technique in polymer characterization; information on the molecular structure of polymers can be deduced from the repeating unit mass and the end group mass. In addition, molecular mass values for low dispersity samples can also be determined by MALDI-TOF-MS. For high dispersity polymer samples, however, MALDI-TOF-MS alone cannot provide accurate mass results due to differences in ionization probability and detection sensitivity of molecules with different masses [19]. Despite the wide application of MALDI-TOF-MS in polymer analysis, no reports on the characterization of PBT have been published so far.

Although SEC or MALDI-TOF-MS can be used discretely to characterize polymer samples, their combination would be more powerful and would overcome most of the problems that are associated with the two characterization methods when applied separately [19–25]. In SEC–MALDI-TOF-MS, a high polydisperse PBT sample is first separated into low polydisperse fractions by SEC, and each fraction is consecutively analyzed by MALDI-TOF-MS. The acquired mass data on the fractions can then be used to construct an absolute SEC calibration curve. Molecular mass values are thus only derived from the PBT sample under investigation.

In this contribution, we introduce the use of the HFIP–chloroform mixed solvent as the mobile phase in the SEC analysis of PBT. Furthermore, we present a method for the analysis of PBT by MALDI-TOF-MS; the usefulness of several matrices and different sample deposition procedures has been investigated and results—including the end group analysis of PBT samples—are discussed. Finally, combination of SEC (off line) and MALDI-TOF-MS has allowed for a comparison between molecular mass (distribution) data (i) based on PS standards and (ii) based on absolute MALDI-TOF-MS calibration.

2. Experimental

The investigated PBT samples and some of their properties are listed in Table 1. PBT-A is a low-molecular-mass sample; the other, higher-molecular-mass, PBT samples are commercial products from different manufacturers. PBT-A was prepared by melt transesterfication and subsequent polycondensation of dimethyl terephthalate with a 1.3-fold molar excess of 1,4-butanediol using tetrabutyl titanate as the catalyst. The transesterfication was carried out at a temperature between 100 and 150 °C, and the

Table 1
Viscosity and end group titration data on various PBT samples

Name	Intrinsic viscosity (ml/g)	–OH (mmol/kg)	–COOH (mmol/kg)
PBT-A	7.8	1500	80
PBT-B	47.4	157	33
PBT-C	69.0	67	41
PBT-D	90.1	55	18
PBT-E	73.9	47	30
PBT-F	68.3	49	49

polycondensation was performed by increasing the temperature further to 250 °C. Deep vacuum was not applied in order to obtain a low-molecular-mass polymer. PBT-A was acquired as flakes and was analyzed without further modification. The intrinsic viscosities shown in Table 1 were measured in *m*-cresol at 25.0±0.05 °C with an Ubelohde viscometer using a viscotimer. The amount of hydroxyl end-groups was determined by esterification of the PBT polymers with anthracenoylchloride at 25 °C in HFIP using pyridine as the base, followed by high-performance liquid chromatography (HPLC) analysis using UV detection and applying anthracenoylhexanoate as the internal standard. The amount of carboxylic end-groups was analyzed by dissolving the sample in *o*-cresol, dilution with chloroform and photometrical titration with a standard solution of potassium hydroxide in ethanol using bromocresol green as the indicator.

Narrow polystyrene standards were obtained from Polymer Labs (Amherst, MA, USA). The MALDI-TOF-MS matrices, α-cyano-4-hydroxycinnamic acid (CHCA), 2,5-dihydroxybenzoic acid (DHB), dithranol, norharmane, 2-(4-hydroxyphenylazo)benzoic acid (HABA) and 2,4,6-trihydroxyacetonphenone (THAP), were purchased from Aldrich (Milwaukee, WI, USA). Chloroform and THF (both from Biosolve, Valkenswaard, Netherlands) were solvents of HPLC grade and were used without further purification. The sample solutions were prepared by dissolving the polymers in pure HFIP (from Fluka, Zwijndrecht, The Netherlands), followed by dilution with chloroform to reach the required HFIP concentration of 2 or 5% (both v/v).

Two SEC columns from Polymer Labs, mixed-E (300×7.5 mm I.D., 3 μm particles, linear molecular mass range up to 30 000) and minimixed-C (250×4.6 mm I.D., 5 μm particles, linear molecular mass range 200–2 000 000), were employed for the SEC separations. PBT-A was separated with the mixed-E column at a mobile phase flow-rate of 1 ml/min, while the other samples were analyzed using the minimixed-C column at a flow-rate of 0.3 ml/min. The mobile phase was delivered by an LC-10 AT pump (Shimadzu, Kyoto, Japan). Samples were injected with a Midas autosampler (Spark Holland, Emmen, Netherlands) and detected with a UV–Vis detector (SPD-10AV vp, Shimadzu) operated at 254 nm. The chromatographic data were collected and calculated using DAX software (PP van Mierlo, Eindhoven, Netherlands).

The MALDI-TOF-MS measurements were performed with a Voyager-DE Pro instrument (PerSeptive Biosystems, Framingham, MA, USA) equipped with a 337-nm nitrogen laser, capable of executing both linear and reflector modes. Spectra were acquired by summing spectra from 200 laser shots. Unless noted otherwise, the matrices were dissolved in THF at a concentration of ~20 mg/ml; the polymers were dissolved in 2% HFIP in chloroform. The MALDI-TOF-MS spots were prepared by either depositing a mixed solution of PBT and matrix, or usually, by consecutively depositing PBT and matrix, one on top of the other, using a two-step sample deposition procedure. In the two-step procedures, one solution (of either PBT or matrix) was first spotted onto the target plate and air dried, before the second solution was loaded. Good quality spectra could only be obtained by applying matrix first followed by the PBT solution.

In the combined SEC (off-line)–MALDI-TOF-MS experiments, the chromatographic peaks of the polymers were divided into nine parts of 20 s [20]. The corresponding fractions were concentrated, and then pipetted on top of the THAP matrix that had already been spotted on the plate (two-step sample deposi-

tion procedure). The MALDI-TOF-MS measurements were carried out in the linear mode with delayed extraction.

3. Results and discussion

3.1. SEC measurements on PBT using HFIP–chloroform as eluent

PBT is insoluble in pure chloroform, but it becomes soluble in chloroform with just a few percent of added HFIP. Six PBT samples (PBT-A–PBT-F) have been analyzed using the mixed HFIP–chloroform eluent at two different HFIP concentrations of 2 and 5% (v/v). On the mixed-E column, the oligomers in PBT-A can be separated quite well, as can be seen in Fig. 1. The SEC chromatograms of the five other samples are quite similar to each other; illustrative chromatograms of PBT-C are displayed in Fig. 2.

SEC requires calibration for the calculation of molecular masses and molecular mass distributions. Narrow PS standards are widely used for this purpose, giving molecular masses relative to these

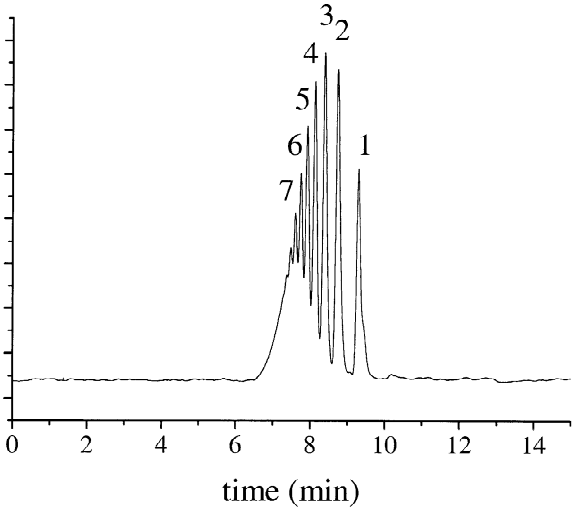


Fig. 1. SEC chromatogram of the low-molecular-mass PBT-A sample. Oligomer structure: H–[O–$(CH_2)_4$–OOC–C_6H_4CO]$_n$–O$(CH_2)_4$OH. Conditions: mixed-E column (300×7.5 mm I.D., 3 μm particles), 2% (v/v) HFIP in $CHCl_3$ mobile phase, flow of 1 ml/min, UV detection at 254 nm.

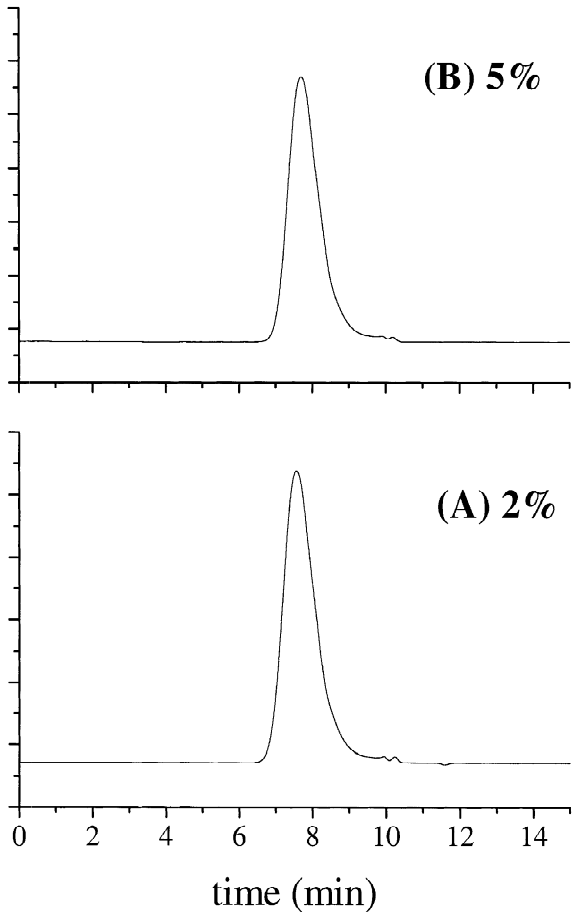


Fig. 2. SEC chromatogram of the PBT-C sample; mobile phases of (A) 2% (v/v) HFIP in $CHCl_3$, and (B) 5% (v/v) HFIP in $CHCl_3$. Conditions: minimixed-C column (250×4.6 mm I.D., 5 μm particles), flow of 0.3 ml/min, UV detection at 254 nm.

standards. Fortunately, PS standards are soluble in the mixed solvent of HFIP and chloroform and can thus be employed for calibration. In pure HFIP, PS standards cannot be used. Hence, HFIP soluble standards like poly(methyl methacrylate) (PMMA) should be applied [6,17]. The molecular mass data based on PS calibration standards are listed in Table 2. It can be seen from this table that the chromatography results at a 2% HFIP level agree reasonably well with those at a 5% level, especially when it is considered that the used minimixed-C column has a quite broad molecular mass operating domain (see Experimental section). We have chosen the lower

Table 2
Molecular mass (distribution) data of poly(butylene terephthalate) (PBT) samples determined by SEC using PS standards[a]

	2% (v/v) HFIP			5% (v/v) HFIP		
	M_p[b]	M_n[c]	PD[d]	M_p[b]	M_n[c]	PD[d]
PBT-B	41 100	14 300	2.7	38 300	15 000	2.3
PBT-C	62 200	20 600	3.0	53 200	21 100	2.5
PBT-D	91 100	22 900	4.1	74 500	26 700	2.8
PBT-E	62 600	19 300	3.2	64 800	23 400	2.8
PBT-F	46 500	13 100	3.3	51 600	19 300	2.8

Two 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) concentrations in chloroform are used.

[a] SEC conditions: column minimixed-C (250×4.6 mm I.D., 5 μm particles), mobile phase flow at 0.3 ml/min, UV detection at 254 nm.

[b] M_p, molecular mass at chromatography peak top.

[c] M_n, number-average molecular mass.

[d] PD, polydispersity, equals M_w (weight-average molecular mass) divided by M_n.

level of 2% (v/v) HFIP in chloroform for the combined SEC–MALDI-TOF-MS experiments (vide infra).

3.2. MALDI-TOF-MS measurements on PBT

The key step in MALDI-TOF-MS is to find a suitable matrix for the polymer under investigation. Six matrices (CHCA, DHB, dithranol, norharmane, HABA and THAP) have been tried to analyze PBT. A difficulty in these experiments is that different solvents must be used for the PBT sample on the one hand and for the matrix on the other. PBT can be dissolved in HFIP or in a mixed solvent of HFIP and $CHCl_3$, whereas all matrices are easily soluble in THF. Only dithranol can be dissolved in $CHCl_3$, and HABA in HFIP. Unfortunately, neither dithranol nor HABA are suitable matrices for PBT. Using the other matrices, only low-molecular-mass oligomer ions are observed if a mixed solution of matrix (in THF) and PBT (in 2% HFIP in $CHCl_3$) is deposited onto the MALDI-TOF-MS plate (see Fig. 3A for an example). Possibly, the incompatibility between solvents for PBT and matrix results in phase separated PBT as opposed to embedded PBT molecules. Much better results are obtained by using a two-step sample deposition procedure, which is carried out by first depositing the THF solution of the matrix onto the plate, followed by loading the chloroform–HFIP solution of the sample on top of the dried matrix. First depositing the sample and then the matrix has also been tried, but this yields unsatisfactory spectra. Of all the matrices tested, THAP gives the best results, and therefore all following MALDI-TOF-MS data were acquired by using the two-step sample

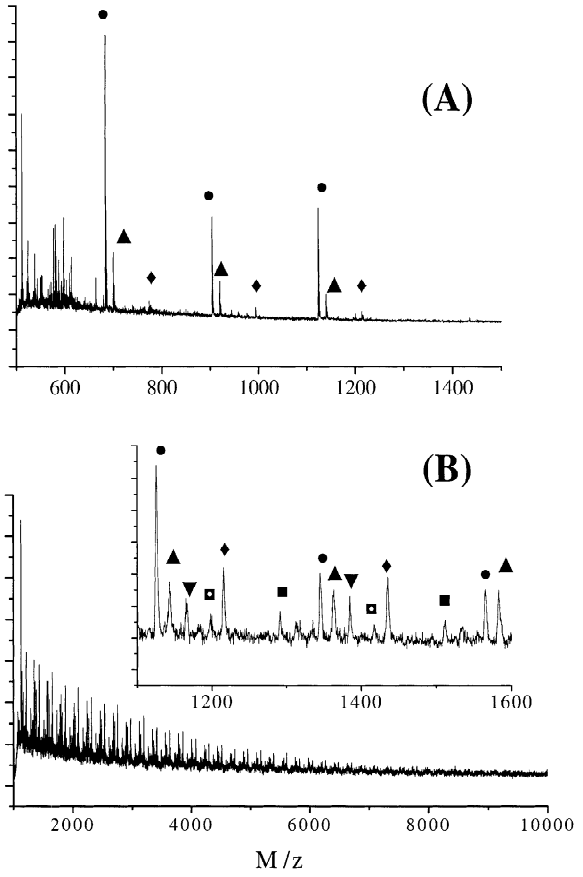


Fig. 3. MALDI-TOF-MS spectra of PBT-C using 2,4,6-trihydroxyacetophenone (THAP) as the matrix. MALDI-TOF-MS conditions: Voyager-DE with a 337-nm nitrogen laser, linear mode; PBT dissolved in 2% (v/v) HFIP in $CHCl_3$ and matrix in tetrahydrofuran; the spot prepared by (A) depositing a mixed solution of PBT and matrix, and (B) a two-step deposition procedure of spotting PBT on top of the matrix. Marked mass peaks are Na^+-adducts of: ● cyclic PBT, or $HOOC–C_6H_4CO–[O–(CH_2)_4–OOC–C_6H_4CO]_n–O–(CH_2)_2CH{=}CH_2$; ▲ $H–[O–(CH_2)_4–OOC–C_6H_4CO]_n–OH$; ▼ $H–[O–(CH_2)_4–OOC–C_6H_4CO]_n–ONa$; ◘ $H–[O–(CH_2)_4–OOC–C_6H_4CO]_n–O–(CH_2)_2CH{=}CH_2$; ♦ $H–[O–(CH_2)_4–OOC–C_6H_4CO]_n–O(CH_2)_4OH$; and ■ $HOOC–C_6H_4CO–[O–(CH_2)_4–OOC–C_6H_4CO]_n–OH$.

deposition protocol in which PBT was spotted on top of a THAP matrix. A typical result displayed in Fig. 3B shows a MALDI-TOF-MS spectrum of PBT-C. Compared to Fig. 3A, PBT molecules with much higher masses can clearly be detected. Except for PBT-A, which mainly contains oligomers of low molecular mass, MS spectra similar to that shown in Fig. 3B have been recorded for the other PBT samples.

The spectrum in Fig. 3B shows repeating clusters with a period of 220 (the molecular mass of the monomeric unit). Different peaks in one cluster correspond to molecules with different end-group functionalities. We have assigned these end groups and results are shown in Fig. 3B and in Table 3. From the PBT polymer structure it is easy to understand that a linear PBT molecule can be capped with an alcohol, a carboxylic acid or a vinyl end-group (the latter originates from elimination of water). Cyclic molecules without end groups are also possible, but these can not be distinguished from linear PBT molecules with a vinyl and a carboxylic acid end group, as they have the same molecular mass. All identified peaks are sodium adducts. Even double sodium adduct ions with masses of $m/z = 23 + 220n + 40$ are detected; these adducts may have been originally present in the sample, or may have been formed in the laser desorption process through the reaction of a –COOH group with a ubiquitous sodium impurity.

We have not extensively tried to quantitatively analyze the gathered data on the end group functionalities, since the relative intensities of peaks within one cluster (i) are not reproducible due to the inhomogeneity of the sample spot, (ii) depend on the chosen cluster and (iii) may be of different sensitivity for molecules with different functionality. In future, if more control over MALDI-TOF-MS measurements becomes possible, quantitative analyses of end groups may be feasible, so that MALDI-TOF-MS could then be used instead of tedious end group titrations.

The determination of absolute average molecular masses and molecular mass distributions of the PBT samples cannot be based on MALDI-TOF-MS measurements on crude PBT samples, because the polydispersity of these samples is too high. The combination of SEC with MALDI-TOF-MS is required for such determinations.

3.3. The analysis of PBT by combination of SEC (off line) and MALDI-TOF-MS

The low-molecular-mass sample PBT-A has been separated into its pure oligomer components by SEC and, consecutively, the collected fractions have been analyzed with MALDI-TOF-MS, revealing that the oligomers have the structure H–[O–$(CH_2)_4$–OOC–$C_6H_4CO]_n$–O$(CH_2)_4$OH. Table 4 compares the actually measured molecular masses of the oligomers as obtained by MALDI-TOF-MS to those determined by solely using SEC and PS calibration standards. A significant positive deviation from the absolute mass values is observed when SEC with polystyrene calibration is used, indicating that PBT has a more rigid conformation in 2% (v/v) HFIP in $CHCl_3$ than polystyrene. It is interesting to note that the relative deviation increases considerably with increasing oligomer size.

Table 3
End-group analysis of PBT-C by MALDI-TOF-MS (Fig. 3B)

General structure: X–[O–$(CH_2)_4$–OOC–$C_6H_4CO]_n$–Y		
$[Na+M]^+$ ion at m/z	X	Y
$23+220n$	Cyclic	Cyclic
	–OC–C_6H_4COOH	–O$(CH_2)_2$–CH=CH_2
$23+220n+18$	–H	–OH
$23+220n+40$	–H	–ONa
$23+220n+72$	–H	–O$(CH_2)_2$–CH=CH_2
$23+220n+90$	–H	–O–$(CH_2)_4$–OH
$23+220n+166$	–OC–C_6H_4COOH	OH

Table 4
PBT oligomer masses determined by MALDI-TOF-MS (absolute values) compared to those obtained by SEC using polystyrene standards (relative values)

n[a]	1	2	3	4	5	6	7
MALDI-TOF-MS[a]	310	530	750	970	1190	1410	1630
SEC[b,c]	410	810	1250	1720	2210	2720	3250

[a] Oligomer structure: H–[O–$(CH_2)_4$–OOC–C_6H_4CO]$_n$–O$(CH_2)_4$OH (Fig. 1).
[b] Values at peak top, M_p.
[c] SEC conditions: column mixed-E (300×7.5 mm I.D., 3 μm particles), mobile phase 2% (v/v) HFIP in $CHCl_3$, flow of 1 ml/min, UV detection at 254 nm.

Analogous to sample PBT-A, the polydisperse samples PBT-B, PBT-C and PBT-D have been fractionated by SEC and thereafter analyzed by MALDI-TOF-MS. As an example, Fig. 4 shows the MALDI-TOF-MS spectra of three SEC fractions of PBT-C. Under the applied experimental conditions, the polydispersity of the individual SEC fractions as measured by MALDI-TOF-MS is ~1.08, a figure that allows for an accurate determination of the average molecular mass [19,23,26]. By using these values to construct an SEC calibration line (Fig. 5), absolute molecular masses based on PBT itself can be acquired.

Unfortunately, only SEC fractions with molecular masses below 10 000 can be analyzed properly with MALDI-TOF-MS. This limitation may be related to (i) the incompatibility of the solvents for PBT on one hand and matrix on the other, leading to PBT molecules—especially those of higher molecular mass—that are not well-embedded into the matrix and to (ii) the low PBT concentrations in the matrix (the PBT amount collected after fractionation is quite small). Despite the fact that only PBT of molecular masses below 10 000 can be measured with MALDI-TOF-MS, linear extrapolation of the absolute calibration curve is reasonable, because minimixed-C columns have a wide linear range up to MW $2\cdot10^{-6}$ (based on polystyrene) [27].

Table 5 lists the molecular mass data of the PBT samples as measured by SEC based on polystyrene calibration standards and MALDI-TOF-MS calibration. For comparison, the number-average molecular masses as determined by titration are also included. Titration gives the number of –OH and –COOH end groups in a certain amount of PBT polymer sample, and the number-average molecular mass (M_n) of the PBT can be calculated from these values by the formula,

$$M_n = \frac{2000}{\sum C_i} \quad (1)$$

where ΣC_i is the total mole amount of end group in 1 kg of polymer (mol/kg). For the values shown in Table 5 it is assumed that the PBT molecules are all linear and only contain –OH and –COOH end groups. From the MALDI-TOF-MS results presented in the previous section, it is obvious that this assumption is not correct, so that the M_n values determined via titration data (given in Table 1) and Eq. (1) are overrated to a certain extent.

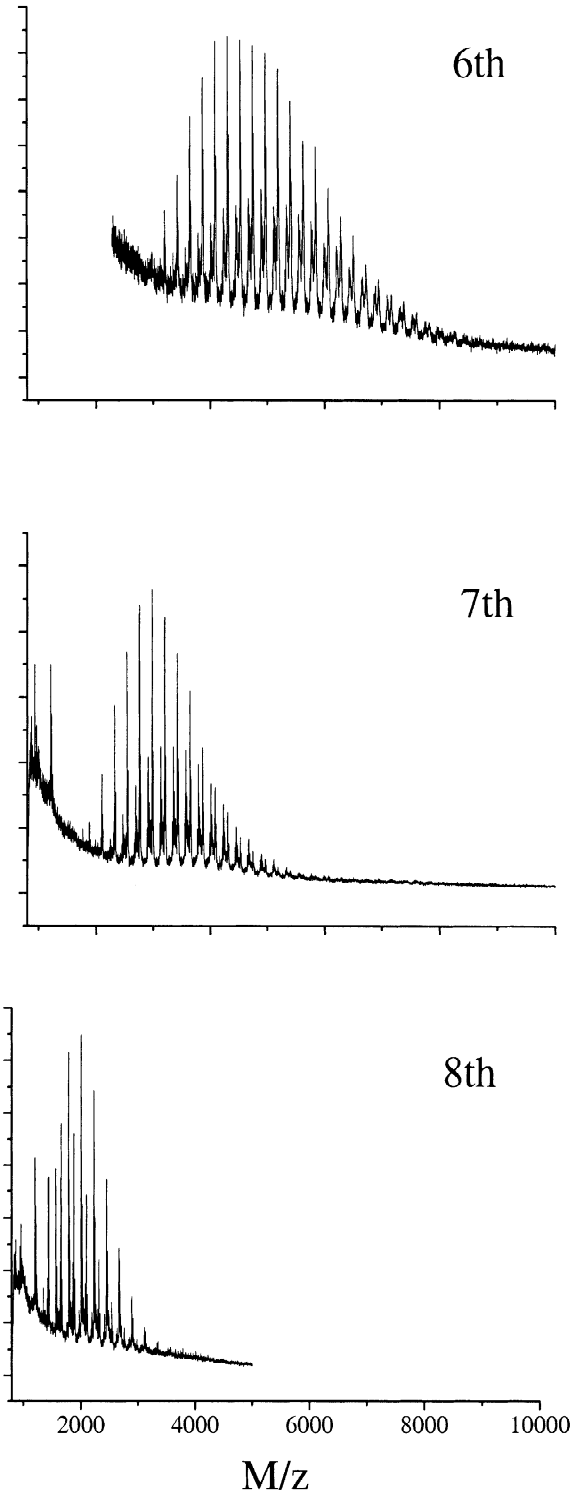
Similar to what has already been seen for the oligomers (Table 4), relative calibration with polystyrene standards leads to an overrated molecular mass. When the M_p values in Tables 4 and 5 are compared, it is clear that considerably higher deviations are found for the polymers than for the oligomers. Additionally, one sees that the polydispersity values based on relative and absolute calibration differ greatly. The following reasoning will explain these observations.

In the SEC of PBT or PS samples the relation between molecular mass and elution volume can be described by the following equations,

$$\text{Log } M_{\text{PBT}} = A_{\text{PBT}} - B_{\text{PBT}}V \quad (2)$$

$$\text{Log } M_{\text{PS}} = A_{\text{PS}} - B_{\text{PS}}V \quad (3)$$

where M_{PBT} and M_{PS} are the molecular masses corresponding to an elution volume V, and A_{PBT}, B_{PBT}, A_{PS} and B_{PS} are system constants related to PBT or PS. If, for example, polystyrene standards



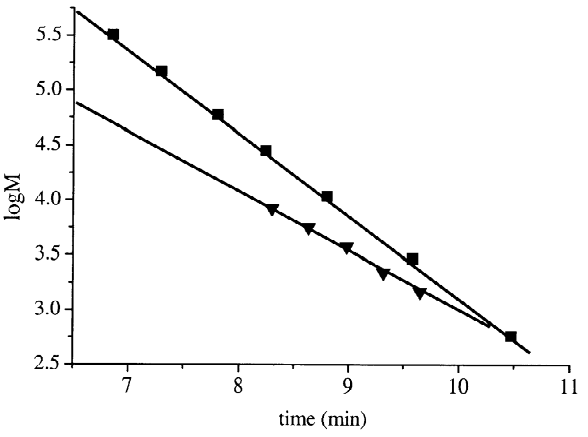


Fig. 5. SEC calibration curves based on polystyrene standards and on PBT standards: ■ calibration curve based on polystyrene standards; and ▲ calibration curve based on SEC–MALDI-TOF-MS data of PBT-C.

are used for calibration, the molecular mass of a PBT sample can be calculated by assuming,

$$\text{Log } M_{\text{PBT}} = \log M_{\text{PS}} = A_{\text{PS}} - B_{\text{PS}}V \quad (4)$$

(it is assumed that PBT and PS have similar hydrodynamic volumes at similar molecular masses). However, PBT has a more rigid molecular structure than PS, so that the A_{PBT} and B_{PBT} values are considerably lower than their corresponding A_{PS} and B_{PS} values. Therefore, deviations will occur in the calibration of PBT samples using PS standards. The extent of this deviation can be estimated by combining Eqs. (2), (3), (6) and (7):

$$\frac{M_{\text{PS}}}{M_{\text{PBT}}} = 10^{A_{\text{PS}} - A_{\text{PBT}}} \cdot 10^{-(B_{\text{PS}} - B_{\text{PBT}})V} \quad (5)$$

$$A_{\text{PS}} > A_{\text{PBT}} \quad (6)$$

$$B_{\text{PS}} > B_{\text{PBT}} \quad (7)$$

Clearly from Eq. (5), $M_{\text{PS}}/M_{\text{PBT}}$ is an exponential

Fig. 4. MALDI-TOF-MS spectra of PBT-C SEC fractions six to eight. SEC conditions: column minimixed-C (250×4.6 mm I.D., 5 μm particles), mobile phase 2% (v/v) HFIP in $CHCl_3$ at a flow of 0.3 ml/min. MALDI-TOF-MS conditions: Voyager-DE with a 337-nm nitrogen laser, linear mode; spot prepared by a two-step deposition procedure in which PBT is loaded on top of the THAP matrix.

Table 5
Molecular mass (distribution) data obtained by SEC using polystyrene calibration standards compared to those obtained with MALDI-TOF-MS calibration[a]

	SEC–polystyrene (relative)			SEC–MALDI-TOF-MS (absolute)			Titration[b]
	M_p[c]	M_n[d]	PD[e]	M_p[c]	M_n[d]	PD[e]	M_n[d]
PBT-B	41 100	14 300	2.7	12 400	6600	1.7	10 500
PBT-C	62 200	20 600	3.0	18 500	9000	1.9	18 500
PBT-D	91 100	22 900	4.1	23 000	11 500	1.9	27 400

Molecular masses derived from end group titration data are also included.

[a] SEC conditions: column minimixed-C (250×4.6 mm I.D., 5 μm particles), mobile phase 2% (v%) HFIP in $CHCl_3$ at 0.3 ml/min, UV detection at 254 nm. MALDI-TOF-MS conditions: Voyager-DE with a 337-nm nitrogen laser, linear mode; spot prepared by a two-step deposition procedure of loading PBT on top of the THAP matrix.

[b] Assuming PBT samples only have –OH and –COOH end groups (Table 1).

[c] M_p, molecular mass at chromatography peak top.

[d] M_n, number-average molecular mass.

[e] PD, polydispersity, equals M_w (weight-average molecular mass) divided by M_n.

function of V, and much greater deviations can be expected at lower elution volumes (for high-molecular-mass molecules). Because M_w is averaging the molecular masses at a power of two, the deviation for M_w is more pronounced than that for M_n. Therefore, if SEC analysis of PBT is based on polystyrene, not only the number-average molecular masses, but also the polydispersity values will be overestimated. The absolute calibration data provided by the combined SEC–MALDI-TOF-MS measurements show how big this overestimation actually is.

4. Conclusions

In this paper we report on methods that can be used to analyze poly(butylene terephthalate) with SEC, MALDI-TOF-MS and combined SEC–MALDI-TOF-MS. Qualitative end-group analyses of PBT have become accessible, and truly quantitative molecular masses and molecular mass distributions of PBT can be determined with the presented methods. The applicability of this work may extend to polymers similar to PBT, such as PET and co-polymers of PBT or PET.

Acknowledgements

The authors acknowledge fruitful discussions with many colleagues at DSM Research in Geleen and at the Eindhoven University of Technology. We are also grateful to the referee for his critical comments.

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