

Matrix-assisted laser desorption/ionization behavior of neat linear and cyclic poly(L-lactide)s and their blends

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Rationale: Numerous new tin catalysts that enable the synthesis of cyclic poly(lactides) with broad variation in their molecular mass were recently developed. The abundance of cyclics in matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra is, however, frequently reported to greatly exceed that of linears. Thus, the MALDI ionization behavior of various end-capped linear poly(L-lactide)s and one cyclic poly(L-lactide) was investigated and compared.

Methods: Neat compounds and various blends of cyclic and linear species were prepared and studied under identical conditions with regard to sample preparation and instrumental condition, except for the laser power. For this purpose, two different MALDI-TOF mass spectrometers were applied.

Results: Our results reveal that cyclics indeed show a slightly better ionization in MALDI, although their ionization as a neat compound seems to be less effective than that of linear poly(lactides). The ionization of most linear poly(lactides) investigated does not depend on the end group structure. However, linear poly(lactides) containing 12-bromododecyl end groups reveal an unexpected saturation effect that is not caused by fragmentation of the polymer or the end group, or by electronic saturation of the detector digitizer. Furthermore, poly(lactides) with a 2-bromoethyl end group did not show such a saturation effect.

Conclusions: An overestimation of cyclic species in MALDI-TOF mass spectra of poly(L-lactide)s must be considered, but the commonly assumed peak suppression of linear polymers in mixtures of both structures can be excluded.

1 | INTRODUCTION

Since its introduction in the early 1990s, matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) has suffered from its inability to provide quantitative results. Peak discrimination is a common problem in MALDI, especially when mixtures of compounds are measured. Synthetic polymers can be regarded as a kind of mixture because they always consist of various long polymer chains with different degrees of polymerization

and molar mass, which is referred to as molar mass distribution (MMD). Moreover, they often exhibit an additional chemical heterogeneity distribution, expressed by different end groups and other structural variations (e.g., tacticity and copolymer composition). Apart from these structural variations, other effects caused by sample preparation issues (e.g., matrix and cationizing salt) and instrumental parameters (laser power) significantly influence the ionization/desorption step in MALDI and need to be considered too.

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Only a few examples shall be given to highlight the complexity of ionization in a MALDI instrument. Compared with molar mass and MMD data provided by size-exclusion chromatography (SEC), MALDI spectra often exhibit mass distributions with narrower dispersities and show a loss of peak intensity in the higher mass regions.¹ This indicates a mass-dependent ionization behavior and/or a mass-dependent detector sensitivity. Thus, when blends of lower- and higher-mass polymers with identical structures were investigated, the ionization of higher-mass homologous often seemed to be discriminated against.² A variation in the matrix or the addition of different cationization agents (salts) can change these results. Examples on how the matrix choice affects the molecular weight distribution and the analysis of mixtures of polymers having different masses have been presented by several groups. Matrix vaporability and ionization efficiency, crystallinity, and homogeneity of matrix/sample spots were found to affect the quality of spectra.³⁻⁷ Likewise, the influence of the cationizing agent was a matter of investigation from the early MALDI beginnings.^{8,9} Often these salts were added to enable better end group differentiation in complex spectra. It was also reported, however, that the variation in dopants due to different cationization efficiency changed the intensity of the original polymer distribution and shifted its maximum.^{2,10} An attempt to optimize the MALDI-TOF MS sample preparation of polymers was made by a statistical design of experiments, which focused on a variation in matrix, matrix/sample ratio, peak resolution, and signal-to-noise ratio (S/N).⁶ Others showed that the molar mixing ratio of several polymers depends not only on the matrix/polymer combination but also on the solvent.¹¹ The influence of the applied laser energy was also a matter of investigation.¹²

As mentioned before, other important issues caused by the polymer structure must also be considered. Soon after MALDI was introduced for polymer analyses, it became clear that the ionization efficiency strongly depends on the nature of the polymer end group, even when the structure of the repeating units is identical.¹³⁻¹⁵ This is important when polymer degradation that often results in various products with different end groups is investigated. Here, the use of liquid chromatographic techniques (especially chromatography at the “critical” point of adsorption) in combination with quantitative detectors often shows a mismatch with MS results, which is expressed by an overestimation or suppression of lactides in MALDI spectra.^{16,17} Many polymer synthesis processes (e.g., reversible addition-fragmentation transfer polymerization – RAFT, and ring-opening polymerization – ROP) reveal side reactions (e.g., hydrolysis, termination by the solvent, ring-chain equilibrium, cyclization by intramolecular back-biting) that also result in a formation of different polymer end groups, including ring formation.¹⁸⁻²⁵ For example, it was reported that the ion intensities of α - and β -cyclodextrins were much larger than those of the linear ones (maltohexaose and maltoheptaose).²⁶ Moreover, differences in ionization efficiencies between α - and β -cyclodextrins showed an additional effect caused by the size of the alkali metal cation. It was supposed that the number of coordination sites and the binding energies were responsible for these effects.

Determining and quantifying cyclic polymers is a major problem in the synthesis and analysis of polymers. A general opinion is that cyclic

polymers exhibit a much higher ionization tendency, as demonstrated in an early paper dealing with mixtures of cyclic and linear polyethylene terephthalate (PET) oligomers.²⁷ Even after complete chromatographic separation of cyclic structures from linear structures, the cyclic structures will be regenerated in the bulk material (e.g., in PET bottles) due to thermodynamic reasons.

Cyclic polymers can be intentionally synthesized via ring-expansion polymerization (REP) of cyclic monomers (e.g., lactides and ϵ -caprolactone).^{28,29} As in any other polycondensation, typically dispersities $\bar{D} \geq 2$ are obtained. These values are too high for a reliable MALDI-TOF MS analysis because both instrumental and desorption/ionization issues cause a mass discrimination of polymer species.³⁰⁻³³ Combined with the aforementioned assumed overestimation of cyclic polymer species, using MALDI-TOF MS to reliably determine the exact amount of cyclic or linear polymers in mixtures is problematic. Thus, it is important to know the structure-dependent MALDI response of linear and cyclic polymers and their mixtures, especially when cyclic structures predominate in MALDI-TOF mass spectra.

In this paper we describe a systematic investigation of linear poly(L-lactide)s synthesized by ROP and their mixtures with cyclic poly(L-lactide)s obtained by REP. The MALDI responses of both neat polymers and mixtures were determined at different laser energies in linear, and particularly, reflectron modes.

Poly(L-lactide)s were selected for this study for two reasons. First, polylactide is an important, technically produced, biosourced, and biodegradable material. Second, we have recently developed numerous new tin catalysts that enable the synthesis of cyclic polylactides with broad variation in molecular mass, so that cyclic and linear polylactides with similar low molecular masses and molecular mass distributions are accessible.³⁴⁻³⁷

2 | EXPERIMENTAL

2.1 | Materials

L-Lactide (TCI Chemicals, Eschborn, Germany) was recrystallized from “Toluene 99.89% extra dry” purchased from ACROS Chemicals (Geel, Belgium). Tin(II)-2-ethylhexanoate (SnOct₂), 4-nitrobenzylalcohol, and benzylamine were purchased from Alfa Aesar (Karlsruhe, Germany) and used as received. Cyclic polylactide was prepared using spirocyclic catalysts, tin(IV) *tert*-butoxide and 2,2'-dihydroxy-1,1-bisnaphthol, as described previously.³⁷

2.2 | Syntheses of poly(L-lactide)s

2.2.1 | 4-Nitrobenzylalcohol, 11-undecenol, and 12-bromododecanol as initiator

4-Nitrobenzylalcohol (0.1 mmol) was weighed into a flame-dried 50-mL Erlenmeyer flask, and L-lactide (50 mmol) was added under a blanket of argon. A 0.5 M solution of SnOct₂ in toluene (0.1 mL) was then injected using a syringe. The reaction vessel was closed with a

glass stopper and steel spring and immersed in an oil bath preheated to 120°C. After 6 h, when the entire reaction mixture had solidified, the polylactide was broken into pieces with a spatula and removed from the reaction vessel.

The polymerizations initiated with 11-undecanol, bromoethanol, and 12-bromododecanol were performed analogously. The neat alcohols were weighed into the Erlenmeyer flask.

2.2.2 | Benzylamine as initiator

L-Lactide (50 mmol) was weighed under argon into a 50-mL Erlenmeyer flask, and a 5 M solution of benzylamine (0.2 mL) and a 0.5 M solution of SnOct₂ in toluene (0.1 mL) were injected with a syringe. The polymerization was performed as described earlier.

2.2.3 | Cyclic poly(lactide)

SnNaph₂ (0.5 mmol) was weighed into a 50 mL Erlenmeyer flask; L-lactide (50 mmol) and a magnetic stirring bar were added under a blanket of argon. The polymerization was performed at 120°C for 20 h, and the solid polylactide was mechanically isolated.

All poly(L-lactide)s were stored and characterized without purification for two reasons. First, dissolution and precipitation enhance the risk of hydrolysis because a larger surface is created. Second, in the case of cyclic polylactides, cleavage of one single bond per molecule suffices to change the structure from cyclic to linear.

2.3 | Nuclear magnetic resonance spectroscopy

¹H nuclear magnetic resonance (NMR) data of cyclic and linear polylactides were recorded using a Mercury-400 (MHz) NMR spectrometer (Varian, Palo Alto, CA, USA) and are shown in Figure S1 (supporting information). Samples were dissolved in CDCl₃ and measured with a relaxation delay of 2 (resp. 10). Thirty-two (resp. 64) scan repetitions were performed. To determine molecular masses, the integrals of characteristic bands of end group protons (-CH₂-O-, 4.4 ppm; CH₂-Br, 3.4 ppm; aromatic protons, 8.2 ppm) were related to those of the polymer unit (CH 5.2, ppm; CH₃ 1.6 ppm).

2.4 | SEC

SEC was performed using a modular system consisting of an isocratic pump (1 mL min⁻¹) and a refractive index detector (RI-501-Shodex, Munich, Germany) at 40°C. Chloroform was used as eluent. Samples were manually injected (100 μL, 2–4 mg mL⁻¹). For instrument control and data calculation, Clarity software (GPC extension, DataApex, Prague, Czech Republic) was used. The calibration was performed using polystyrene standard sets (Polymer Standards Service – PSS, Mainz, Germany).

2.5 | MALDI-TOF MS/laser adjustment

Two mass spectrometers (Autoflex Smartbeam and Autoflex Max, both from Bruker Daltonik, Bremen, Germany) were used for all investigations. Spectra were recorded in linear mode at 200 Hz (Autoflex Smartbeam) and 2000 Hz (Autoflex Max) laser shot rate. DCTB (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene] malononitrile, 10 mg mL⁻¹, tetrahydrofuran–THF) was used as a matrix and doped with potassium trifluoroacetate (KTFA 2 mg mL⁻¹, THF) to selectively enable the formation of potassium adduct ions. About 50 μL of the matrix solution was pre-mixed with 20 μL of dissolved polylactides (3 mg mL⁻¹, chloroform) (v/v). Finally, 1 μL of this solution was deposited on a stainless-steel target. Multiple spots of each mixture were prepared. About 2000 single spectra recorded on different positions of each spot were accumulated for one spectrum. This procedure was repeated three times for every single experiment using fresh spots. Experimental (concentration, mixing ratio, etc.) and instrumental conditions (voltages, delay time, peak suppression, etc.) were kept constant for all experiments, except for the laser energy, which varied from 10% to 50%. Because a frequency-tripled Nd:YAG laser (355 nm) with a structured focus profile (Smartbeam, Bruker Daltonik) was used, absolute laser energy values cannot be given.³⁸

The average molecular masses were calculated using the instrument software PolyTools (Bruker Daltonik) at two different laser intensities (30% and 40%). They showed only minor differences (maximum one monomer unit mass) and are compared with SEC and NMR mass data in Table S1 (supporting information).

A compilation of measured and experimentally obtained MALDI masses of all investigated polylactides is shown in Table S2 (supporting information).

3 | RESULTS AND DISCUSSION

3.1 | Cyclic and linear poly(L-lactide)s

To avoid an additional influence of the molecular masses on the ionization behavior, polylactides with almost-identical masses and narrow dispersities were synthesized and used for the experiments. SEC measurements confirmed narrow dispersities but showed higher molecular masses especially of linear polymers (see Figure S2, supporting information). This, however, is not surprising, because the hydrodynamic volume of linear polylactides differs significantly (+30%) from that of the polystyrene standard used for calibration.³⁹ On the contrary, recent investigations have also shown that the hydrodynamic volume of cyclic polylactides is comparable with that of polystyrenes.⁴⁰ Figure 1 shows a series of MALDI-TOF mass spectra of cyclic poly(L-lactide) and two linear analogues capped with 4-nitrobenzylalcohol and benzylamine recorded at different laser energies. All spectra exhibited a main distribution with peak-to-peak distances of 72 *m/z* units and a second, less-intense peak distribution (again with 72 *m/z* unit distances). These two series can be attributed

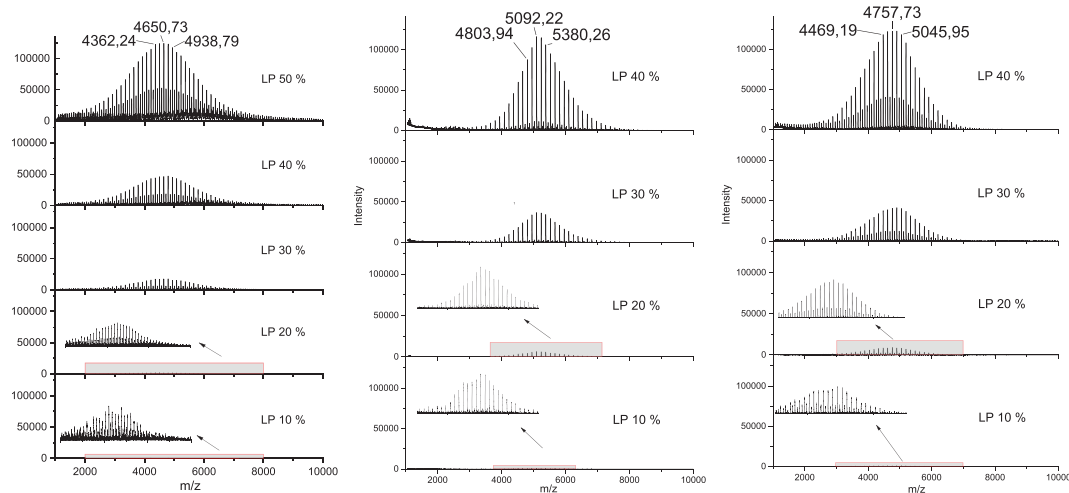


FIGURE 1 MALDI-TOF mass spectra of (left) cyclic poly(L-lactide), (middle) 4-nitrobenzylalcohol-capped linear, and (right) benzylamine-capped linear poly(L-lactides) at different laser energies [Color figure can be viewed at wileyonlinelibrary.com]

to polylactides with even (main product) and odd numbers of monomer units formed by transesterification during polymerization.⁴¹ Due to the addition of potassium trifluoroacetate as dopant, in all spectra only singly charged K^+ adduct ions were found.

Spectra could already be recorded for all polymers independent of their individual structure at 10% laser energy. As shown in the insets of Figure 1, these spectra are very noisy and are of very low intensity. Thus, this laser intensity can be regarded as shortly above the threshold energy necessary for sufficient ionization of these polymers. Interestingly, the intensity of cyclic polylactides in general is lower than that of the linear polylactides. Considering the value of the most intense peak of each distribution, similar peak intensities could be obtained at 50% laser energy for cyclic polymers, whereas they could already be observed at 40% laser energy for both linear species. This point is in contrast to the often-expressed opinion that cyclic species a priori reveal better ionization behavior in MALDI, which results in an overestimation of cyclic species in mixtures. A possible reason might be the end group structure of linear polylactides. Both linear polymers contain aromatic end groups, which might be able to coordinate cations in a sandwich structure.

Such a behavior is considered to be responsible for the ionization of polystyrenes by silver cations. However, it is still not clear where exactly adduct ion formation occurs in a polymer chain. Some data show that the ionization of nonpolar polymers (e.g., waxes and oligo ethylene) proceeds much better or becomes possible in the first place after the introduction of a polar end group.⁴²⁻⁴⁴ Likewise, an increasing polarity by modification of nonpolar double bonds improved the quality of MALDI spectra significantly.⁴⁵ As already mentioned, an influence of chain end groups was described by Montaudo and co-workers for blends of nylon 6 and hydroxyl-terminated polybutyleneterephthalate (PBT). However, their investigations were carried out using low mass oligomers (< 2000 Da).^{14,46} Therefore, a possible influence of end groups on the ionization behavior of poly(L-lactide)s was checked by an additional series of experiments involving linear polymers with rather nonpolar end groups. The corresponding MALDI spectra are shown in Figure 2.

Again, MALDI-TOF mass spectra beginning at 10% laser energy were obtained. Their intensity increased with increasing laser intensity. These data are summarized in Figure 3, where the means of maximum peak intensities (three measures) of all investigated

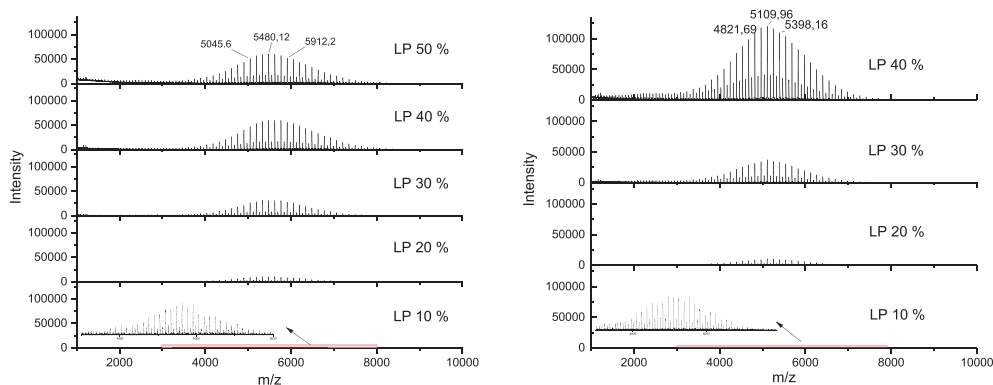


FIGURE 2 MALDI-TOF mass spectra of (left) 12-bromododecanol-capped linear and (right) 11-undecenol-capped linear poly(L-lactides) at different laser energies [Color figure can be viewed at wileyonlinelibrary.com]

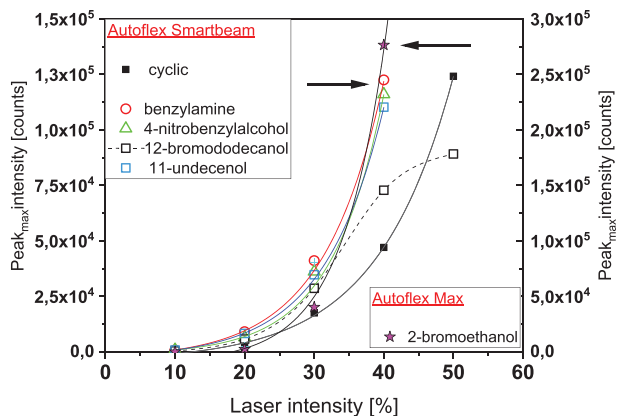


FIGURE 3 Peak intensities (peak max distribution) of cyclic and linear end-capped poly (L-lactide) depending on the laser intensities (averaged values of three single measurements) measured with two different mass spectrometers [Color figure can be viewed at wileyonlinelibrary.com]

linear and cyclic polyactides were plotted versus the laser intensities varying from 10% to 50%. In Figures S3A–S3D (supporting information) the data of Figure 3 are presented for each linear polyactide, revealing the individual deviations. Laser energies higher than 50% were not used, because at these values a complete ablation of sample/matrix material was observed. At first glance, the results clearly contradict a possible end group influence. The peak intensities of the linear 11-undecenol-capped polymer are almost identical to those of the two polymers having aromatic end groups. A similar behavior can also be found for the 12-bromododecanol-capped linear species up to a laser energy of 30%. At higher laser energies a deviation from other linear polymers was found to begin, indicating a saturation effect. Apart from a supposed end group effect changing the ionization in general, other processes might also contribute. In an earlier paper of McCullough and co-workers dealing with MALDI-TOF MS of poly (alkylthiophene)s, fragmentation of bromine end groups depending on the laser power was reported.⁴⁷ This fragmentation

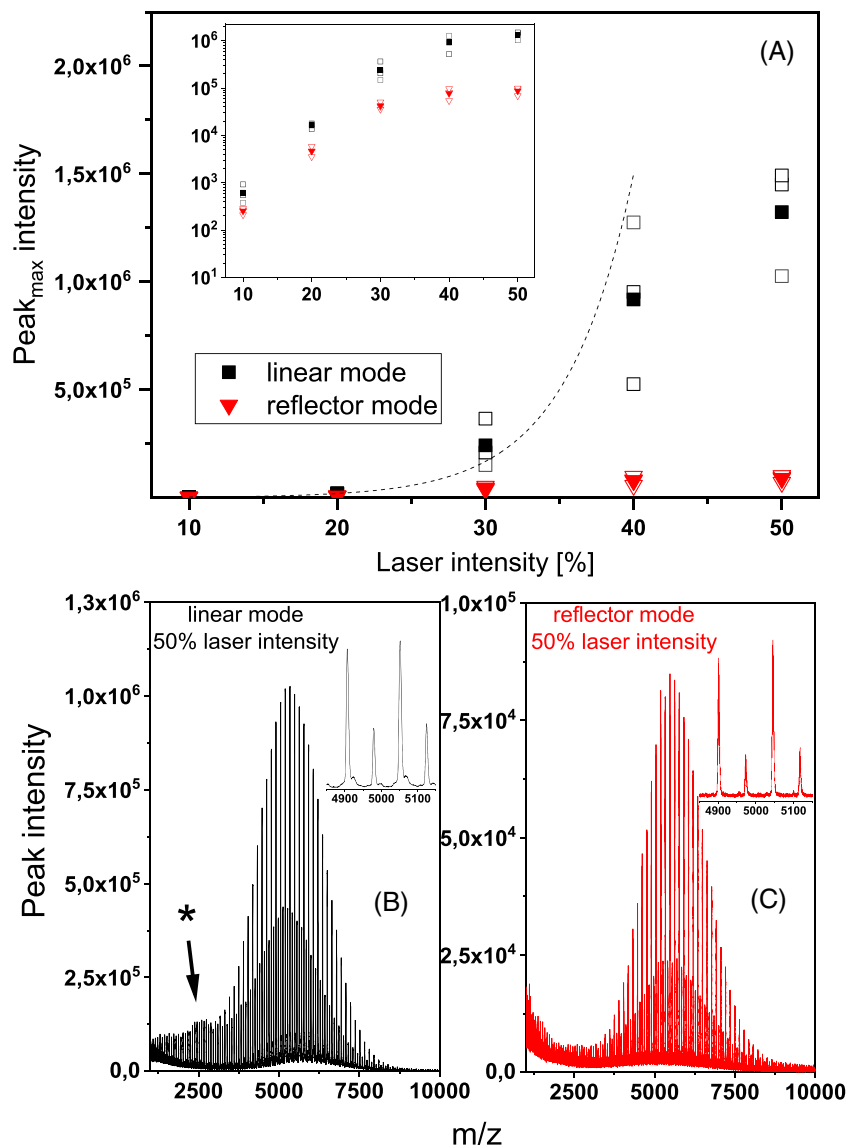


FIGURE 4 Peak intensity of linear 12-bromododecanol end-capped poly(L-lactide) at higher laser intensity measured in A, linear and reflector mode and B and C, MALDI-TOF mass spectra recorded in both modes at 50% laser energy; the inset in (A) shows data plotted in log scale [Color figure can be viewed at wileyonlinelibrary.com]

occurred especially at the shorter polymer chains, whereas longer chains remained widely unaffected, because these chains were able to disperse the energy over a greater number of bonds.

A similar effect could be caused by the bromine itself. However, a shift in the molecular mass distribution due to fragmentation (in source) was not observed. Likewise, a peak shift caused by a formation of allyl bonds due to a loss of bromine (or HBr), as reported by other groups, could not be found in mass spectra recorded in linear mode.^{48,49} Therefore, additional measurements were performed at higher laser energy (50%) in linear and reflector modes using the Autoflex Max mass spectrometer. As shown in Figure 4A the previously found deviation from exponential behavior, indicated by the dashed line, was again observed. This deviation became more evident at even higher laser energy of 50%. The corresponding MALDI-TOF mass spectrum is shown in Figure 4B. Only a very small region, indicated by an asterisk, might indicate the formation of a small number of fragments formed in the source of the instrument at comparatively high laser energies. Because additional fragmentation can also occur during the flight in the drift tube (post-source decay) our experiments with bromine end-capped linear poly lactides were repeated in the reflector mode of the instrument. The data, shown in Figure 4C, clearly exclude the formation of fragments generated by in- and post-source decay. Additional peaks caused by polymer fragments or by end group separation and other non-resolved peaks characteristic for the occurrence of metastable ions were not detectable. The deviation from exponential increase of signal intensities at higher laser energies could also be observed at lower intensity level in the reflector mode. This becomes much more visible in the inset showing a log scale plot. Moreover, the shape of the mass distribution curves and its maximum (m/z 5343 in linear and 5477 in reflector mode) and the ratio of typically found even- and odd-numbered poly lactides were almost identical in both modes. This rather supports our assumption of a possible dissipation of an excess of laser energy by the bromine atoms. To check this unexpected behavior, another linear poly lactide with bromine-containing end groups (2-bromoethanol-capped) was investigated. Here, the bromine atom was located close to the polymer backbone in contrast to the 12-bromododecanol-capped end group structure, where the bromine is located at the end of a long aliphatic structure ($-C_{12}H_{14}-Br$). Surprisingly, data shown in Figure 3 (right ordinate) did not reveal any peak saturation. Although measured on a different instrument (Autoflex Max) with different instrumental conditions, the exponential increase in the peak intensities matched well with the curves of other linear poly lactides obtained previously with the Autoflex Smartbeam instrument. Likewise, the corresponding MALDI-TOF mass spectra recorded at these high laser energies in both linear and reflector modes (see Figure S4, supporting information) did not show any peaks caused by fragmentation due to an excess of laser energy. In addition to the expected 2-bromoethanol end group series, a second, less intense peak series that could be attributed to linear hydroxyl-terminated poly lactides was found. Because these additional peaks could already be observed at lower laser intensities, their formation by fragmentation of the bromoethanol end group is rather unlikely. They

were probably formed as byproducts in the polymerization process or formed afterward by hydrolysis of bromoethanol end groups.

Our results indicate that the ionization of linear poly lactides in the investigated mass range is not affected by the end group structure and thus does not occur at the end groups of linear poly lactides (with one exception). The postulated dissipation of excess laser energy by bromine seemed to occur only when bromine is part of a long aliphatic end group structure. Poly lactides with brominated short-chain end groups (bromoethanol) or long aliphatic end groups (undecanol) without bromine did not reveal a comparable behavior. Future systematic investigations are intended to shed more light on the nature of this process.

3.2 | Blends of cyclic with linear poly(L-lactide)s

Based on these results, four blends consisting of cyclic and different linear poly lactides were prepared and investigated with regard to their intensity ratio at various laser energies. The first blend was composed of cyclic and linear 11-undecenol-capped poly lactides. The results are displayed in Figures 5 and 6 (MALDI mass spectra are shown in Figure S5, supporting information). As shown in Figure 3, the intensity of both linear and cyclic species in a blend again exponentially increases with increasing laser energies. In contrast to the

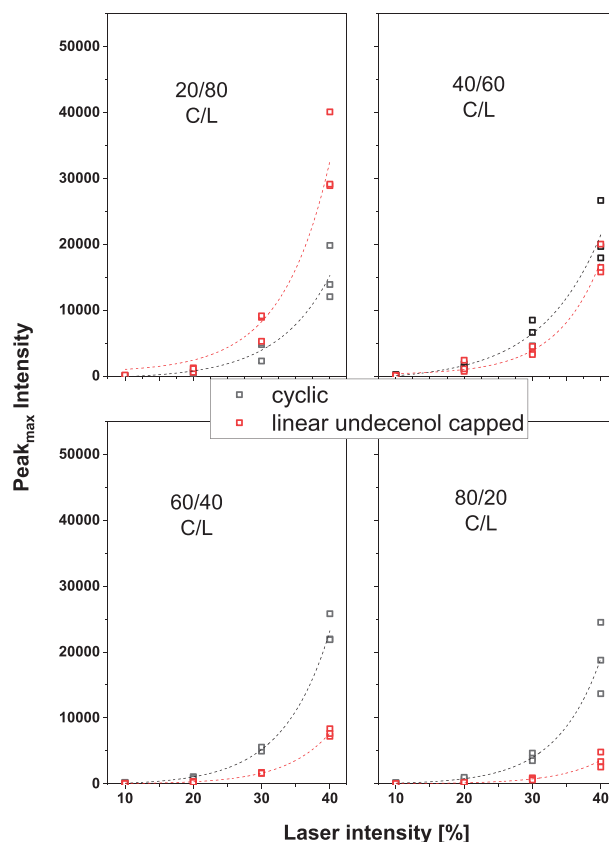


FIGURE 5 Peak intensities of four blends of cyclic and linear 11-undecenol-capped poly lactides (exponential fitting of mean values of three measurements) [Color figure can be viewed at wileyonlinelibrary.com]

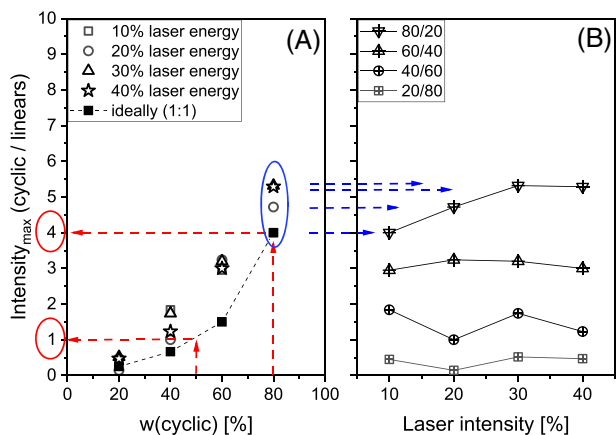


FIGURE 6 Intensity ratio of cyclic and linear undecenol-capped polyactides of four blends versus the amount of cyclic species in the mixtures (for better comparison a graph showing an “ideally” 1:1 response of both species is plotted, dotted line) (A) and at different laser intensities (B) [Color figure can be viewed at wileyonlinelibrary.com]

measurements of the neat compounds (see Figure 3), cyclic structures show a higher abundance in blends than linear 11-undecenol-capped polyactides. In a mixture with a fourfold excess of linear polymers (80/20 L/C) the peak intensities of linear species are only approximately twice as high as those of the cyclic species. However, even at a 40/60 C/L ratio the intensity of peaks representing cyclic polyactides exceeds that of the linear polymers. At C/L 60/40 their intensities are approximately three times higher than those of linear species. With an even higher excess of cyclic polyactides (80/20) peaks representing linear species are only visible at a laser power value above 20%. This is shown in a different way in Figure 6A where the absolute value of the overexpression of the cyclic peak intensity at different laser power values is shown as a plot of the intensity ratio versus the amount of cyclics. For example, supposing an identical ionization behavior of cyclics and linears, a 1:1 mixture of both species should result in a value of one, whereas a mixture containing 80% cyclics (4:1) at this ideal ionization behavior should show a fourfold higher signal intensity of cyclics (see red arrows in Figure 6A). However, this could not be observed. All values in Figure 6A were higher than an “ideal” 1:1 response for both species would provide.

Interestingly, the intensity ratios of both species in mixtures in general seem to be less affected by the applied laser energies, especially at those values that are typically used (20–40%). This is expressed by Figure 6B, where the intensity ratio of cyclic-to-linears of four different blends is plotted versus the laser intensity, as indicated by the blue arrows for a mixture containing 80% cyclics.

In another experiment these measurements were repeated using blends of cyclic and 4-nitrobenzylalcohol-capped linear polyactides. Characteristic MALDI mass spectra of blends recorded at different laser energies are shown in Figure S6 (supporting information). As shown in Figures 7 and 8 similar trends regarding peak intensities and intensity ratios in blends were found. Again, an exponential increase in the peak intensities was observed with increasing laser intensities, accompanied by a higher response of those peaks

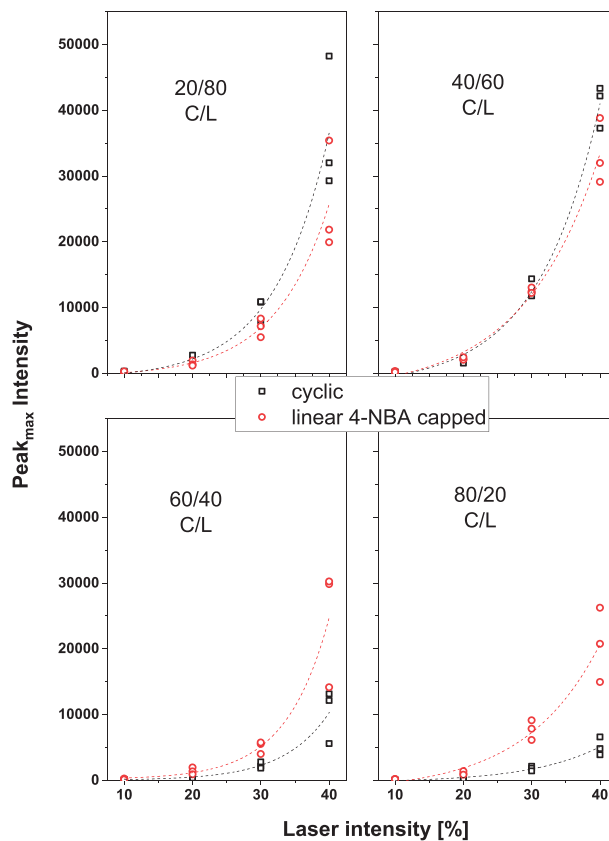


FIGURE 7 Peak intensities of four blends of cyclic and linear 4-NBA-capped polyactides (exponential fitting of mean values of three measurements) [Color figure can be viewed at wileyonlinelibrary.com]

characteristic for cyclic polymers. In an analogy to the results presented earlier, the ratio of peak intensities of cyclics-to-linears investigated for four blends is widely unaffected by the applied laser energy. Interestingly, a blend with lower amounts of cyclic polyactides showed the largest overestimation of cyclic peaks (3–4 times), whereas blends with a large excess of cyclics (80%) reveal the ideal 1:1 abundances of cyclic and linear species (see Figure 8A).

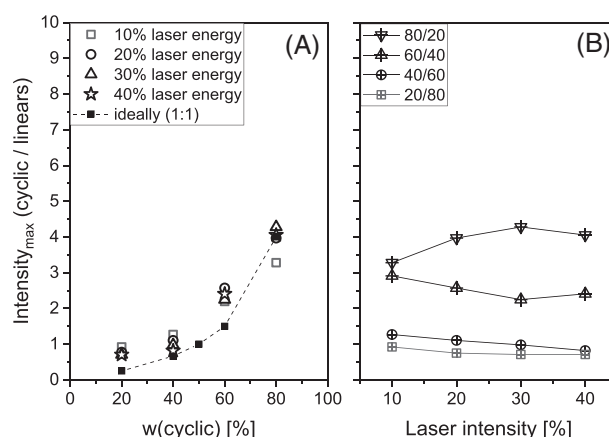


FIGURE 8 Intensity ratio of cyclic and linear 4-NBA-capped polyactides of four blends versus the amount of cyclic species in the mixtures (with a graph showing an “ideally” 1:1 response of both species, dotted line) (A) and at different laser intensities (B)

3.3 | Blends of two linear poly(L-lactide)s

In a final experiment three blends of those two linear polylactides used before in blends with the cyclic analogues were investigated at different laser energies up to 50%. Their mass spectra are shown in Figure S8 (supporting information). The peak intensity information from these mass spectra (see Figure 9) reveals only a slightly higher abundance of linear 4-nitrobenzyl-capped polylactides in blends with linear 11-undecenol-capped species. The laser intensities at a 50/50 ratio were almost similar over a broad range. This is shown in a different way in Figure 10A. Moreover, especially in the laser intensity range of 30–40%, the peak intensity ratio of both linear polylactides remained unaffected by the blend composition (see Figure 10B). The results shown in this figure also indicate that a medium laser intensity might perform best. In other words, working slightly above threshold levels, as often recommended for soft ionization, seems to be disadvantageous for MALDI measurements of polymer blends. Obviously, a higher amount of laser energy is required to enable stable and reproducible ionization conditions in the MALDI process.

These data allow for the following conclusions.

I—The steady increase in the laser intensity caused an exponential increase in the peak intensities of both linear and cyclic polylactides.

II—With one exception, ionization of linear polylactides (in the investigated molecular mass range) is not significantly affected by the polarity of the end groups, whether as neat polymer or in mixtures with cyclic polylactides.

III—At higher laser energies the presence of bromine in combination with long aliphatic end groups seems to cause a dissipation of excess laser energy. Other possible mechanisms such

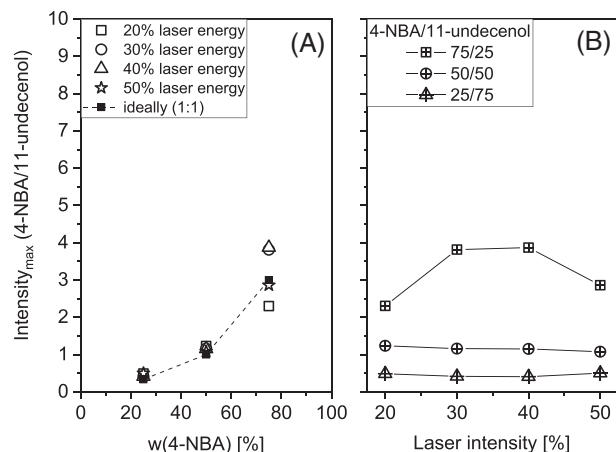


FIGURE 10 Intensity ratio of linear 4-NBA- and 11-undecenol-capped polylactides in three blends versus the amount of 4-NBA species in the mixtures (with a graph showing an “ideally” 1:1 response of both species, dotted line) (A) and at different laser intensities (B)

as in-source and post-source fragmentation processes were excluded, for example, by measurements in the reflector mode.

IV—The variation in the laser energy shows only little effect on the intensity ratio of cyclic-to-linear polylactides in blends. Nevertheless, this ratio is almost always above the ideal 1:1 intensity ratio for cyclic species; that is, cyclic polylactides in general show higher responses than linear polylactides.

V—The higher response of cyclic polylactides in the MALDI mass spectra is far less distinct than frequently reported for other polymers.

VI—The response of two linear species in blends is almost similar. This clearly supports our assumption that ionization in MALDI is probably unaffected by the end group structure.

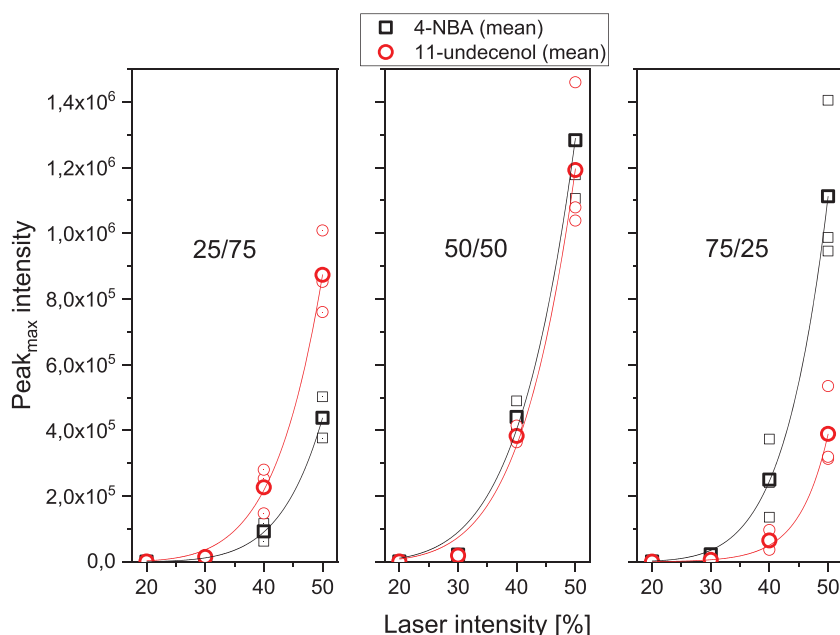


FIGURE 9 Peak intensities of three blends of linear 4-NBA- and 11-undecenol-capped polylactides and exponential fitting of mean values of these measurements [Color figure can be viewed at wileyonlinelibrary.com]

VII—To achieve stable ionization conditions for polymer blends, laser energies significantly over threshold values seem to be favorable.

4 | SUMMARY

In conclusion, our results show that an overestimation of cyclic species in MALDI-TOF mass spectra of polylactides must be considered, but a peak suppression of linear polymers in mixtures of both architectures can be excluded. This also means that polylactides showing only peaks of cyclic compounds in their MALDI-TOF mass spectra do not contain a significant fraction of linear analogues. This result is also widely independent of the applied laser intensities and of the blend composition. In contrast to other results obtained for other polymers (e.g., PA and PBT), end group ionization efficiency appears to be a less significant parameter in determining the peak intensities in the MALDI spectra of blends of cyclic and linear and blends of two linear polylactides studied in this work.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

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