# Structure Elucidation of Linear Polyesters via MALDI/ToF-Mass Spectrometry

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## Introduction

Due to their versatility, polyesters are popular in different industrial applications such as bottles, fibers, and binders. To understand the influence of molecular structures on crucial properties, several analytical methods are available. Besides the quantification of functional groups via titration, the determination of molar mass by gel permeation chromatography (GPC) belongs to conventionally applied analyses. Combining both the characterization of functional groups and molar mass distribution, MALDI/ToF-mass spectrometry (MS) reveals to be a powerful tool which shall be compared with conventional methods.

**Table 1:** Overview of results for PES-COOH comparing titration, GPC, and MALDI/ToF-MS. MALDI/ToF-MS combines information of terminating groups, mass distribution with $M_n$ and $M_w$, as well as further structure elucidation.

| PES-COOH | Titration | GPC | MALDI/ToF-MS |
|---|---|---|---|
| *n* (COOH) / mmol | 0.50 | - | 0.58 |
| *x* (COOH) / mol% | 91 | - | 94 |
| *n* (OH) / mmol | 0.05 | - | 0.04 |
| *x* (OH) / mol% | 9 | - | 6 |
| $M_n$ / g mol$^{-1}$ | 3 620 | 3 230 | 3 260 |
| $M_w$ / g mol$^{-1}$ | - | 7 230 | 4 230 |
| further information | - | mass distribution | mass distribution<br>structure elucidation |

## Experimental and Results

For the comparison of the analytical methods mentioned above, different polyesters (PES) were synthesized using isophthalic acid and neopentyl glycol as monomers (Fig. 1). For carboxyl terminated PES-COOH the acid component was used in excess, PES-OH was synthesized with an excess of neopentyl glycol.

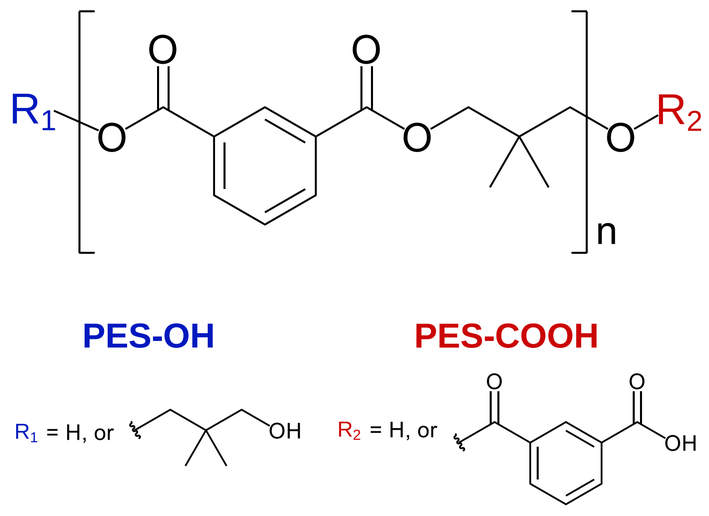


**Figure 1:** Structure of linear polyesters from isophthalic acid and neopentyl glycol. Excess of one component leads to different functionalization on $R_1$ and $R_2$.

**Titration** methods for determination of acid and hydroxyl value additionally allowed the calculation of the number average molar mass ($M_n$). Further information of the molar mass can be obtained by **GPC** (Fig. 2). Results of both methods are summarized in Table 1. Inaccuracies are assumed in both methods, especially determination of hydroxyl values showed poor reproducibility.

**MALDI/ToF-mass spectra** are shown in Fig. 3. The recorded *m*/*z* region up to 10 000 revealed similar distributions for PES-OH and PES-COOH. A detail of the spectra is interpreted in Fig. 4. Interestingly, MALDI/ToF-MS not only revealed combinations of COOH- and OH-terminating groups, but also the formation of cyclic polyesters with masses of up to 2 000 to 3 000 g mol$^{-1}$.

Peak integration gave mass distributions of the individual series as can be seen in Fig. 5. Obtained peak areas were used for calculation of end group ratio as well as $M_n$ and $M_w$. The low value for $M_w$ can be explained by the limited mass range of the MALDI/ToF-MS measurement.

Results of presented characterization methods for PES-COOH are summarized in Table 1.

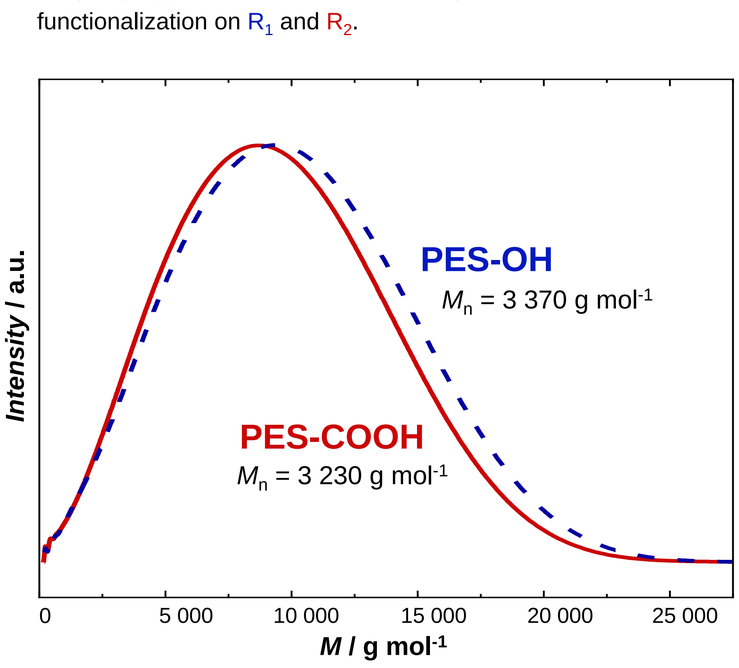


**Figure 2:** GPC results for PES-COOH and -OH. The molecular weight *M* was calculated from retention volume of the samples by calibration with polystyrene standards.

## Conclusion

MALDI/ToF-MS combines investigation of both terminating groups and molar mass distribution instead of isolated analysis of those important characteristics by titration and GPC. Additional to qualitative results obtained by classic interpretation of spectra, peak integration allows quantification and determination of $M_n$ and $M_w$ and end group ratio.

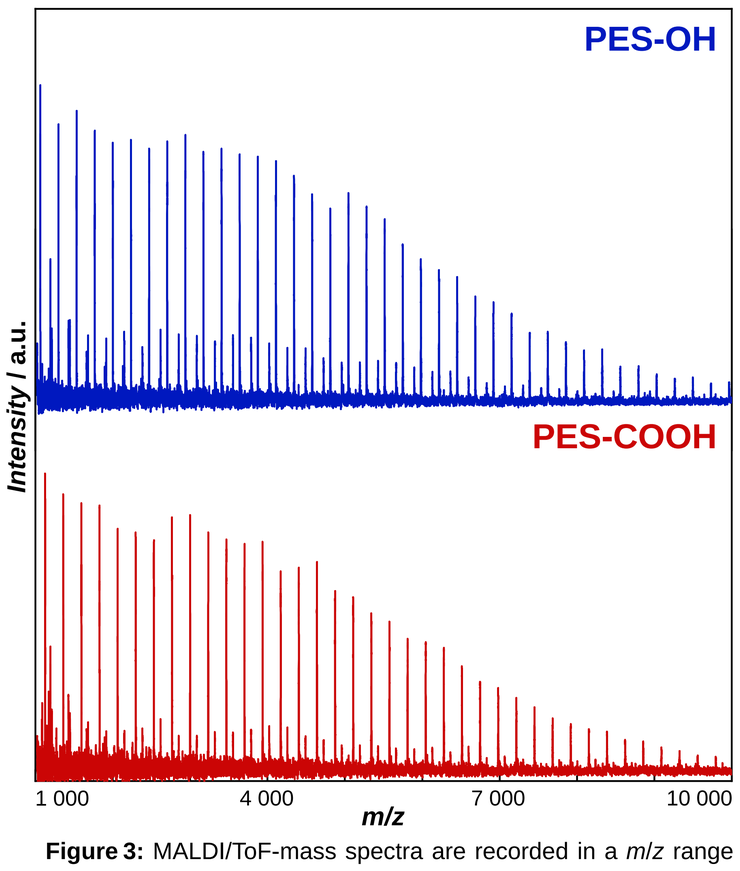


**Figure 3:** MALDI/ToF-mass spectra are recorded in a *m*/*z* range of 1 000 to 10 000. Both polyesters show similar molecular weight distributions, but discrimination of higher masses is assumed.

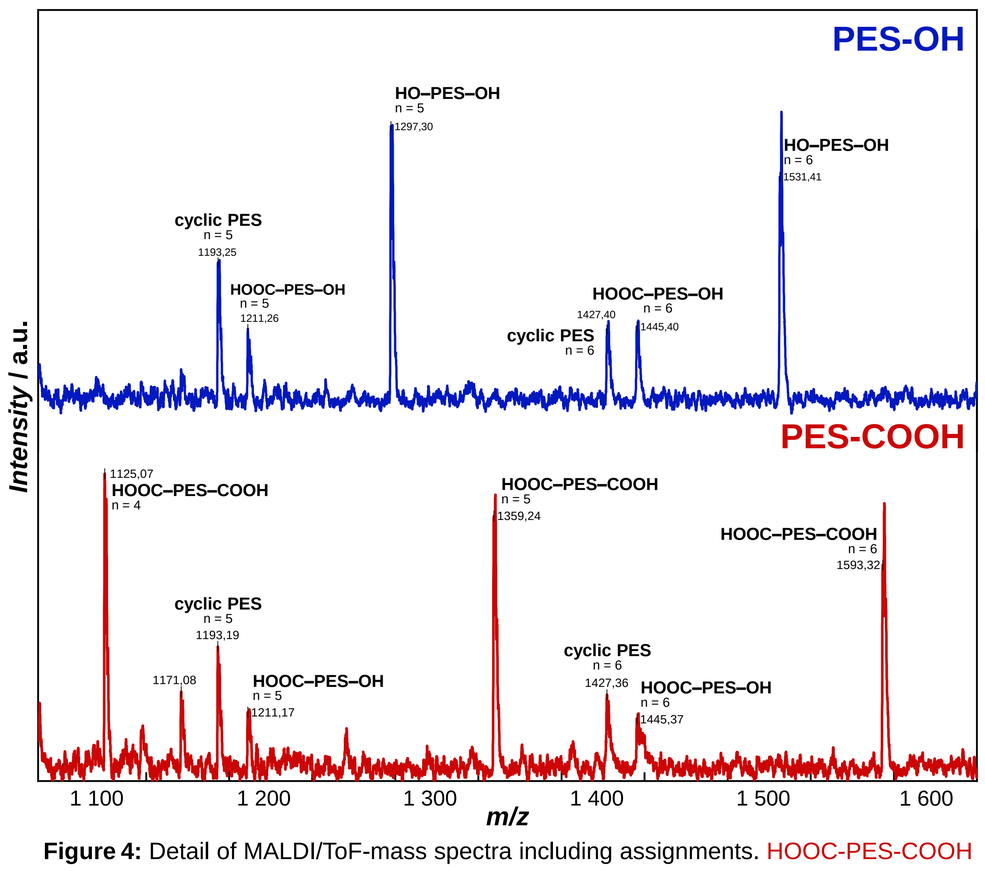


**Figure 4:** Detail of MALDI/ToF-mass spectra including assignments. HOOC-PES-COOH or HO-PES-OH main series were obtained according to monomer ratio. Both spectra reveal polyesters with mixed end groups (HOOC-PES-OH) as well as cyclic PES.

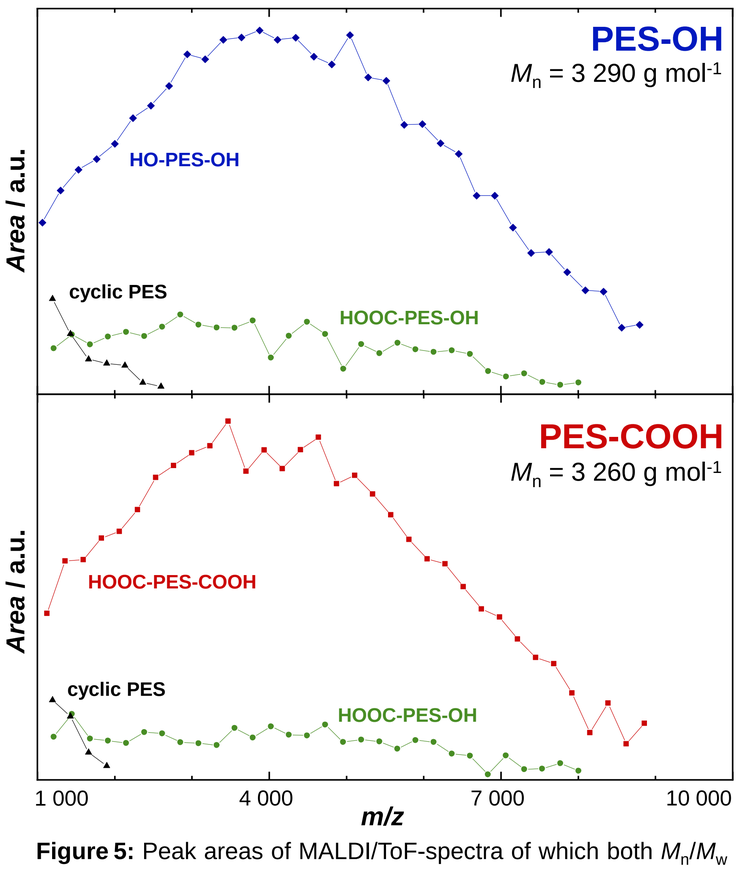


**Figure 5:** Peak areas of MALDI/ToF-spectra of which both $M_n/M_w$ as well as ratio of terminating groups can be calculated. Cyclic polyesters are only formed to a *m*/*z* < 2000–3000.