Article

Semiquantitative Approach for Polyester Characterization Using Matrix-Assisted Laser Desorption Ionization/Time-of-Flight Mass Spectrometry Approved by ^{1}H NMR

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ABSTRACT: Matrix-assisted laser desorption ionization/time-of-flight (MALDI/ToF) mass spectrometry and ^{1}H NMR were used for the structural investigation of isophthalic and maleic acid copolyesters with neopentyl glycol. Since both methods provided information on the ratio of incorporated acid components and terminating groups, results were compared and linear correlations ($R^2 = 0.96-0.98$) could be found. This suggests that MALDI/ToF MS is a suitable tool for the semiquantitative characterization of polyester systems. For the isophthalic/maleic acid ratio, MALDI results yielded constantly lower values than ^{1}H NMR, which was attributed to varying ionization efficiencies of homo- and copolyesters. Ratios of carboxylic and hydroxylic terminating groups, which are conventionally still measured by time consuming complex titrations, were measured with MALDI and ^{1}H NMR and were in good agreement. Both methods either excluded or distinguished unreacted monomers in the polyester bulk in contrast to acid−base titrations where those monomers severely distort the results. Additional structural information could be gained including the observation of cyclic structures (MALDI), E/Z isomerism from maleic to fumaric acid, and the statistical distribution of the acid components within the polyester chain (^{1}H NMR). While ^{1}H NMR peak assignments have to be verified by ^{13}C NMR and multidimensional techniques, MALDI/ToF MS provides a straightforward technique that can be applied to other polyester systems without major alterations.
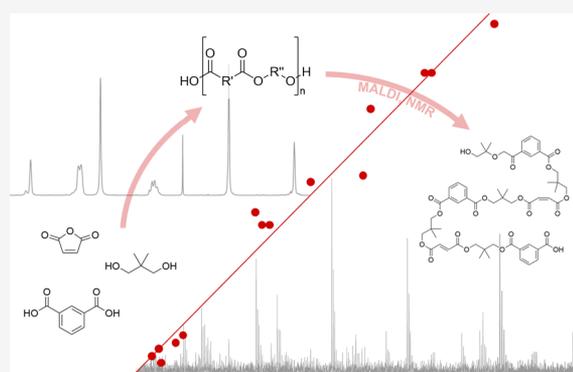
Since the 1920s, polyesters have been extensively studied, and still, current research deals with enhancing kinetic models,[1−4] introducing innovative monomers,[5−7] finding new applications,[8−12] or applying special analytical techniques.[13−16] This interest can be explained by the great versatility of this polymer group arising from numerous suitable monomers. Apart from necessary carboxyl and hydroxyl moieties for esterification, monomers often carry additional functional groups. Those functionalities, either within the polymer chain or as side groups, influence the material's properties severely. To enhance the understanding of structure−property relationships, detailed structural investigation of synthesized polyesters is crucial.

Introduced in the 1950s, nuclear magnetic resonance (NMR) provides one possibility to examine polyester compositions. A major advantage of NMR compared to other methods is its ability to distinguish different isomers, which was first described for polyesters containing 1,4-cyclohexanedicarboxylic acid.[17] Soon, reports on E/Z isomerism of maleic to fumaric acid in unsaturated polyesters followed. Quantification of isomeric ratios proved to be necessary because polyesters exhibited different properties.[18]

Similar to the differentiation of isomers due to separated chemical shifts, the composition of a more-component polyester could be investigated, including quantification of comonomers.[19] The presence of at least two isomers or two comonomers caused peak splitting of diol signals. While this splitting was used to prove randomness of polyester sequences,[20] it also complicated the interpretation of spectra. Additional information gathered from NMR techniques included reaction kinetics[21−24] and quantification of terminating groups using different derivatization methods.[25−27]

Unlike NMR, mass spectrometry (MS) using matrix-assisted laser desorption ionization (MALDI) usually coupled with a time-of-flight detector (ToF) represents a tool especially introduced for analysis of large fragile molecules.[28] Its availability since the 1980s caused a revival of academic

research in the field of polyesters. MALDI/ToF MS provided the first proof-of-ring formation during polyester synthesis, which was followed by a reform of polycondensation theory.[1] Next to cyclic structures, polyesters with different terminating groups as well as varying comonomer incorporation could be identified due to their distinct m/z ratios.[29] Detailed structural characterization of a polyester illuminating the monomer sequence has been performed using MALDI with collision-induced dissociation (CID) fragmentation.[30] Due to the separation according to mass, molecular weight distributions and calculation of number and weight average molecular masses could be determined. However, this application was limited to analytes with low polydispersity since higher masses were significantly suppressed at suitable acceleration voltages and low laser power.[29] A way to overcome this problem was found by Montaudo M. and Montaudo G. by measuring SEC fractions.[31,32] Additional dependence of signal intensities on ionizability of molecules and sample preparation led to the broad consent that results from MALDI/ToF MS are purely qualitatively.[1,29,33]

The aim of this work was a detailed structural investigation of three-component polyester systems composed of neopentyl glycol, isophthalic acid, and maleic anhydride. To overcome the problems arising from conventional bulk analytical techniques, such as acid value and hydroxyl number titrations, ^{1}H NMR and MALDI/ToF MS methods were established as an alternative approach.

■ EXPERIMENTAL SECTION

Polyester Synthesis. Neopentyl glycol (NPG), isophthalic acid (IPA), and maleic anhydride (MA) were chosen as monomers for polyester synthesis. NPG (>99%) from Perstorp Holding AB, Sweden, and IPA (>99%) from Indorama Ventures Química S.L.U. were used. Maleic anhydride (≥98%) was purchased from Alfa Aesar. All chemicals were used without further purification. Amounts of monomers, which are summarized in Table 1, were calculated to yield a constant theoretical acid value, except for IPA(OH), which was synthesized with an excess of neopentyl glycol.

Table 1. Composition and Reaction Conditions of the IPA and IPA/MA Polyesters that Have Been Discussed in Detail

sample	mole fraction (%)			T (°C)
	NPG	IPA	MA	
IPA-1	0.49	0.51		240
IPA-2				200
IPA/MA-1	0.49	0.21	0.30	220
IPA/MA-2				200
IPA/MA-3	0.49	0.30	0.21	180
IPA/MA-4	0.49	0.41	0.10	200

Polyester syntheses were performed in bulk in a 0.5 L reaction vessel with a four-neck lid. The apparatus was flushed with nitrogen. A heating mantle and an overhead stirrer were used. After melting NPG in the reaction vessel, 0.9 mmol of a stabilizer, 1.1 mmol of a tin catalyst, the acid components, and a retainer were added. The reaction mixture was heated to final temperatures of 180−240 °C. After 5−7 h, synthesis was carried on under reduced pressure for 4 h. Finally, the melt of the polyester resins was poured onto aluminum plates and grinded after cooling down. Unless otherwise noted, polyesters

were analyzed without further purification. The reason for temperature variation was the observation of gelation in the synthesis of maleic acid homo- and copolyesters with high maleic acid ratios.

MALDI/ToF Mass Spectrometry. MALDI/ToF mass spectra were recorded on a Bruker Autoflex III smartbeam. 2,5-Dihydroxybenzoic acid (DHB; Acros Organics, 99%) was used as the matrix, and sodium trifluoroacetate (Fluka, 99%) was added as the ionization agent. Solutions of the matrix (10 mg mL^{-1}), sample (10 mg mL^{-1}), and sodium salt (1 mg mL^{-1}) in tetrahydrofuran (THF; Carl Roth, ROTISOLV HPLC, unstabilized) were mixed in a ratio of 100:10:1 and applied to the MALDI target via the dried droplet method. In contrast to previous findings,[34] low matrix concentrations were preferred since those promoted rapid evaporation of THF, leading to a suppression of spot inhomogeneity. Peak integration and deconvolution were performed by the Bruker FlexAnalysis 3.0 software. For quantificative calculations, the peak areas of Na and K adducts were added.

NMR. NMR spectra of samples were recorded on a Bruker Avance 300 MHz. For ^{1}H NMR, about 15 mg of the polyester was dissolved in 0.6 mL of chloroform-d (VWR Chemicals, 99.8%) and 5 mg of N,N-dimethylformamide (DMF; VWR Chemicals, 99.5%) was added. DMF was used as an internal standard, which allowed for determination of the acid value and hydroxyl number. Peaks were given in ppm relative to tetramethylsilane. Assignments were partly described in literature[20,21,23,24] and validated by ^{13}C NMR and 2D experiments for which 20−25 mg of the sample was dissolved in 0.6 mL of CDCl$_3$. Additionally, selected samples were fractionated by precipitation using THF and water to investigate oligoesters.

Size Exclusion Chromatography. Molecular weight distributions were examined by size exclusion chromatography (SEC) measurements. The SEC setup included a PU-2086 Plus pump (Jasco), a 728 autosampler (Bischoff), and a UV-975 detector (Jasco) adjusted to a wavelength of 260 nm. Phenogel columns with pore sizes of 100, 500, and 1000 Å were used for separation. Samples were dissolved in THF using concentrations of 2−3 mg mL^{-1}. The system was calibrated using polystyrene standards. Spectra were processed manually. After baseline correction, data upwards of 202 g mol^{-1}, corresponding to NPG-MA dimers, were used to calculate the polystyrene equivalents of number and weight average molecular masses (M_n and M_w) as well as the polydispersity index Đ.

Acid−Base Titration. Terminating groups of polyesters were conventionally quantified by titration with potassium hydroxide. Results are expressed as acid value (AV) and hydroxyl number (HN), which describe the mass of potassium hydroxide in milligrams needed for the neutralization of respective terminating groups per gram of polyester resin. Definitions are given in eqs 1 and 2.

$$\text{acid value (AV)} = \frac{(n_{\text{COOH}}/\text{mmol}) \cdot (M_{\text{KOH}}/\text{g mol}^{-1})}{m_{\text{PES}}/\text{g}}$$

$$(1)$$

$$\text{hydroxyl number (HN)} = \frac{(n_{\text{OH}}/\text{mmol}) \cdot (M_{\text{KOH}}/\text{g mol}^{-1})}{m_{\text{PES}}/\text{g}}$$
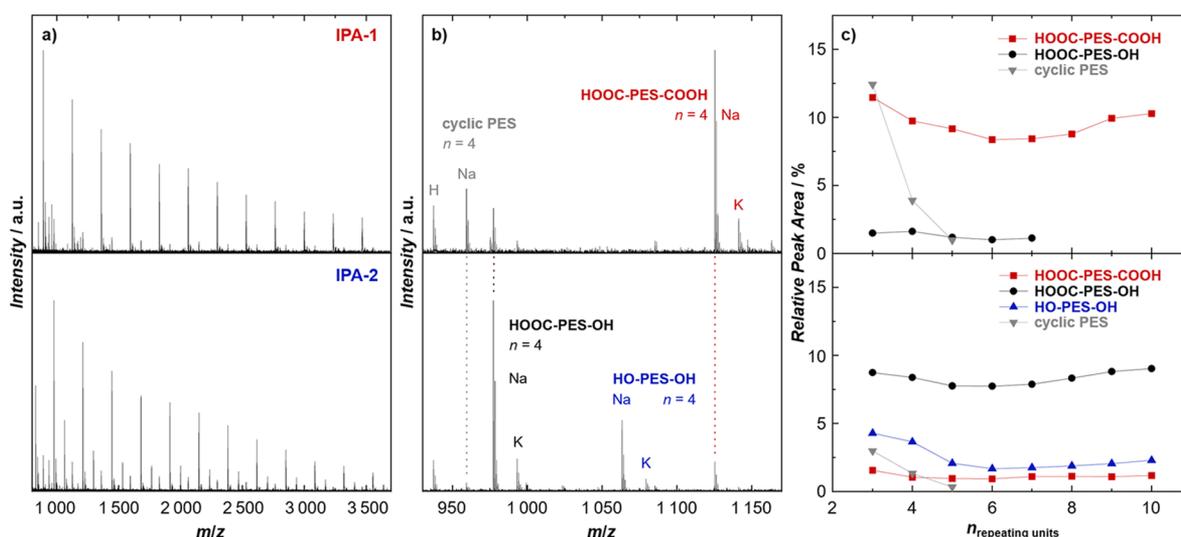
$$(2)$$

Figure 1. (a) MALDI/ToF mass spectrum of homopolyesters IPA-1 and IPA-2 for which different main series were obtained, as highlighted in detail (b), including peak assignments. (c) Distribution of series depending on the number of repeating units. Apart from cyclic structures, which only occurred for an n of up to 5, proportions of terminating groups seemed sufficiently continuous for estimations.

For determination of acid values, samples were dissolved in THF and directly titrated against 0.1 M ethanolic KOH solution (Carl Roth, volumetric standard). Hydroxyl numbers were determined by an indirect method based on DIN EN ISO 4629-1:2016-12.[35] Resins were derivatized with an excess of acetic anhydride (VWR Chemicals, 98%). Upon water addition, the excessive anhydride reacted to acetic acid, which was finally titrated using again a 0.1 M KOH solution in ethanol.

RESULTS AND DISCUSSION

MALDI/ToF MS. MALDI/ToF mass spectra and estimation of end group distribution of NPG-IPA homopolyesters are shown in.

Figure 1. Regarding a broader section of the spectra (800–3700 Da) revealed a decrease of intensity toward higher m/z ratios. On the one hand, such distributions are typical for polycondensates; on the other hand, suppression of higher masses must be kept in mind. Further, different main and side series were observed for polyesters IPA-1 and IPA-2, which are equal in educt composition but differ in reaction temperatures. SEC measurements confirmed lower molecular weights for IPA-2 (M_w = 2900 g mol^{-1}, Đ = 2.0) compared to IPA-1 (M_w = 6000 g mol^{-1}, Đ = 2.6).

A detailed look (Figure 1b) revealed the presence of four different possible constitutions for an identical number of repeating units (n): two carboxylic (HOOC-PES-COOH), two hydroxylic (HO-PES-OH), or mixed (HOOC-PES-OH) terminating groups, and cyclic structures. Peak integration allowed for an estimation of polyester composition for each n, which is displayed in Figure 1c. While formation of cyclic PES was limited to lower molecular weights, proportions of different terminating groups were comparatively stable.

The integrals could further be used to calculate the ratio of carboxylic and hydroxylic end groups, expressed as x_{COOH} calculated using eq 3. COOH and OH were the sums of according peak areas, including the equal share of series with mixed terminating groups. Calculations of x_{COOH} were carried out for each n. Relative standard deviations of 1−10% enforced the assumption that distribution of terminating groups was

constant enough for an estimation. This was important for side series with low intensities whose integration results at higher m/z values lost reliability and thus were excluded from calculations.

$$x_{COOH}/\% = \frac{COOH}{COOH + OH} \cdot 100 \tag{3}$$

For copolyesters of at least three components, MALDI/ToF mass spectra did include information not only about ring formation and end group distribution but also about comonomer incorporation. An example for spectrum interpretation of the investigated NPG-IPA/MA system is given in Figure 2. Again, integration of peaks gave an estimation of
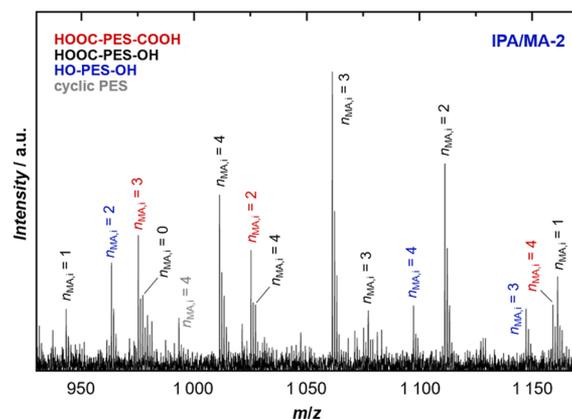

Figure 2. Detail of the MALDI/ToF mass spectrum of copolyester IPA/MA-2. Number of signals increased due to series varying both in terminating groups and maleic acid units.

x_{COOH}. For determination of maleic acid incorporation, the proportion of MA ($x_{MA,i}$) compared to the total number of acid units was calculated for each molecule i (eq 4). The total number of incorporated maleic acid units expressed as x_{MA} was then calculated from eq 5. Figure 3 displays the distribution of series with different numbers of incorporated maleic acid per total repeating units.

$$x_{MA,i} = \frac{n_{MA,i}}{n_{COOH,i}} \tag{4}$$

$$x_{MA}/\% = \frac{\sum (Area_i \cdot x_{MA,i})}{\sum Area_i} \cdot 100 \tag{5}$$
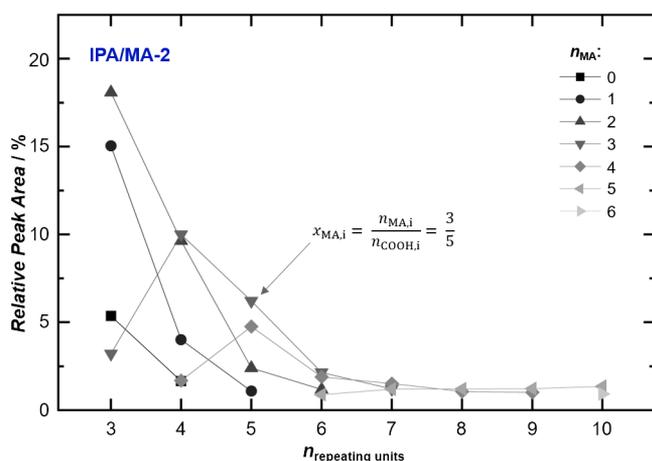

Figure 3. Distribution of series with different numbers of maleic acid units (n_{MA}), including an example for calculation of $x_{MA,i}$.

Since MALDI/ToF MS is usually regarded as a non-quantitative method, results only served for estimation of carboxylic/hydroxylic terminating groups and IPA/MA ratios. To investigate the error of calculated values, samples IPA/MA-1 and IPA/MA-2 were chosen for reproducibility tests. As shown in Table 2, standard deviations (STD) for determination of x_{COOH} were 3−8%, while errors in x_{MA} were smaller with an STD of 1%.

Table 2. Reproducibility of MALDI/ToF MS Results for x_{COOH} and x_{MA} of Samples IPA/MA-1 and IPA/MA-2, Including Mean Values

	IPA/MA-1		IPA/MA-2	
	x_{COOH} (%)	x_{MA} (%)	x_{COOH} (%)	x_{MA} (%)
1	78	44	53	52
2	71	45	34	55
3	71	46	40	54
mean	73	45	42	54

Calculation of molar masses using MALDI spectra was performed, but discussion of such was discarded because the results were strongly depending on the presence of maleic acid. For homopolyesters, M_n values lay in the range of 1550−1600, and M_w values lay between 2100 and 2200 g mol^{-1}. For copolyesters, M_n of 700−1050 and M_w of 750−1300 g mol^{-1} were obtained. Since far more compositions are possible for copolyesters, signal intensities soon dropped to a level with poor signal-to-noise ratios. The chosen m/z ratio of 600−4000 was too small to obtain the whole mass range of homopolyesters, leading to false small polydispersity indices of only up to 1.4 and results for M_n and M_w, which are not comparable to values obtained from SEC measurements.

^{1}H NMR. Different from mass spectrometry, ^{1}H NMR gives information of the bulk instead of distinct molecules. This for example complicated the spectrum interpretation of samples

with significant amounts of oligomers, which could be simply excluded from MS by examining only higher m/z ranges. Further, ^{1}H NMR shifts depend on isomerism. Hence, not only was additional structure elucidation regarding E/Z isomerism of fumaric and maleic acid provided, but the fine structure of the spectra also became more complex.

Therefore, NPG-IPA homopolyesters are discussed first. Spectra of two samples are shown in Figure 4, and assignments
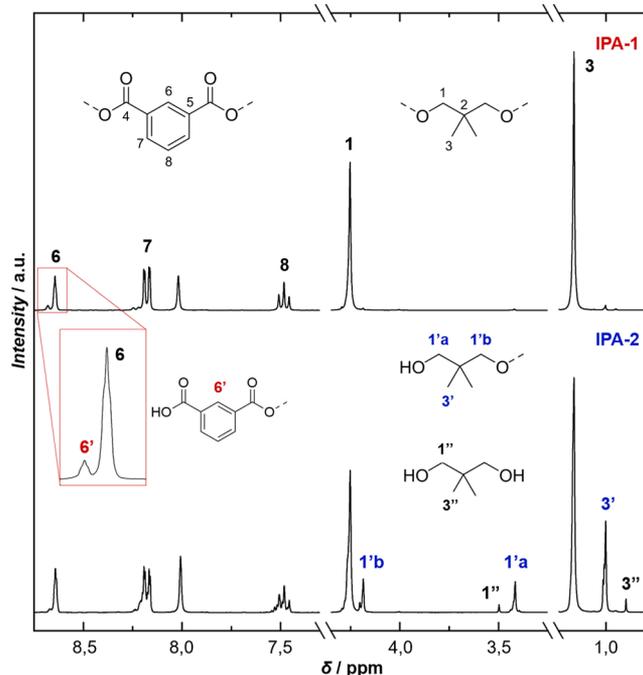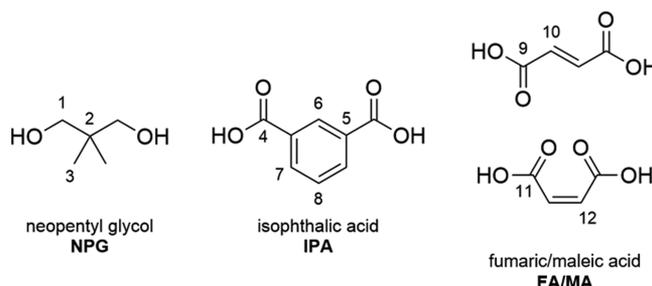

Figure 4. ^{1}H NMR spectra of homopolyesters IPA-1 and IPA-2, including assignments. Additional peaks for sample 2 were observed due to significant amounts of monoesters and oligomers.

Chart 1. Numbering of Carbon Atoms of Possible Polyester Components (Neopentyl Glycol, Isophthalic, Fumaric, and Maleic Acid) for NMR Assignments

are given in Chart 1. Proton and ^{13}C shifts are summarized in Tables 3 and 4, respectively. Next to the main signals for IPA and NPG in polyester chains, also, small peaks could be found that belonged to terminating isophthalic acid (6′) or neopentyl glycol (1′a, 1′b, and 3′) moieties. While splitting of diol signals in several polyester compositions was explained in literature,[20,21,23,24] the assignment of isophthalic acid end groups was confirmed by 2D NMR experiments. As described in detail for poly(lactic acid),[36] further peak splitting in both IPA and

Table 3. ^{1}H NMR Shifts (CDCl$_3$, 300 MHz) for IPA/MA Polyesters with NPG, Including Monoesters (e.g., HO-NPG)

δ (ppm)	assignment	δ (ppm)	assignment
8.68	6′(IPA-COOH)	4.19	1′b(IPA-NPG-OH)
8.64	6(IPA)	3.49	1″(free NPG)
8.18	7(IPA)	3.41	1a(IPA-NPG-OH)
7.48	8(IPA)	3.33−3.31	1′a(FA/MA-NPG-OH)
6.83	10(FA)	1.20−0.85	3, 3′, 3″
6.23	12(MA)	1.00	3′(IPA-NPG-OH)
4.32−3.90	1, 1a, 1b, 1′b	0.90	3″(free NPG)

Table 4. ^{13}C NMR Shifts (CDCl$_3$, 70 MHz) for IPA/MA Polyesters with NPG, Including Monoesters

δ (ppm)	assignment	δ (ppm)	assignment
165.4	4(IPA)	130.0	5(IPA)
165.1	9(MA)	129.9	12(MA)
164.7	11(FA)	128.8	8(IPA)
134.4	7′(IPA-COOH)	70.2−69.9	1(IPA/MA/FA-NPG)
133.9	7(IPA)	68.3	1′(IPA-NPG-OH)
133.6	10(FA)	68.2	1′(FA/MA-NPG-OH)
131.3	6′(IPA-COOH)	35.5−34.9	2(NPG, splitting analogous to ^{1}H NMR)
130.6	5′(IPA-COOH)	22.1−21.6	3(NPG, splitting)

NPG shift regions were attributed to significant amounts of oligomers.

While in MALDI/ToF MS terminating groups could be clearly identified and x_{COOH} was estimated by integration of respective peaks, there were two steps necessary for ^{1}H NMR. The amount of carboxyl terminating groups was determined by integration of peak 6′. Although this peak was the most distinct for IPA monoesters, inaccuracies were caused by poor separation to the polyester peak. Here, deconvolution was

tested but discarded because neither peak exhibited a Gaussian shape. For determination of hydroxyl terminating groups, the NPG monoester peak 1′a was used since there were no interferences with other peaks.

The use of an internal standard, in this case, N,N-dimethylformamide, allowed for calculation of the absolute acid value (AV) and hydroxyl number (HN), which were already defined in eqs 1 and 2. The proportion of carboxyl terminating groups (x_{COOH}) was then determined according to eq 3 where n_{COOH} and n_{OH} replaced COOH and OH, respectively.

^{1}H NMR spectra of two samples with IPA/MA ratios of 4:6, which exhibited different degrees of isomerism, are shown in Figure 5. E/Z isomerism could be calculated by integration of desolated peaks at 6.85 ppm for fumaric acid (E) and 6.25 ppm for maleic acid (Z), according to literature[18,37] and is expressed as x_{FA}. Although a small peak was obtained next to the maleic acid peak at 6.29 ppm, 2D NMR experiments showed that it cannot be attributed to MA monoester analogous to IPA. Since this extra peak was only observed for polyesters with small molecular weights (M_w = 2500−4500 g mol^{-1}), it could be caused by oligomers instead. Hence, ^{1}H NMR only allowed calculation of a partial acid value describing the isophthalic terminating groups.

Regarding Figure 5b, a great influence of the number of acid components on the methylenic and methylic regions of NPG was obvious. Neglecting signals of mono- and oligoesters, examined samples exhibited up to eight peaks caused by different possible configurations compared to one singlet per region in NPG-IPA homopolyesters. Methylic peaks of samples with high x_{FA} values at 1.17, 1.09, and 1.02 ppm were caused by the sequences IPA-NPG-IPA, IPA-NPG-FA or FA-NPG-IPA, and FA-NPG-FA, respectively. Additional splitting could be observed for the two methylenic groups, which were differently affected in asymmetric sequences like IPA-NPG-FA.

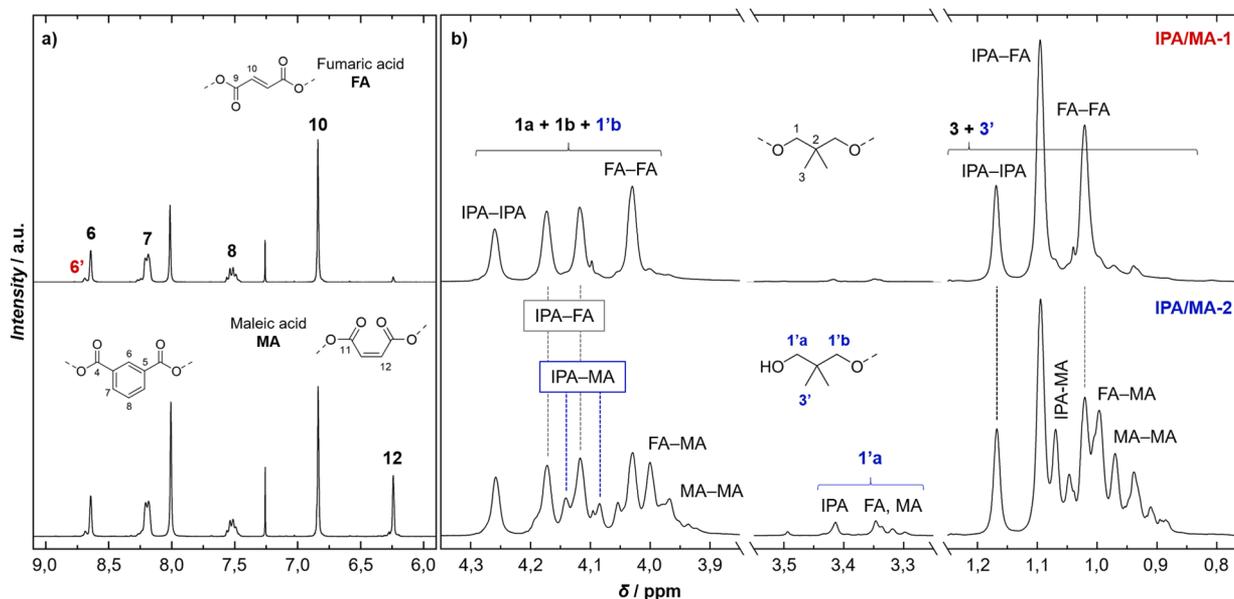Adding a significant amount of MA fraction led to further peak splitting due to an increasing number of possible

Figure 5. ^{1}H NMR spectra of samples IPA/MA-1 and IPA/MA-2 split into the (a) acid shift region and (b) NPG region. The latter underwent peak splitting caused by different sequences like IPA-NPG-IPA and IPA-NPG-FA. To ensure readability, only NPG neighbors were used for peak assignments in the graph (e.g., IPA-IPA and IPA-FA).

sequences. Peak proportions for discussed copolyesters are shown in Figure 6 and compared to their probabilities for the
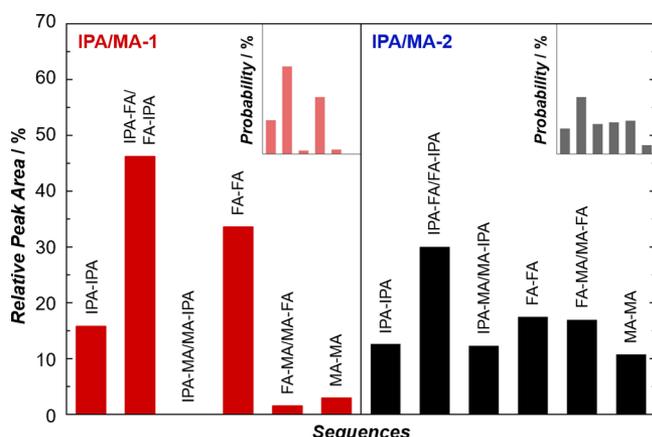

Figure 6. Peak splitting in ^{1}H NMR can be explained by different FA/MA ratios, leading to varying probabilities of polyester sequences. Experimental and theoretical distributions are compared.

determined IPA/FA/MA ratios. Experimental data from both methylenic and methyl regions fit the theoretical values satisfactorily, confirming peak assignments. The graph displays mean values of both regions. As expected, inaccuracies occurred at integration of small peaks, which were surrounded by more intense signals as well as in the high field parts of both NPG regions. Peaks with lower shifts could on the one hand be explained by NPG-FA/MA monoesters identified by 2D NMR experiments as well as oligomers, as confirmed after fractionation by precipitation.

Comparison of MALDI/ToF MS and ^{1}H NMR Results. Both MALDI/ToF MS and ^{1}H NMR provided structural information of investigated two- and three-component polyesters. While ring formation was exclusively revealed using mass spectrometry, E/Z isomerism and statistical distribution of monomers could only be observed in NMR. However, acid-to-alcohol as well as isophthalic-to-maleic acid ratios could be determined from both methods. In the following, results for the fraction of maleic acid, x_{MA}, and the defined x_{COOH} are compared.

First, incorporation of the maleic acid into the polyester chain, expressed by x_{MA}, is discussed. As shown in Figure 7, a linear correlation of MALDI/ToF MS and NMR results was found. The coefficient of determination, R^2, amounted to 0.98. This confirmed that MALDI/ToF MS did not only provide qualitative information but also yielded semiquantitative results for the investigated polyester system as well.

However, regarding Figure 7, absolute x_{MA} values were shifted, and NMR results yielding higher numbers. Since NMR peaks of isophthalic, fumaric, and maleic acid units were well separated, integration could only cause small inaccuracies of NMR results. Hence, it can be assumed that the maleic acid content was underestimated by MALDI/ToF MS. The deviation was likely to be caused by a different ionizability of homo- and copolyesters.

Results concerning the ratio of terminating groups are shown in Figure 8. Again, NMR and MALDI/ToF MS results correlated well, although homo- and copolyesters showed slightly different trends. While the correlation for homopolyesters exhibited deviances for low x_{COOH} values, values for high x_{COOH} were in good agreement. Results for the
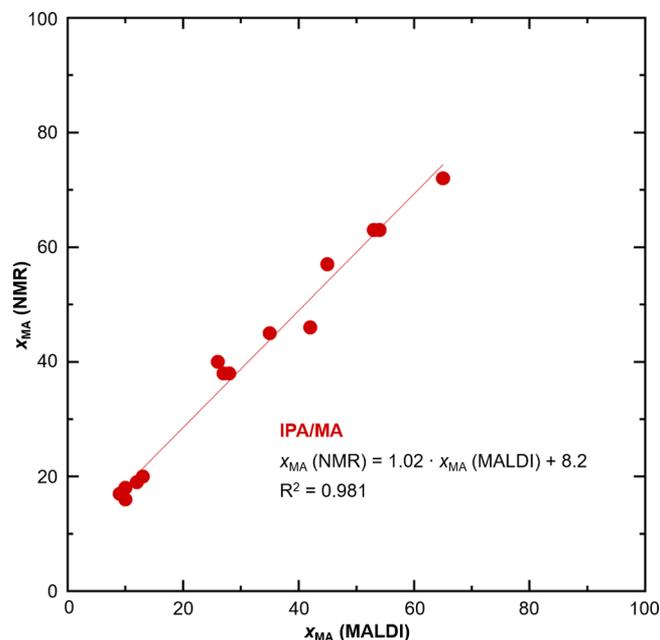

Figure 7. Linear correlation ($R^2 = 0.98$) for MALDI/ToF MS and NMR results concerning the incorporation of maleic acid (x_{MA}).
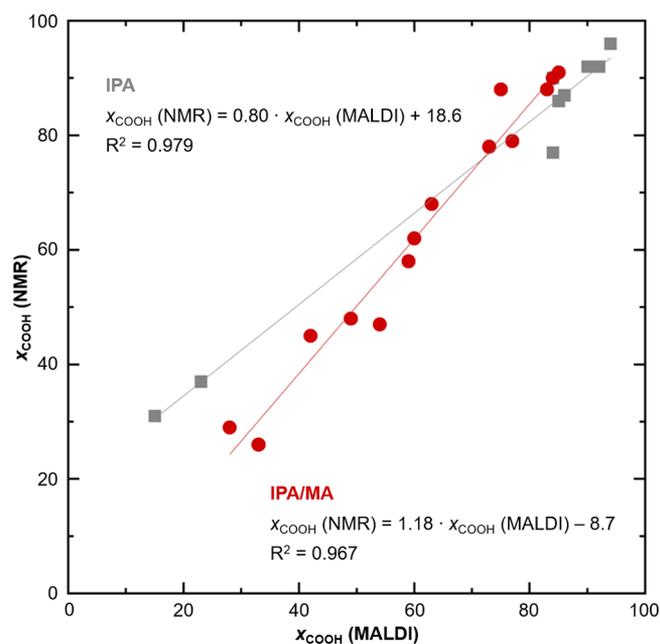

Figure 8. MALDI/ToF MS and NMR results concerning the ratio of terminating groups (x_{COOH}). A linear correlation could be found for both NPG-IPA homo- and NPG-IPA/MA copolyesters ($R^2 = 0.98$ and 0.97, respectively).

terminating group ratio in copolyesters showed greater variances. In contrast to x_{MA}, this deviation could be caused by both the NMR and MALDI method. In NMR, overlapping of isophthalic mono- and polyester peaks might have led to inaccurate determination of acid terminating groups. For the copolyester series, neither fumaric nor maleic monoesters could be distinguished, and hence, x_{COOH} will be underestimated if copolyesters bear a significant amount of fumaric or maleic terminating groups. The unequal slopes of the calibration curves could additionally be explained by the fact that polyester chains bearing various structural elements show

Table 5. Results for x_{MA} and x_{COOH} from MALDI, NMR, and Acid−Base Titration, Including SEC Results

.	x_{MA} (%)		x_{COOH} (%)			SEC	
samples	MALDI	NMR	MALDI	NMR	titration	M_w	Đ
IPA-1			94	96	83	6000	2.6
IPA-2			23	37	63	2910	2.0
IPA/MA-1	45	57	73	78	78	12070	4.2
IPA/MA-2	54	63	42	45	66	5970	2.9
IPA/MA-3	42	46	28	29	62	2540	2.1
IPA/MA-4	13	20	59	58	75	6800	2.6

different ionization efficiencies in MALDI.[33] A verification of this theory was not possible as the synthesis of a homopolyester with maleic anhydride has not yet been possible due to gelation of the reaction mixture.

To further investigate the ratio of terminating groups, conventional acid−base titration was carried out to determine the acid value and hydroxyl number. However, x_{COOH} from titration deviated significantly from both NMR and MALDI values, and some examples are given in Table 5. Due to different reaction conditions, polyester samples contained unreacted monomers to varying extents, which distorted titration results. Such unreacted monomers did not influence NMR results because isophthalic acid was not dissolved in $CDCl_3$, maleic anhydride was not found in any sample, and methylenic protons of free neopentyl glycol caused an isolated peak. Likewise, MALDI results were not affected by choosing an m/z range from 600 to 4000, which excluded both monomers and small oligomers. Especially, polyesters with low x_{COOH} and low molecular weights contained significant amounts of free isophthalic acid, which increased values from titration by up to 40%. Thus, NMR and MALDI were both more suitable to characterize terminating groups compared to conventional titration.

CONCLUSIONS

Polyesters from isophthalic acid, maleic anhydride, and neopentyl glycol were synthesized and characterized by MALDI/ToF mass spectrometry, ^{1}H and ^{13}C NMR, size exclusion chromatography, and acid−base titration. Both MALDI/ToF MS and ^{1}H NMR provided information on the ratio of incorporated acids and terminating groups, expressed as x_{MA} and x_{COOH}, respectively. Although MALDI is commonly regarded as a purely qualitative method for structure elucidation, values of x_{MA} and x_{COOH} were in good agreement with ^{1}H NMR results, and coefficients of determination ranged from 0.97 to 0.98.

While calculation of x_{MA} from ^{1}H NMR spectra was straightforward, determination of x_{COOH} included integration of comparatively small peaks originating from monoesters. Additionally, fumaric or maleic monoesters did not separate from the polyester peaks and thus could not be included in the result. The presence of oligomers complicated spectra and had to be verified by ^{13}C NMR, fractionation by precipitation, and SEC. In MALDI/ToF MS, on the other hand, information on both the terminating group and acid incorporation was given by each individual peak. Oligomers could easily be excluded by choosing a suitable m/z range. However, changes in the polyester structure caused different ionizabilities, leading to a not perfectly linear correlation between peak areas and structural features of the polymer.

Nonetheless, the good agreement of results from both methods suggested that MALDI/ToF MS could be used for a semiquantitative analysis of the investigated polyester system. Regarding the ratio between isophthalic and maleic acid, a calibration with ^{1}H NMR would be recommended to determine the underestimation of absolute values in MALDI. For the ratio of terminating groups, both methods not only bore disadvantages but also excluded unreacted monomers, which were found in the polyester bulk to varying extents. Since these resulted in incorrect ratios of terminating groups using conventional acid−base titration, both MALDI/ToF MS and ^{1}H NMR are to be considered superior.

For new polyester systems, the NMR method has to be adapted to an extent where peak assignments have to be verified by 2D experiments and fractionation. In addition, monoester peaks depend on the chemical shift of individual monomers and thus could be unidentifiable as in the case of maleic and fumaric acid. Analysis via MALDI/ToF MS, on the other hand, provides information of distinct molecules and can be applied to other polyester compositions without principal alterations.

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Author Contributions

K.M.S. has conducted the experiments, K.M.S and C.S. have written the manuscript, all authors discussed and interpreted the results, and I.G. and D.H. have written the project proposal.

Notes

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