# Solventless Liquid Oligoesters Analyzed by MALDI−ToF−MS

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ABSTRACT: MALDI−ToF−MS mass spectra of copolymers contain a lot of information on both chain-length distribution (CLD) and chemical composition distribution (CCD). In this paper, two random solventless liquid oligoesters were synthesized by an esterification of 1,4-butanediol with adipic acid and isophthalic acid or glutaric acid, respectively. The thus obtained oligoesters contain two different repeat units and may therefore be regarded as a copolymer. A copolymer fingerprint analysis has been used to study the microstructure of the copolymers for which it was observed that the copolymers can be described very well using Bernoullian chain statistics.

## Introduction

Solventless liquid oligoesters (SLOs) have been recently synthesized to prepare solventless liquid coatings in an endeavor toward the development of environmentally friendly coatings by eliminating volatile organic compounds (VOCs).[1−5] Hydroxyl-end-capped SLOs have been successfully used to prepare low surface-energy (as low as 10 mN/m) polymeric films with partially fluorinated (blocked) polyisocyanates via the surface segregation of fluorinated species.[6,7] The SLOs can also be partially fluorinated and then reacted with polyisocyanates to prepare films with a low surface energy.[8] Such thin layers with low surface energy may introduce many interesting properties to a coating, such as hydrophobicity/lipophobicity, excellent chemical resistance, low coefficient of friction, and so on. Recently MALDI−ToF−MS was successfully employed to identify end groups and end group distributions for a model oligoester (from a single diacid and a single diol) for SLOs.[9] In this paper, MALDI−ToF−MS is used to characterize the microstructure of two SLOs that were synthesized by condensation polymerization between a single diol and two diacids. The interpretation of the resulting MALDI−ToF−MS mass spectra is carried out by in-house developed software.[10]

## Experimental Section

**Materials.** The diacids, including adipic acid (AA, >99%), glutaric acid (GA, >99%), and isophthalic acid (IPA, ≥99%), and 1,4-butanediol (BDO, ≥99%) were purchased from Merck and used as received. A tin catalyst for direct esterification, butylchlorotin dihydroxide, with a trademark of FASTCAT 4101, was obtained from Atofina, France.

**Polymer Synthesis.** The synthesis of SLOs was detailed elsewhere.[8,9] A typical example of SLOs used in this study was prepared as follows. To a 250 mL four-neck flask equipped with a mechanical stirrer, Dean−Stark trap, reflux condenser, thermometer, and nitrogen inlet were added BDO (36.04 g, 0.400 mol), AA (21.95 g, 0.150 mol), IPA (25.04 g, 0.151 mol), and FASTCAT 4101 (0.1% of the total weight). The flask was gradually heated to 200 °C over 0.5 h and then kept at 200 °C until the amount of water collected in the Dean−Stark trap reached 70% of the theoretical amount (ca. 0.6 mol). The obtained SLO was dried under vacuum at 40 °C for 2 days to remove the trace amount of water. The acid number and hydroxyl number for the SLO were determined by titration[8] to be 5.8 and 86.8 mg of KOH/g, respectively, indicating that about 7% of end groups for this SLO was COOH.

A second SLO, synthesized in a similar way as described above was obtained after polymerization with BDO, AA, and GA as starting materials (molar ratio BDO:AA:GA = 0.403:0.150:0.150).

**Polymer Analysis.** MALDI−ToF−MS analysis was carried out on a Voyager DE-STR from Applied Biosystems. The matrix used for the analysis is *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) which was synthesized according to literature procedures.[11] The matrix was dissolved in THF at a concentration of 40 mg·mL$^{-1}$. Potassium trifluoracetate (Aldrich, 98%) was used as cationization agent and was added to THF at typical concentrations of 1 mg·mL$^{-1}$. The polymer was dissolved in THF at approximately 2 mg·mL$^{-1}$. In a typical MALDI−ToF−MS experiment, the matrix, salt, and polymer solution were premixed in a ratio of 10:1:5. The premixed solutions were handspotted on the target-well and left to dry. All mass spectra were recorded in the reflector mode and are the result of approximately 5000 individual laser shots. Mass spectra were baseline corrected with the advanced baseline correction mode from the Data Explorer software from Applied Biosystems. For a correct interpretation of MALDI−ToF−MS mass spectra, isotopic patterns of single polymer chains need to be integrated in the mass domain.[12] Due to the complexity of copolymer mass spectra this integration procedure cannot be readily applied, and therefore, these mass spectra were analyzed using a homemade program written in Visual Basic 6.0. This program needs the molecular formulas of the repeat units, end groups and cation as an input for a full mass spectral analysis.[10]

$^1$H NMR spectra were recorded on a Varian 400 spectrometer operating at 400.162 MHz at 25 °C. $CDCl_3$ (with TMS as an internal standard) was used as a solvent.

## Results and Discussion

The theoretical mass of a single charged copolymer in a typical MALDI−ToF−MS analysis can be calculated by use of eq 1.

$$m = n_A M_A + n_B M_B + E_I + E_{II} + M^+ \qquad (1)$$

in which the mass of the copolymer is related to the chemical composition ($n_A$ and $n_B$) of the copolymer,

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**Table 1. Structures of the Monomers Used to Prepare the SLOs and Possible Polymer Structures with Different End Groups**

| Diol | Diacid |
|---|---|
| HO—$(CH_2)_4$—OH | HO—C(=O)—$X_i$—C(=O)—OH |
| 1,4-butanediol | $X_A = (CH_2)_4$ AA |
| | $X_B = C_6H_4$ IPA or |
| | $X_B = (CH_2)_3$ GA |

Possible oligoester structures

I H—[O—$(CH_2)_4$—O—C(=O)—$X_i$—C(=O)—O—$(CH_2)_4$—O]$_{n_A,m_B}$—OH

II H—[O—$(CH_2)_4$—O—C(=O)—$X_i$—C(=O)—O]$_{n_A,m_B}$—H

III HO—C(=O)—$X_i$—C(=O)—[O—$(CH_2)_4$—O—C(=O)—$X_i$—C(=O)—O]$_{n_A,m_B}$—H

IV [O—$(CH_2)_4$—O—C(=O)—$X_i$—C(=O)]$_{n_A,m_B}$

consisting of the monomeric units ($M_A$ and $M_B$), and the masses of the end groups ($E_I$ and/or $E_{II}$) plus cationization agent ($M^+$).

The oligoesters described in this study were synthesized by condensation polymerization between 1,4-butanediol (BDO) and a mixture of adipic acid (AA) and isophthalic acid (IPA) or glutaric acid (GA) as shown in Table 1. For reasons of convenience the first system will from now on be denoted as AA-IPA whereas the latter will be denoted as AA-GA. Upon reaction, the diol and the two diacids form two new repeat units, A (containing BDO and AA) with a mass equal to $M_A$ and B (containing BDO and IPA or GA) with a mass equal to $M_B$. The formed oligoester may contain a number of different end groups as shown in Table 1.

Depending on the reaction conditions the polymer may contain predominantly two OH (structure **I**), two COOH (structure **III**), or one of each end group (structure **II**). Another possibility is the formation of cyclic structures (structure **IV**). As mentioned in the Experimental Section, in both polymerizations the diol was added in a molar ratio of 4:3 compared to the diacids, thus favoring the formation of polymer chains having two OH end groups (structure **I**, Table 1).

Figure 1a,b shows an overall impression of the MALDI−ToF−MS mass spectra for the two SLOs, whereas Figure 2 highlights a part of the mass spectrum with oligoester chains containing 6 repeat units. Inspection of Figure 2a,b and Table 2 indeed confirms that the most prevalent structure in both systems is the structure having two OH end groups.

Parts a and b of Figure 3, which give enlargements of parts a and b of Figure 1, demonstrate the part of the MALDI−ToF−MS mass spectra with low intensity peaks. Figure 3a,b combined with Table 2 indicate that in both systems oligoesters bearing both COOH and OH end groups (structure **II**, Table 1) are formed. Furthermore, there is some evidence for the formation of cyclic oligoesters (structure **IV**, Table 1).

**Copolymer Fingerprint.** Because of the complexity of having two different repeat units, the MALDI−ToF−MS mass spectra were examined by a copolymer fingerprint analysis as has been successfully outlined in our previous paper on the analysis of polystyrene-*block*-polyisoprene by MALDI−ToF−MS.[10] The computer program used to analyze the spectrum can only analyze one type of copolymer chain at the time. Although oligoesters with different end groups are present (Figure 3a,b), the copolymer fingerprint analysis was performed only on those oligoesters bearing two OH end groups (structure **I**, Table 1) as these have the highest intensities. For both SLOs, structure **I** can be considered as a copolymer consisting of two repeat units, i.e. $n_A$ units of repeat unit A (containing 1,4-butanediol and adipic acid) with mass $M_A = 200.236$ g mol$^{-1}$ and $n_B$ units of repeat unit B (containing 1,4-butanediol and isophthalic acid or glutaric acid), with masses $M_B = 220.225$ g mol$^{-1}$ or $M_B = 186.208$ g mol$^{-1}$, and two end groups $E_I = 89.11$ g mol$^{-1}$ and $E_{II} = 1.008$ g mol$^{-1}$. The MALDI−ToF−MS analysis was carried out with potassium ($M^+ = 39.098$ g mol$^{-1}$) as cation. With knowledge of these masses the computer program calculates the theoretical mass of a copolymer by using eq 1. The results of this analysis are shown in Figure 4a,b in which the MALDI−ToF−MS mass spectra for both SLOs are transferred to a matrix of $n_A \times n_B$ repeat units.

MALDI−ToF−MS as an analytical tool has proven itself as a robust tool for the determination of low polydisperse molecular weight distributions. Suddaby et al.[13] and Wilcek-Vera et al.[14] however demonstrated that average chemical compositions of copolymers determined by MALDI−ToF−MS can deviate from $^1$H NMR. Speculations regarding these observed differences are believed to be related toward mass discrimination due to differences in ionization efficiencies. In an investigation on oligoesters by Koster et al.[15] it was also

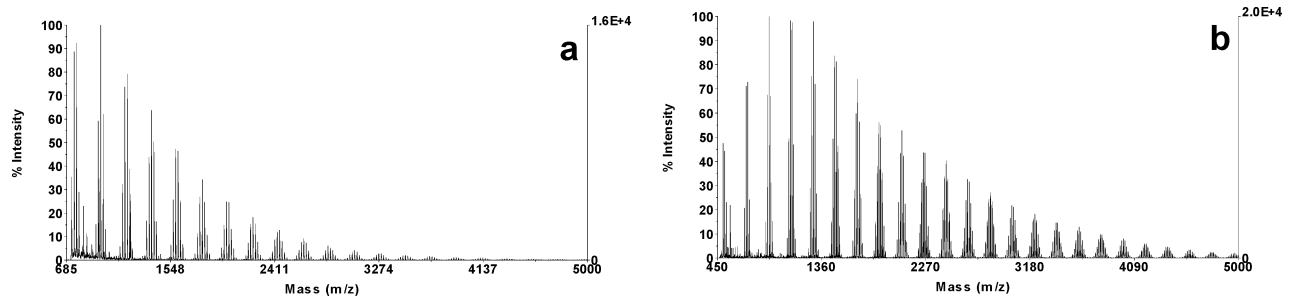


**Figure 1.** MALDI−ToF−MS mass spectra for the SLOs prepared from a condensation reaction between (a) 1,4-butanediol, adipic acid, and isophthalic acid (AA-IPA) and (b) 1,4-butanediol, adipic acid, and glutaric acid (AA-GA).

**Table 2. Theoretical and Experimental Mass of the Most Abundant Isotope for the Structures in Figure 2a,b and Figure 3a,b**

| AA-IPA | | | | AA-GA | | | |
|---|---|---|---|---|---|---|---|
| structure | $(n_{AA},n_{IPA})^a$ | $m_{th}{}^b$ [g mol$^{-1}$] | $m_{exp}{}^b$ [g mol$^{-1}$] | structure | $(n_{GA},n_{AA})^a$ | $m_{th}{}^b$ [g mol$^{-1}$] | $m_{exp}{}^b$ [g mol$^{-1}$] |
| I | (6−0) | 1329.66 | 1329.63 | I | (6−0) | 1245.57 | 1246.29 |
| I | (5−1) | 1349.63 | 1349.60 | I | (5−1) | 1259.58 | 1260.31 |
| I | (4−2) | 1369.60 | 1369.57 | I | (4−2) | 1273.60 | 1274.34 |
| I | (3−3) | 1389.56 | 1389.53 | I | (3−3) | 1287.61 | 1288.36 |
| I | (2−4) | 1409.54 | 1409.51 | I | (2−4) | 1301.63 | 1302.38 |
| I | (1−5) | 1429.50 | 1429.48 | I | (1−5) | 1315.65 | 1316.40 |
| I | (0−6) | 1449.47 | 1449.45 | I | (0−6) | 1329.66 | 1330.43 |
| I | (7−0) | 1529.77 | 1529.75 | I | (7−0) | 1431.66 | 1432.49 |
| I | (6−1) | 1549.74 | 1549.71 | II | (5−2) | 1387.65 | 1388.85 |
| II | (5−2) | 1497.65 | 1497.66 | II | (4−3) | 1401.65 | 1402.49 |
| II | (4−3) | 1517.61 | 1517.61 | II | (3−4) | 1415.66 | 1416.52 |
| II | (3−4) | 1537.58 | 1537.56 | IV | (5−2) | 1369.62 | 1370.43 |
| II | (2−5) | 1557.55 | 1557.55 | IV | (4−3) | 1383.64 | 1384.45 |
| IV | (4−3) | 1499.60 | 1499.63 | IV | (3−4) | 1397.65 | 1398.48 |
| IV | (3−4) | 1519.57 | 1519.62 | IV | (2−5) | 1411.67 | 1412.49 |

[a] The symbols between the brackets refer to the number of repeat units containing adipic acid ($n_{AA}$), isophthalic acid ($n_{IPA}$) or glutaric acid ($n_{GA}$), respectively. [b] The theoretical and experimental masses include the mass of the cation Potassium.

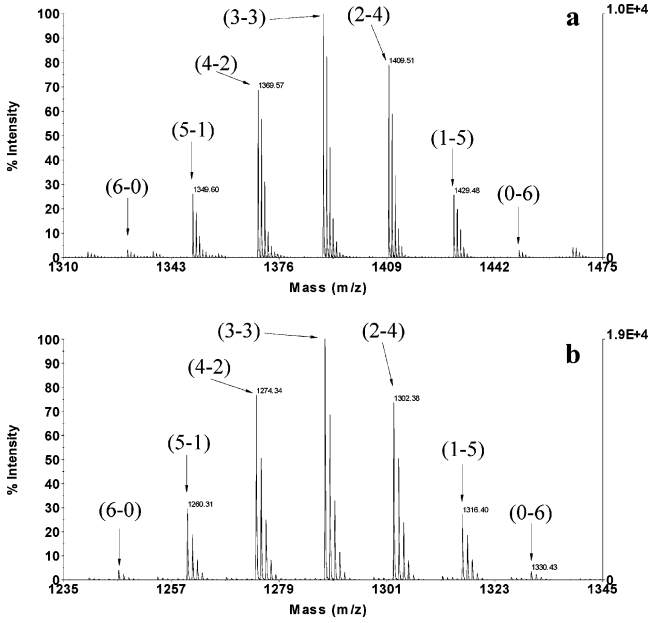


**Figure 2.** Enlargement of Figure 1 for the system AA-IPA (a) between 1310 and 1475 g mol$^{-1}$ and the system AA-GA (b) between 1234 and 1345 g mol$^{-1}$ showing oligoester structures bearing two OH end groups (Table 1, structure **I**) and the number of repeat units equal to 6. The numbers between brackets refer to (a) the amount of AA ($n_{AA}$) vs IPA ($n_{IPA}$) incorporation and (b) the amount of GA ($n_{GA}$) vs AA ($n_{AA}$) incorporation. Theoretical and experimental masses are given in Table 2.

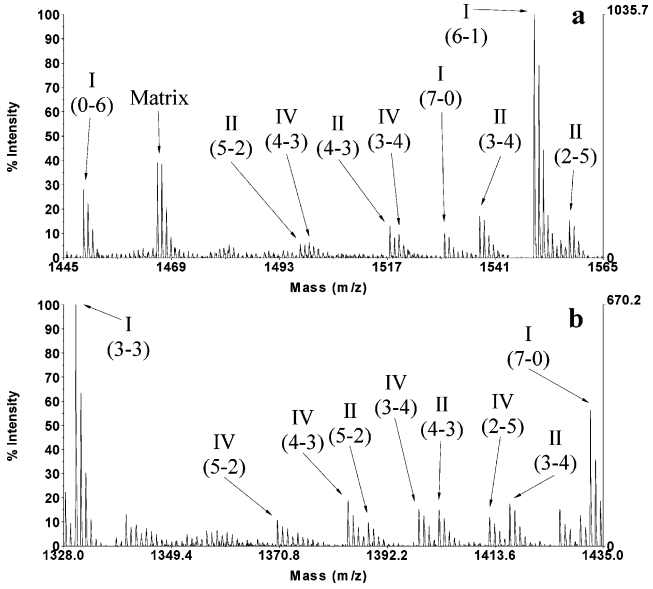


**Figure 3.** Enlargement of Figure 1a,b, respectively, for (a) the system AA-IPA between 1445 and 1565 g mol$^{-1}$ and (b) the system AA-GA between 1328 and 1435 g mol$^{-1}$ identifying oligoesters having both COOH and OH end groups (Table 1, structure **II**) and cyclic structures (Table 1, structure **IV**). The numbers between brackets refer to (a) the amount of AA ($n_{AA}$) vs IPA ($n_{IPA}$) incorporation and (b) the amount of GA ($n_{GA}$) vs AA ($n_{AA}$) incorporation. Theoretical and experimental masses are given in Table 2. Note that the intensity scale is approximately 5−10% of the scale of Figure 2a,b.

observed that the intermolecular structure of an oligoester could have a severe effect on the ionization efficiency when analyzing the oligoesters with an electron-spray-ionization Fourier transform ion-cyclotron-resonance mass spectrometer (ESI FT-ICR MS). On the other hand, both Montaudo et al.[16] and our previous results[10] show that chemical compositions obtained by MALDI−ToF−MS can be successfully compared to $^1$H NMR. Interestingly to note is that the system studied by Montaudo et al. is rather similar to the systems studied in this work On the basis of the entire copolymer fingerprint in Figure 4a,b, the average chemical composition of repeat unit A (containing AA) can be calculated[10] which was determined to be 49.8% for both systems. This is in excellent agreement with the average composition based on the recipe (49.9% and 50.0% incorporation of repeat unit A for the systems AA-IPA and AA-GA, respectively), indicating that mass discrimination due to differences in ionization efficiency do not seem to play a role for these systems. Further proof of the equal incorporation of the two diacids for the system AA-IPA was verified by $^1$H NMR. The proton NMR spectra for AA-GA and AA-IPA are given in Figure 5. For AA-IPA, the ratio of the sum of the integral for the peaks i, j, and k against the integral of the peak e is 0.99, and the integrals for the peaks h and d are the same, both confirming that the two acids (AA and IPA) are equally incorporated into the AA-IPA polymer during condensation polymerization.

As the copolymer fingerprints in Figure 4a,b are symmetrically located along the diagonal, they seem to suggest that the chemical composition is independent of the chain length. To further demonstrate this, the

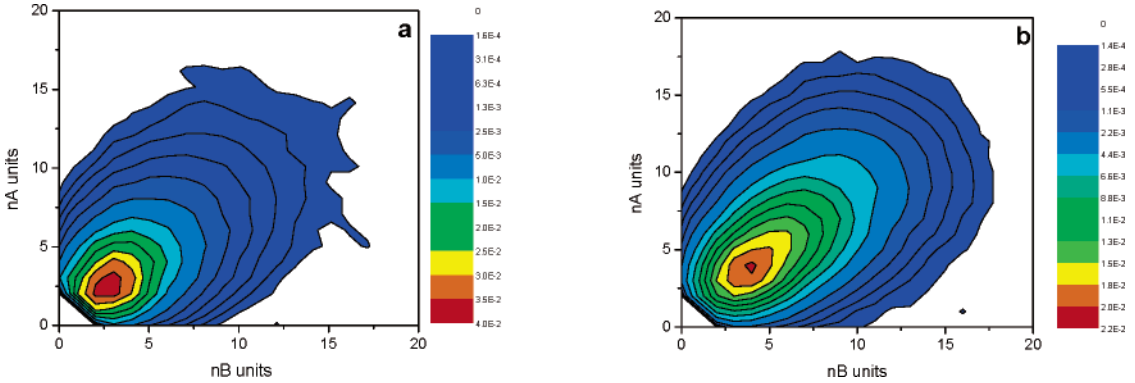


**Figure 4.** Copolymer fingerprint for the solventless liquid oligoesters considering only oligoester chains containing two OH end groups (Table 1, structure **I**) for the system AA-IPA (a) and the system AA-GA (b).

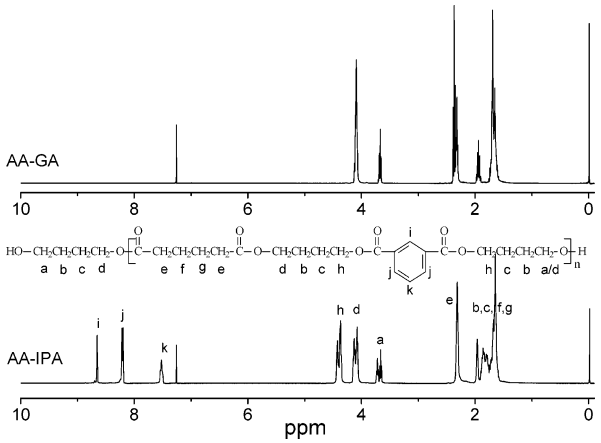


**Figure 5.** $^1$H NMR spectra for polymers AA-GA and AA-IPA.

average chemical composition as a function of the copolymer chain length was evaluated from the obtained copolymer fingerprints. The results of this can be observed in Figure 6a,b, and indeed, Figure 6a,b clearly demonstrates that the chemical composition is independent of the chain length.

**Copolymer Microstructure.** Insight into the copolymer microstructure can result in a better understanding of the underlying polymerization mechanisms. The polymer microstructure can be studied using Bernoullian and Markovian chain statistics.[17,18] The Bernoullian chain statistics are used to model random copolymerizations, whereas Markovian chain statistics allow the modeling of both random and nonrandom copolymerization reactions. If it is assumed that the repeat units are randomly distributed over the copolymer, then the polymer microstructure may be described by Bernoullian chain statistics.

According to Bernoullian chain statistics, the polymer microstructure is solely dependent on the feed composition. The Bernoullian chain statistics state that the chance of finding $n$A units, given the polymeric structure $A_nB_m$, is given by

$$P(n\mathrm{A}|\mathrm{A}_n\mathrm{B}_m) = \frac{(n+m)!}{n!m!}[\mathrm{A}]^n[\mathrm{B}]^m \qquad (2)$$

in which [A] and [B] refer to the feed concentrations of units A and B. In the case of the oligoesters, the concentrations [A] and [B] refer to the adipic acid and isophthalic acid or glutaric acid concentrations, respectively.

Figure 7a−d compares the chemical composition distribution as obtained from a MALDI−ToF−MS experiment with the Bernoullian chain statistics for four different chain lengths. As can be observed from Figure 7a−d, the MALDI−ToF−MS experiments are in excellent agreement with the Bernoullian chain statistics for both SLOs. This good correlation is further supported by Figure 8a,b where the $R^2$ values are listed as a function of chain length for both SLOs. Good correlations are found for chain lengths up to a chain length of 25. The reason for the decreasing $R^2$ values at the higher chain lengths is related to the lower signal-to-noise ratio at the higher end of the spectrum (a chain length of 20 units corresponds to a mass of approximately 4000 g mol$^{-1}$). The good agreement between the

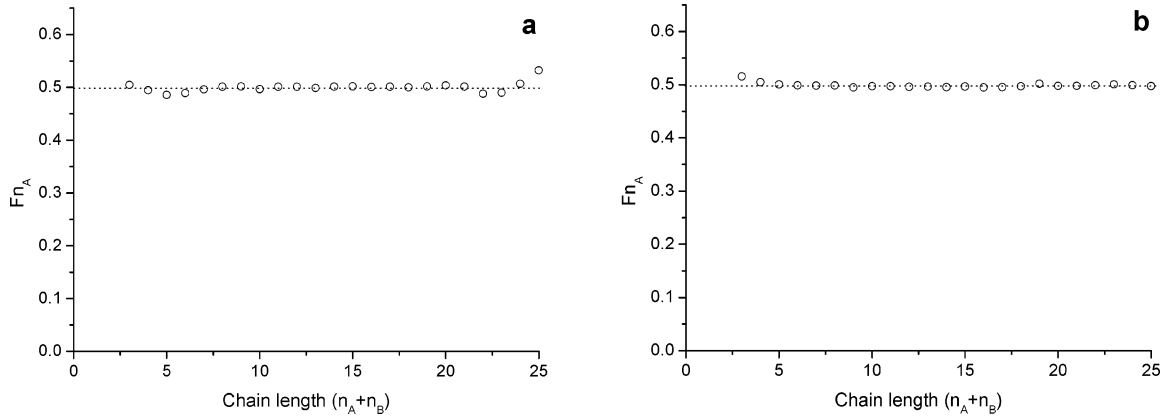


**Figure 6.** Chemical composition ($Fn_A$, ○) of repeat unit A (containing AA) as a function of chain length ($n_A + n_B$) obtained from the copolymer fingerprint for the SLO systems AA-IPA (a) and AA-GA (b). The dotted line indicates the feed composition of the diacids, which were added in equimolar amounts.

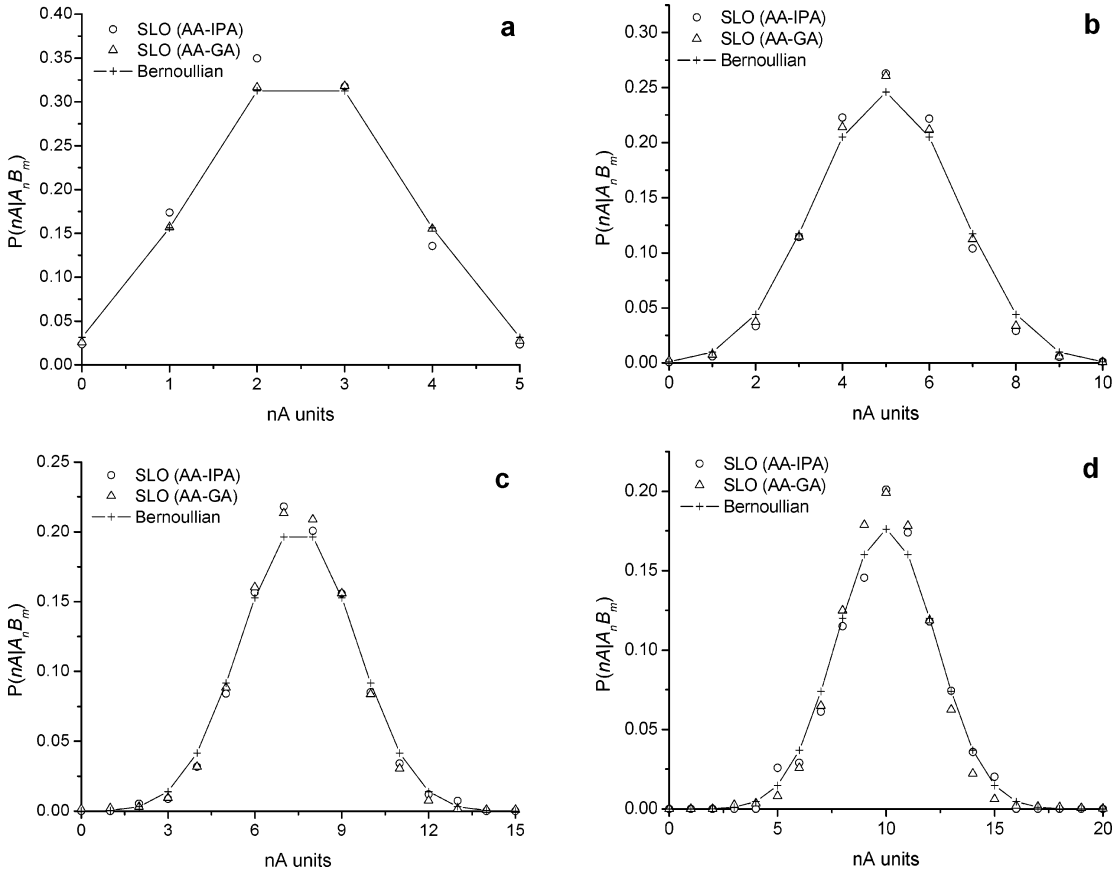


**Figure 7.** Normalized oligoester chemical composition distributions obtained by MALDI−ToF−MS for the systems AA-IPA (○) and AA-GA (△) compared to Bernoullian chain statistics (− + −) evaluated at oligoester chain lengths of 5 (a), 10 (b), 15 (c), and 20 (d) repeat units.

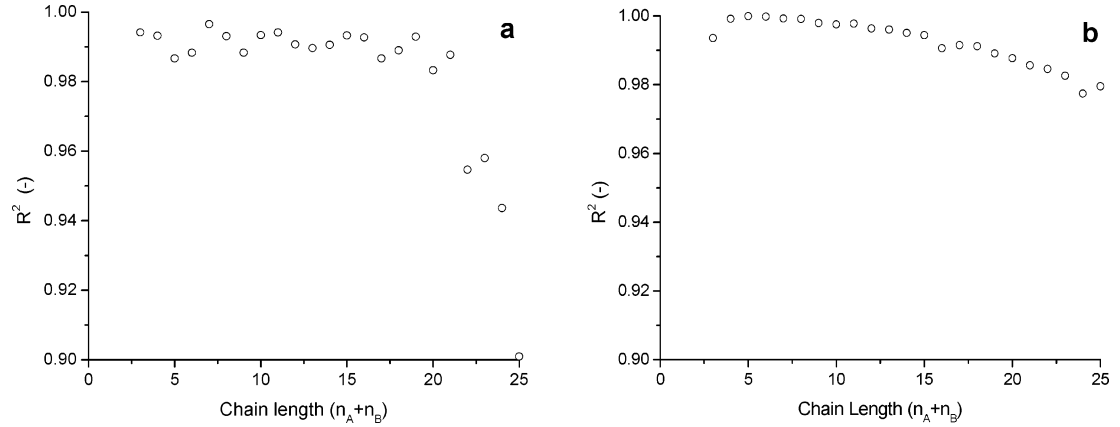


**Figure 8.** $R^2$ values calculated from the comparison between normalized MALDI−ToF−MS chemical composition distributions and Bernoullian chain statistics for the system AA-IPA (a) and the system AA-GA (b) indicating a good correlation between the model and the measurements.

microstructural investigation by MALDI−ToF−MS and Bernoullian chain statistics therefore suggests that the diacids are randomly distributed over the copolymer which may be due to either negligible influences of the reactivity of the diacids, or due to successful transesterification (or a combination of the two).

## Conclusion

MALDI−ToF−MS is a powerful tool in the analysis for copolymers. Not only does it allow for a detailed investigation into the end groups but also it can be successfully applied to get insight into polymer microstructure as has been demonstrated in this paper.

The oligoesters studied in this article were synthesized from 1,4-butanediol, adipic acid, and glutaric acid or isophthalic acid and further analyzed by MALDI−ToF−MS. The results in this paper clearly demonstrate that MALDI−ToF−MS does not necessarily suffer from differences in ionization efficiencies. This was verified by the average chemical compositions determined by MALDI−ToF−MS which clearly reflected the composition of the reaction mixture. Further proof was obtained by comparing the average chemical composition for the system 1,4-butanediol, adipic acid and isophthalic acid to $^1$H NMR. By analyzing the microstructure of the obtained copolymers it was verified that the diacid monomers are randomly distributed along the copolymer as the microstructure could be described using Bernoullian chain statistics.

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