Investigation of three-component Polyesters using MALDI/ToF-Mass Spectrometry

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Introduction

The polymer class of polyesters (PES) offers great versatility due to numerous possible combinations of monomers, their different incorporation in the polymer chain and variations in molecular mass distribution. This makes polyesters suitable for a broad range of applications. A thorough structural investigation of the polymers is crucial to get an understanding for the material's properties. Whereas conventional methods only provide partial structure elucidation, MALDI/ToF-mass spectrometry (MS) includes information about both composition of subunits and molar masses. Therefor, MALDI/ToF-MS is a very powerful tool for polyester analysis.

Experimental

Three polyesters were synthesized according to the general reaction scheme given in Figure 1. Whereas the diacid was unchanged for all polymers, the diol component varied. For the polyester **PES-00** only a C_6 diol was used, which was then partially replaced by a comonomer (C_{10}) in the three-component polyesters **PES-10** (10 %) and **PES-50** (50 %).

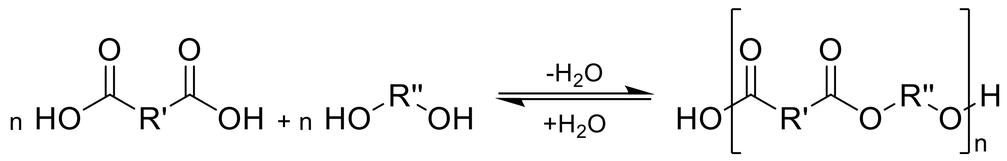


Figure 1: General reaction scheme of polyesters. C_6 and C_{10} diols were used in different ratios (**PES-00**, **PES-10**, and **PES-50** with 0, 10, and 50 % of the C_{10} diol, respectively).

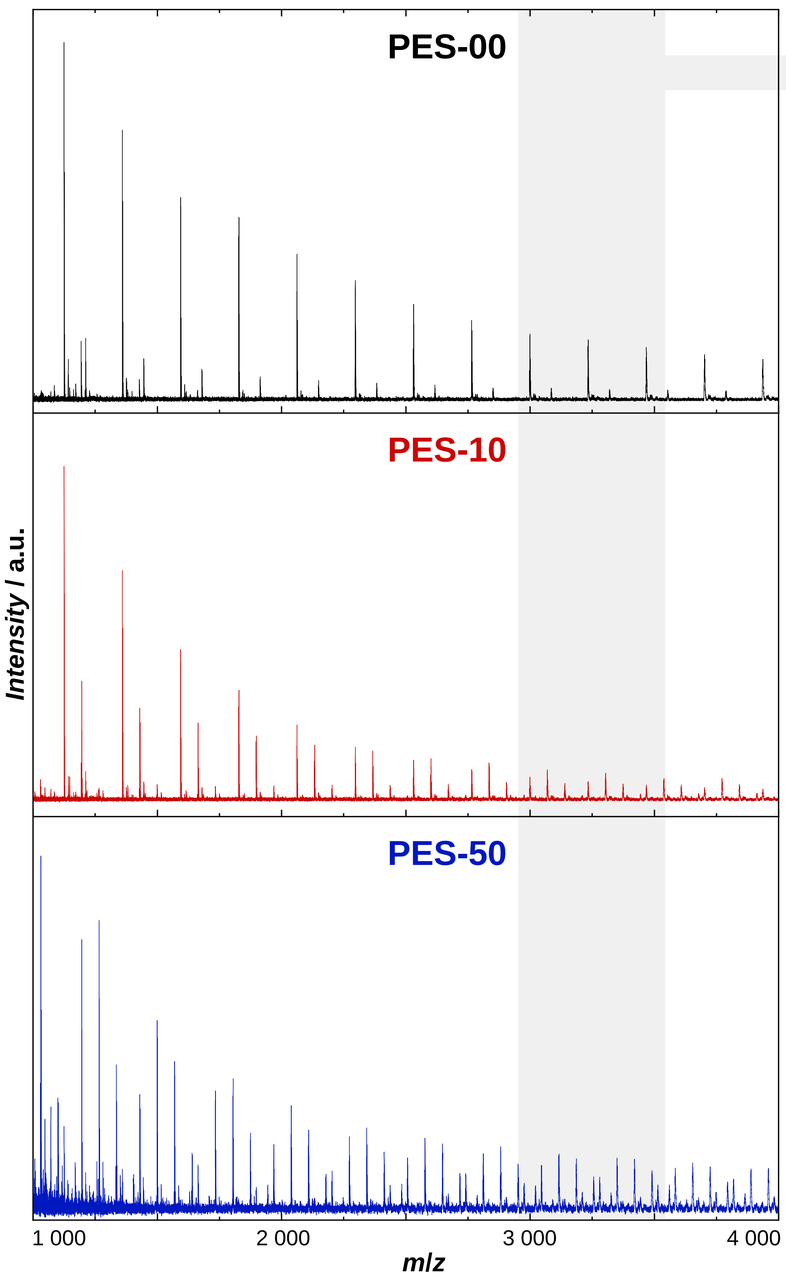


Figure 2: MALDI/ToF-mass spectra of a two-component (**PES-00**) and two three-component polyesters (**PES-10** with 10 % and **PES-50** with 50 % comonomer) in a *m/z* range of 1 000 to 4 000. The complexity of the spectrum increases strongly with a rising amount of comonomer.

Figure 3 (right): Detail of mass spectra reveals series of different terminating groups for **PES-00** (up to 2 000 g mol^{-1} also formation of cyclic polyesters is detected). Series of varying number of incorporated comonomer units can be observed for **PES-10** and **PES-50**.

Detail
- terminating groups (**PES-00**)
- incorporation of comonomer (**PES-10**, **PES-50**)

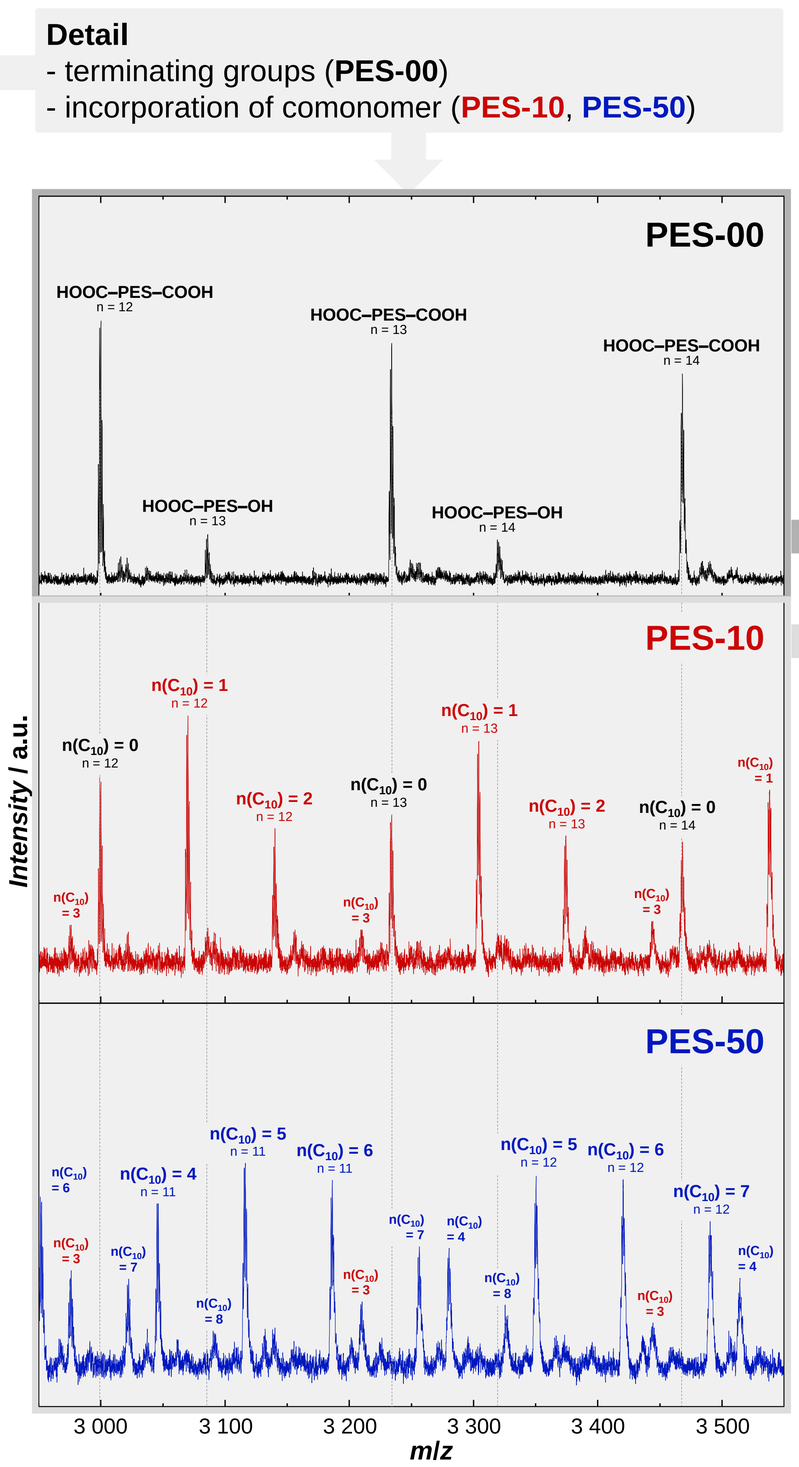
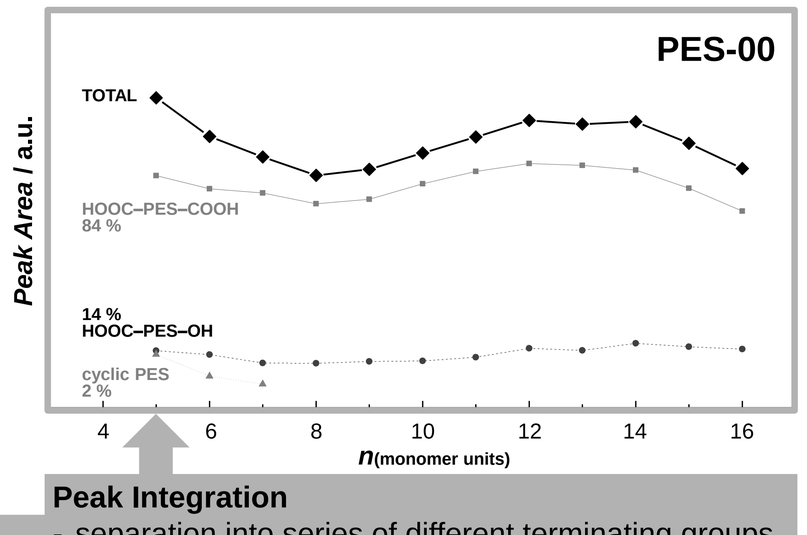
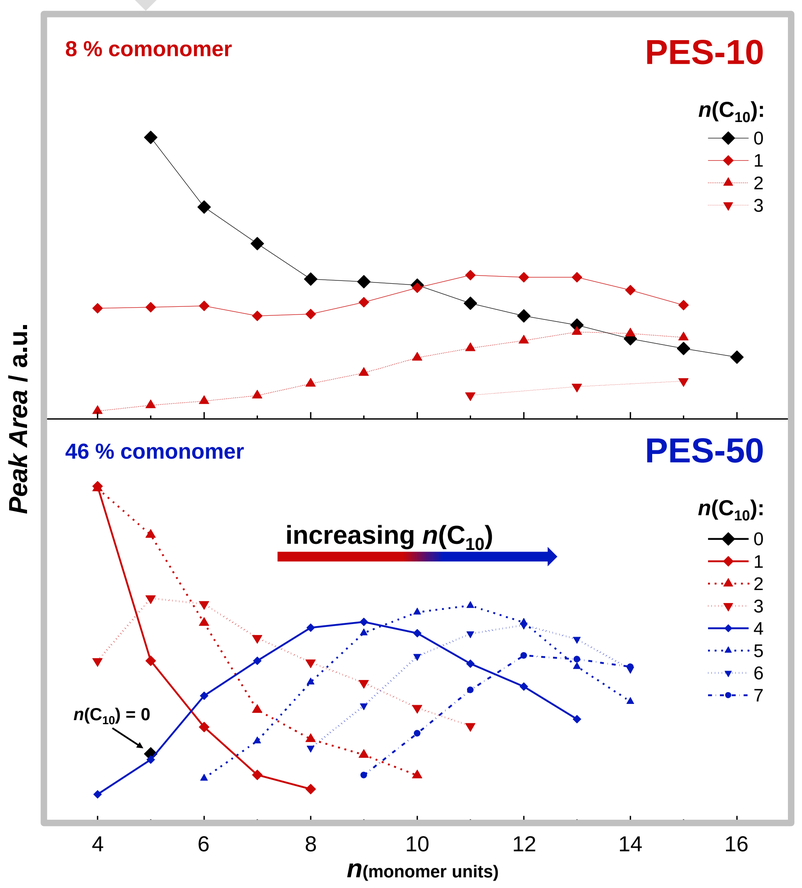


Figure 4, 5 (right): Integration of peaks and separation into different series of either different termination groups (**PES-00**) or varying extent of C_{10} incorporation (**PES-10**, **PES-50**).



Peak Integration
- separation into series of different terminating groups
- calculation of COOH/OH ratios (**PES-00**)
- separation into series of different comonomer amount, sum of all end groups (**PES-10**, **PES-50**)
- calculation of comonomer incorporation



Results

MALDI/ToF-mass spectra of the investigated polyesters **PES-00** (two components), **PES-10** and **PES-50** (3 components) are shown in Fig. 2 with details interpreted in Fig. 3. The details reveal that mainly polyesters with two acidic end groups are present (**HOOC-PES-COOH**). After integration of peaks, ratios of different structures can be calculated and it was found that **HOOC-PES-COOH** accounts for 84 % of the total polyester (Fig. 4).

For 3-component polyesters the series of varying terminating groups get split for each comonomer unit incorporated in the polyester and spectra soon get more complicated. Only 10 % replacement of C_6 to C_{10} causes splitting into 4 series (Fig. 5). For **PES-50** series from $n(C_{10}) = 0–7$ can be integrated satisfactorily and an additional series of 8 C_{10} units per chain starts to emerge at 3 100 *m/z*. Naturally, probability for a higher comonomer incorporation increases with polymer chains length and polyesters with solely C_{10} diols are obtained as well. Finally, comonomer incorporation can be calculated to be 8 % (**PES-10**) and 46 % (**PES-50**).

Conclusion

MALDI/ToF-MS proves to be a powerful tool for the investigation of three-component polyesters. Results include successful identification and quantification of series with varying comonomer incorporation.