Supplementary Information to

Direct access to biocompatible nitroxide containing polymers

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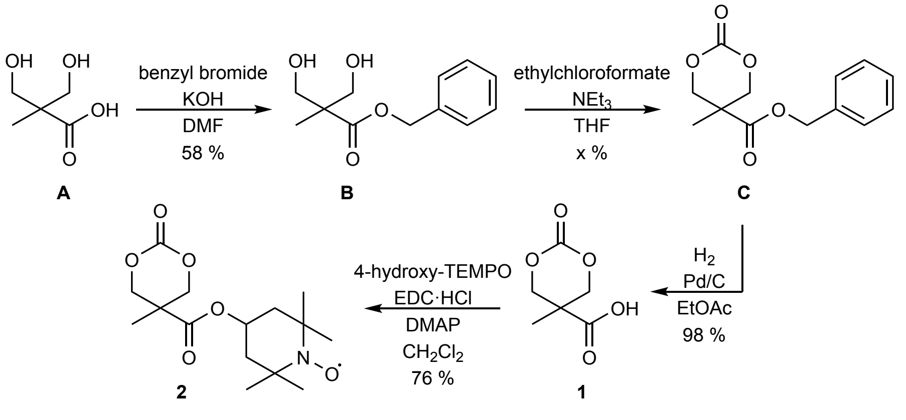
Materials

3-hydroxy-2-(hydroxymethyl)-2-methylpropanoic acid (Sigma Aldrich, 98 %), 4-hydroxy-TEMPO (Sigma Aldrich, 97 %), acetic acid (Thermo Fisher Scientific, AR), acetone (Thermo Fisher Scientific, AR), benzyl bromide (Merck, 98 %), celite (Sigma Aldrich), chloroform (Thermo Fisher Scientific, AR), diethyl ether (Thermo Fisher Scientific, AR), ethyl acetate (Thermo Fisher Scientific, AR), ethyl chloroformate (Sigma Aldrich, 98 %), hydrochloric acid (Thermo Fisher Scientific, AR), hydrogen gas (Supagas, high purity), methylene chloride (Thermo Fisher Scientific, AR), *N*-(3-Dimethylaminopropyl)-*N′*-ethylcarbodiimide hydrochloride (EDC·HCl) (Sigma Aldrich, 98 %), *N,N*-dimethylformamide (Sigma Aldrich, 99 %), palladium catalyst (Sigma Aldrich, 10% on activated charcoal), potassium hydroxide (Chemsupply, AR), sigmacote (Sigma Aldrich), sodium bicarbonate (Thermo Fisher Scientific, AR), sodium sulfate (Thermo Fisher Scientific, AR), tetrahydrofuran (Thermo Fisher Scientific, HPLC grade) were used as received. 1-(3,5-bis(trifluoromethyl)phenyl)-3-cyclohexylthiourea (TU) was prepared according to literature procedure[1] and recrystallised twice from chloroform, *D/L*-lactide (Sigma Aldrich, 99 %) was recrystallized three times from ethyl acetate, propargyl alcohol (Sigma Aldrich, 99 %) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (Sigma Aldrich, 98 %) were distilled from calcium hydride, triethylamine (Sigma Aldrich, 99 %) was dried over potassium hydroxide

Methods

Proton and carbon nuclear magnetic resonance (^{1}H and ^{13}C NMR) spectra were recorded on a *Bruker* System 600 Ascend LH, equipped with an ONP-Probe (5 mm) with z-gradient (^{1}H: 600 MHz, ^{13}C 151 MHz). The δ-scale was normalized relative to the solvent signal of $CHCl_3$ or DMSO for ^{1}H spectra and for ^{13}C spectra on the middle signal of the $CHCl_3$ triplet, or the DMSO quintet, respectively. **High-performance liquid chromatography (HPLC)** was performed with a HP Agilent 1100 HPLC instrument equipped with a Diode Array Detector (254nm) and an Agilent ZORBAX Eclipse Plus C18 (4.6x250mm, 5µm) analytical column (isocratic gradient 70% MeOH in water over 15 minutes with a flow rate of 1 $mL\cdot min^{-1}$). **Electron paramagnetic resonance (EPR)** spectra were recorded on a Magnettech MiniScope MS400 spectrometer using chloroform as a solvent. **Melting points (T_m)** were measured on a Gallenkamp variable temperature apparatus by the capillary method and are uncorrected. The **gel permeation chromatography (GPC)** measurements were conducted on a *PSS* SECurity[2] system consisting of a *PSS* SECurity Degasser, *PSS* SECurity TCC6000 Column Oven (35 °C), *PSS* SDV Column Set (8x150 mm 5 µm Precolumn, 8x300 mm 5 µm Analytical Columns, 100000 Å, 1000 Å and 100 Å) and an *Agilent* 1260 Infinity Isocratic Pump, *Agilent* 1260 Infinity Standard Autosampler, *Agilent* 1260 Infinity Diode Array and Multiple Wavelength Detector (A: 254 nm, B: 360 nm), *Agilent* 1260 Infinity Refractive Index Detector (35 °C). HPLC grade THF, stabilized with BHT, is used as eluent at a flow rate of 1 mL·min^{-1}. Narrow disperse linear poly(styrene) (M_n: 266 g·mol^{-1} to 2.52×10^6 g·mol^{-1}) and poly(methyl methacrylate) (M_n: 202 g·mol^{-1} to 2.2×10^6 g·mol^{-1}) standards (*PSS* ReadyCal) were used as calibrants. All samples were passed over 0.22 µm PTFE membrane filters. Molecular weight and dispersity analysis was performed in *PSS* WinGPC UniChrom software (version 8.2). **High resolution mass spectra (HRMS)** were recorded on a Q Exactive Plus (Orbitrap) mass spectrometer (*Thermo Fisher Scientific,* San Jose, CA, USA) equipped with an HESI II probe. The instrument was calibrated in the m/z range 74-1822 using premixed calibration solutions (*Thermo Scientific*) and for the high mass mode in the m/z range of 600-8000 using ammonium hexafluorophosphate solution. A constant spray voltage of 3.5 kV, a dimensionless sheath gas and a dimensionless auxiliary gas flow rate of 5 and 3 were applied, respectively. The capillary temperature was set to 320 °C, the S-lens RF level was set to 62, and the aux gas heater temperature was set to 50 °C. The sample was injected using a syringe pump with a constant flow rate of 5 µL·min^{-1}. The polymers were analysed using **size exclusion chromatography coupled to a mass spectrometer (SEC-MS)**. Spectra were recorded on a Q Exactive Plus (Orbitrap) mass spectrometer (Thermo Fisher Scientific, San Jose, CA, USA) equipped with an HESI II probe. The instrument was calibrated in the m/z range 74-1822 using premixed calibration solutions (Thermo Scientific) and for the high mass mode in the m/z range of 600-8000 using ammonium hexafluorophosphate solution. A constant spray voltage of 3.5 kV, a dimensionless sheath gas and a dimensionless auxiliary gas flow rate of 10 and 0 were applied, respectively. The capillary temperaturewas set to 320 °C, the S-lens RF level was set to 150, and the aux gas heater temperature was set to 125 °C. The Q Exactive was coupled to an UltiMate 3000 UHPLC System (Dionex, Sunnyvale, CA, USA) consisting of a pump (LPG 3400SD), autosampler (WPS 3000TSL), and a temperature controlled column department (TCC 3000). Separation was performed on two mixed bed size exclusion chromatography columns (Agilent, Mesopore 250 × 4.6 mm, particle diameter 3 µm) with a precolumn (Mesopore 50 × 7.5 mm) operating at 30 °C. THF at a flow rate of 0.30 mL·min^{-1} was used as eluent. The mass spectrometer was coupled to the column in parallel to an UV detector (VWD 3400, Dionex), and a RI-detector (RefractoMax520, ERC, Japan) in a setup described earlier.[2] 0.27 mL·min^{-1} of the eluent were directed through the UV and RI-detector and 30 µL·min-1 were infused into the electrospray source after post-column addition of a 50 µM solution of sodium iodide in methanol at 20 µL·min^{-1} by a micro-flow HPLC syringe pump (Teledyne ISCO, Model 100DM). A 100 µL aliquot of a polymer solution with a concentration of 2 mg·mL^{-1} was injected into the SEC system.

Monomer synthesis



Scheme S1. Synthesis of the cyclic carbonate monomer (**2**) from 2,2-bis(hydroxymethyl) propionic acid (**A**). Literature known synthetic protocols were followed for the introduction of the benzoyl protecting group (**B**), the formation of the cyclic carbonate (**C**), and the removal of the benzoyl protecting group (**1**). Steglich esterification of **1** with 4-hydroxy-TEMPO provides the monomer **2**.

Synthesis of benzyl 3-hydroxy-2-(hydroxymethyl)-2-methylpropanoate (B):

A mixture of 3-hydroxy-2-(hydroxymethyl)-2-methylpropanoic acid (**A**) (10.0 g, 75.0 mmol, 1.0 eq), potassium hydroxide (5.1 g, 91.0 mmol, 1.2), and DMF (50 mL) was heated to 95 °C for 1 h at which point a homogenous solution was formed. Benzyl bromide (8.9 mL, 75.0 mmol, 1.0 eq) was added to the warm solution, and stirring was continued at 95°C for 16 h. The reaction was cooled, and the solvent was removed under vacuum. Diethyl ether (50 mL) and water (50 mL) were added to the residue. The aqueous phase was extracted with diethyl ether two more times. The combined organic layers were washed with water (3 x 50 mL), dried (Na_2SO_4), and the solvent was evaporated. The product was dried in vacuo over night to yield 9.8 g (58 %) of the product as a white crystalline solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ / ppm = 7.40-7.31 (m, 5H, Ph-H), 5.21 (s, 2H, CH_2-Ph), 3.95 and 3.74 (each dd, 2H, CH_2-OH), 2.82 (bt, 2H, OH), 1.08 (s, 3H, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ / ppm = 175.9, 135.8, 128.8, 128.5, 128.0, 68.7, 66.9, 49.4, 17.3. ESI-MS: $[M+Na]^+$ $m/z^{\text{theor.}}$ = 247.09463; m/z^{exp}. = 247.0934; $\Delta m/z$ = 0.0012. $[2M+Na]^+$ $m/z^{\text{theor.}}$ = 471.19949; $m/z^{\text{exp.}}$ = 471.1978; $\Delta m/z$ = 0.0017.

Synthesis of benzyl 5-methyl-2-oxo-1,3-dioxane-5-carboxylate (C):

A solution of 5.0 g benzyl 3-hydroxy-2-(hydroxymethyl)-2-methylpropanoate (**B**) (23.3 mmol, 1 eq) in 120 mL THF was stirred at 0 °C when 6.7 mL ethyl chloroformate (70.1 mmol, 3 eq) were added dropwise. The ice bath was removed, and the solution was stirred at ambient temperature for 30 min. After cooling to 0 °C, 10 mL triethylamine (71.8 mmol, 3 eq) was added dropwise over a period of 30 min. The ice bath was removed, and the mixture was stirred at ambient temperature overnight. The TEA–HCl precipitate was filtered off. The filtrate was concentrated under reduced pressure to obtain a liquid. The residue was recrystallized from ethyl acetate. White crystals were obtained (3.61 g, 62 %).

^{1}H NMR (600 MHz, $CDCl_3$) δ / ppm = 7.40 – 7.32 (m, 5H, Ph-H), 5.22 (s, 2H, CH_2-Ph), 4.70 and 4.20 (each d, ^3J = 10.8 Hz, 2H, carbonate-CH_2), 1.33 (s, 3H, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ / ppm = 171.0, 147.5, 134.9, 128.6 (d), 73.1, 68.1, 40.4, 17.7. ESI-MS: $[M+Na]^+$ $m/z^{\text{theor.}}$ = 273.0739; $m/z^{\text{exp.}}$ = 273.0725; $\Delta m/z$ = 0.0014. $[M+MeOH+Na]^+$ $m/z^{\text{theor.}}$ = 305.1001; $m/z^{\text{exp.}}$ = 305.0986; $\Delta m/z$ = 0.0015. $[2M+Na]^+$ $m/z^{\text{theor.}}$ = 523.1580; $m/z^{\text{exp.}}$ = 523.1562; $\Delta m/z$ = 0.0018.

Synthesis of 5-methyl-2-oxo-1,3-dioxane-5-carboxylic acid (1):

A mixture of 2.0 g of 3-hydroxy-2-(hydroxymethyl)-2-methylpropanoate (**C**) (8.0 mmol, 1.0 eq) and 22.5 mg Pd/C catalyst (10 %w/w, 0.2 mg Pd, 0.02 mmol, 0.003 eq) in 200 mL ethyl acetate was percolated with H_2 gas for 1 h and stirred for additional 4 h under a hydrogen atmosphere. Subsequently, the catalyst is removed by filtration over Celite and the filtrate is evaporated to give 1.24 g (97 %) of a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ / ppm = 4.53 and 4.31 (each d, ^3J=10.5 Hz, 2H, CH_2), 1.16 (s, 3H, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ / ppm = 173.3, 147.4, 72.7, 16.5. ESI-MS: $[M-H]^-$ $m/z^{\text{theor.}}$ = 159.0299; $m/z^{\text{exp.}}$ = 159.0289; $\Delta m/z$ = 0.0010. $[2M-H]^-$ $m/z^{\text{theor.}}$ = 319.0671; $m/z^{\text{exp.}}$ = 319.0664; $\Delta m/z$ = 0.0007.

Synthesis of TEMPO 5-methyl-2-oxo-1,3-dioxane-5-carboxylate (2):

A solution of 400 mg 5-methyl-2-oxo-1,3-dioxane-5-carboxylic acid (**1**) (2.50 mmol, 1.0 eq), 500 mg 4-hydroxy-TEMPO (2.91 mmol, 1.2 eq), and 60 mg DMAP (0.49 mmol, 0.2 eq) in 30 mL dry CH_2Cl_2 was cooled in an ice bath when 730 mg EDC·HCl (3.81 mmol, 1.5 eq) were added portionwise. The orange solution was stirred another 2 h in the ice bath and subsequently at ambient temperature overnight. The reaction mixture was diluted with 25 mL CH_2Cl_2, washed with 1M HCl (4 x 25 mL) and saturated aqueous $NaHCO_3$ solution (3 x 25 mL), dried (Na_2SO_4), and the solvent was removed under reduced pressure. The product was recrystallised from THF to yield 349 mg (63 %) of orange crystals.

^1H NMR (600 MHz, $CDCl_3$) δ / ppm = 4.81 and 4.34 (each bs, 2H, carbonate-CH_2), 1.44 (bs, 3H, carbonate-CH_3). Proton signals corresponding to the TEMPO ring are not visible due to significant broadening by the free radical. After the reduction of the free radical by addition of pentafluorophenyl hydrazine, the protons can be identified: ^1H NMR (600 MHz, $CDCl_3$) δ / ppm = 5.21-5.17 (m, 1H, TEMPO-CH), 4.66 and 4.18 (each d, 2H, carbonate-CH_2), 1.96-1.91 and 1.75-1.66 (each m, 2H, TEMPO-CH_2), 1.30 (s, 3H, carbonate-CH_3), 1.27 and 1.23 (each s, 6H, TEMPO-CH_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ / ppm =166.3 (ester carbonyl-C), 143.8 (carbonate-C), 70.1 (carbonate-CH_2), 39.5 (carbonate-c_{quart}), 14.2 (carbonate-CH_3). Signals for the carbon atoms corresponding to the TEMPO ring are not visible due to the free radical present. ESI-MS: $[M+H]^+$ $m/z^{theor.}$ = 314.1604; $m/z^{exp.}$ = 314.1590; $\Delta m/z$ = 0.0014. $[MH+H]^+$ $m/z^{theor.}$ = 316.1760; $m/z^{exp.}$ = 316.1747; $\Delta m/z$ = 0.0013. $[M+Na]^+$ $m/z^{theor.}$ = 337.1501; $m/z^{exp.}$ = 337.1487; $\Delta m/z$ = 0.0014. $[2M+Na]^+$ $m/z^{theor.}$ = 651.3105; $m/z^{exp.}$ = 651.3082; $\Delta m/z$ = 0.0023. T_m = 138 ± 2 °C.

Representative Procedure for the Ring-Opening Polymerisation (3):

All vessels used for the ROP were silanised using Sigmacote, rinsed with water and acetone and dried in an oven overnight. The reaction vials were transferred into a glovebox. Stock solutions of D/L-lactide (0.69 mM), monomer 5 (0.51 mM), propargyl alcohol (0.12 mM), DBU catalyst (0.05 mM), and TU co-catalyst (0.21 mM) in extra dry THF were prepared. The stock solutions were combined, and the polymerisation was allowed to proceed for variable times. The vials were then removed from the glovebox and the DBU catalyst was quenched by addition of acetic acid. The polymers were precipitated from hexane, isolated by centrifugation, re-precipitated twice (THF/hexane) and finally dried in vacuo.

Details of monomer mass spectrometric analysis

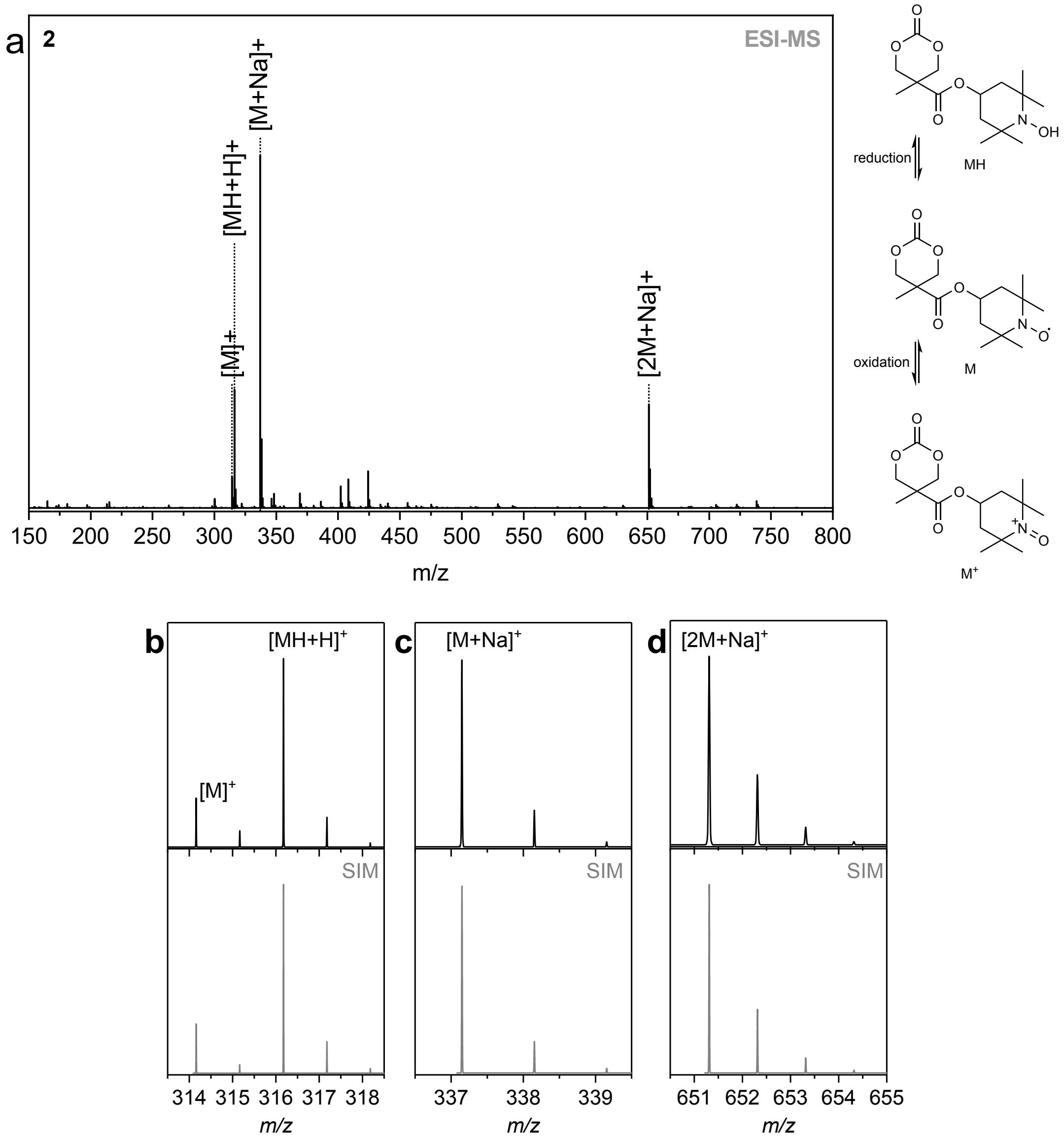


Figure S1. (a) Overview over the high-resolution mass spectrum of **2** in methanol. Please refer to the schematic drawing on the right for a structural assignment of the different oxidation states that can be observed in the mass spectrum. Please refer to **Table S1** for a comparison of the experimentally found m/z ratios to the theoretically expected values. **(b-d)** enlarged view of the main signals of the overview spectrum (top) and comparison to the simulated spectra (bottom).

Table S1. Collation of observed signals in the mass spectrum of **2** in the range of m/z = 150 - 800 and the theoretically expected values for the assigned compositions. The resolution was 30000.

Species	m/z^{exp}	m/z^{theor}	Δ_{ppm}	composition
[M]$^+$	314.1590	314.1598	-2.55	$[C_{15}H_{24}NO_6]^+$
[MH+H]$^+$	316.1747	316.1775	-8.86	$[C_{15}H_{26}NO_6]^+$
[M+Na]$^+$	337.1487	337.1496	-2.67	$[C_{15}H_{24}NO_6Na]^+$
[2M+Na]$^+$	651.3082	651.3099	-2.61	$[C_{30}H_{48}N_2O_{12}Na]^+$

Details of the EPR quantification

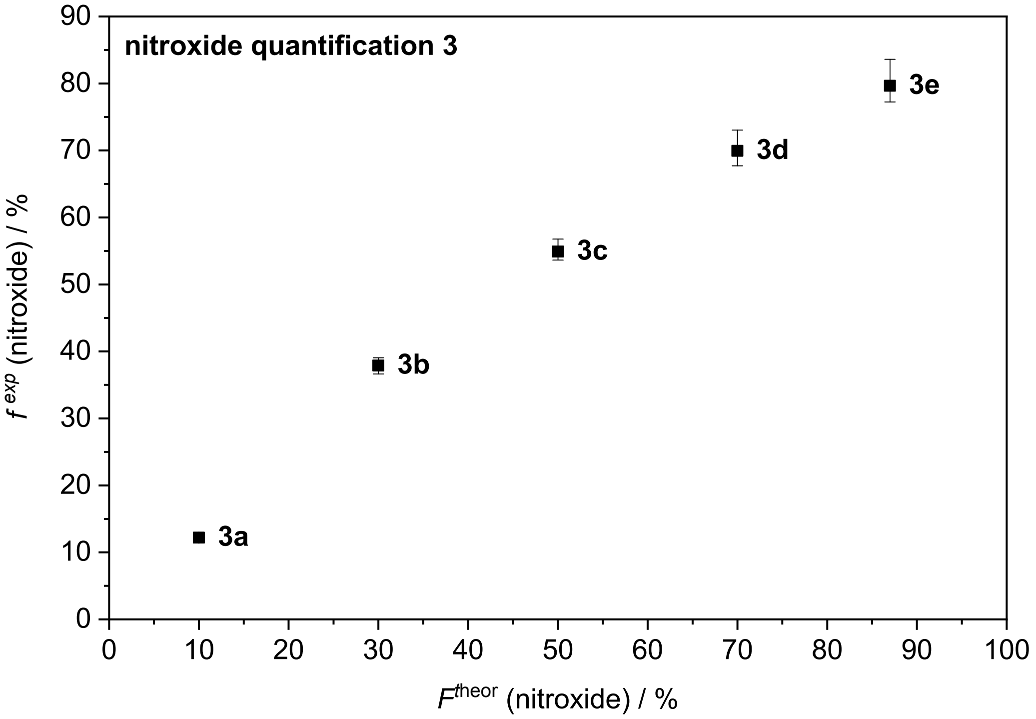


Figure S2. Result of the quantification of the nitroxide content in the polymers **3a-e** using the double integral of the EPR signal after calibration against the nitroxide monomer **2**.

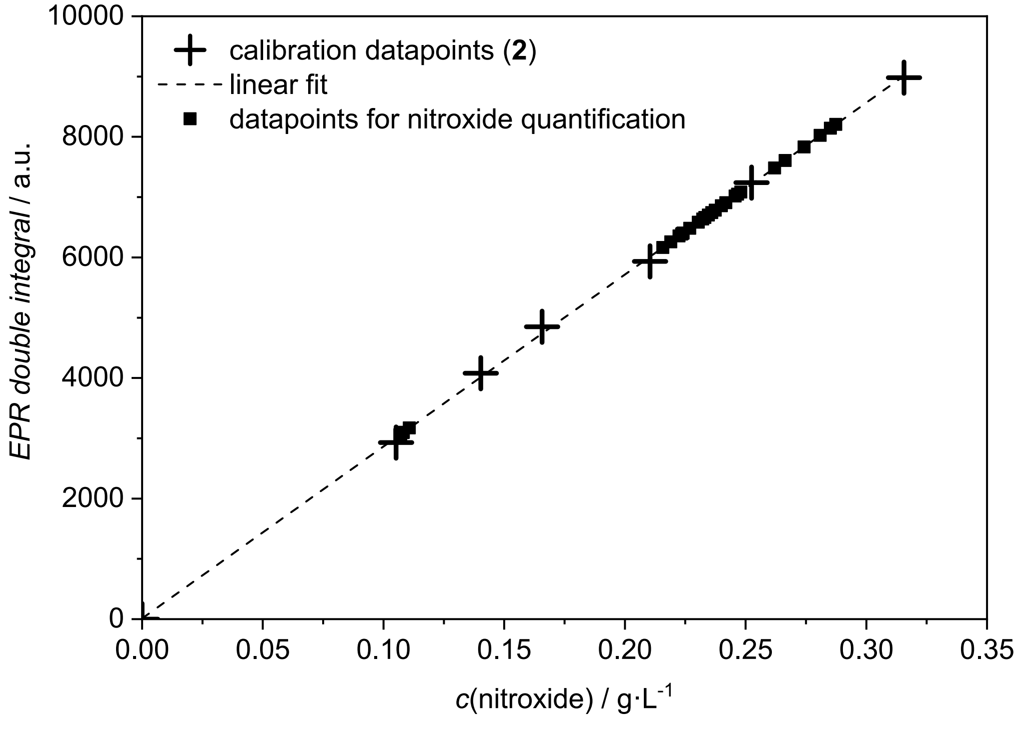
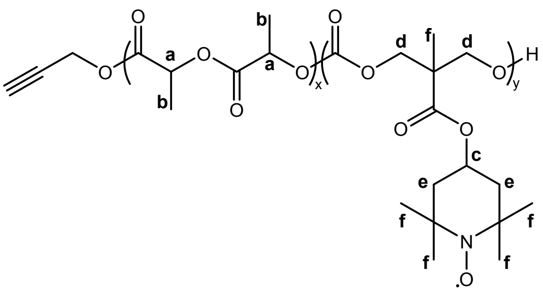


Figure S3. Comparison of the data points acquired for the EPR calibration using monomer **2** (crosses) and the data points acquired to determine the nitroxide content of the polymers **3a**-**e** (squares).

Details of NMR spectroscopy analyses

For NMR spectroscopy quantification the integrals of the polymer proton signals (**Table S2**) were determined and set into relation using various combinations of the signals according to **Eq. 1** which can be resolved for the fraction of monomer B (the nitroxide monomer), **Eq. 3**, considering that the fractions of both monomers will add up to unity (**Eq. 2**). To account for the overlaying signal of the residual pentafluorophenyl hydrazine in the integral of the protons a+c (δ = 5.32-5.05 ppm), the integral of the second peak of pentafluorophenyl hydrazine is used which can be identified at δ = 4.14 - 3.56 ppm and is in a 2:1 ratio to the first peak following **Eq. 4**.



Scheme S1. Annotation of proton signals in the copolymers used in this discussion

$$\frac{I_1}{I_2}=\frac{k\cdot F(LA)+m\cdot F(2)}{l\cdot F(LA)+n\cdot F(2)}$$ **Eq. 1**

$$F(LA)+F(2)=1$$ **Eq. 2**

$$F(2)=\frac{k-\frac{I_1}{I_2}\cdot l}{k-\frac{I_1}{I_2}\cdot l-m+\frac{I_1}{I_2}\cdot n}$$ **Eq. 3**

$$I_{(a+c)}=I_{a+c+\bullet}-\frac{I_\bullet}{2}$$ **Eq. 4**

Table S2. Collation of the signals observed in the NMR spectra of polymer **3a-e** after reduction with pentafluorophenyl hydrazine including the typical integration range used for the quantification and the number of protons in each of the comonomers, LA (lactide), **2** (nitroxide carbonate), or the penta-fluorophenyl hydrazine (●), respectively. Please refer to **Scheme S1** for assignment of the signals.

Signal	**Integration range / ppm**	**Protons in LA (k or l)**	**Protons in 2 (m or n)**	**Protons in ●**
a+c+●	5.32 - 5.05	2	1	1
d	4.41 - 4.15	0	4	
●	4.14 – 3.56	0	0	2
e	2.15 - 1.65	0	4	
b	1.62 - 1.5	6	0	
f	1.5 - 0.8	0	15	

Table S3. Overview over the single results for *F*(**2**) in % for the various signal combinations, as well as the average and standard deviation (s) for polymers **3a-e**.

	a+c | d	**a+c | e**	**a+c | b**	**a+c | f**	**d | b**	**e | b**	**b | f**	**average**	**s**
3a	9.25	9.36	9.82	9.11	9.28	9.38	9.14	9.33	0.24
3b	28.08	30.4	28.58	30.72	28.16	30.08	30.34	29.48	1.15
3c	47.69	44.38	48.24	48.33	47.87	45.54	48.3	47.19	1.58
3d	65.65	66.52	66.15	67.08	65.9	66.34	66.62	66.32	0.48
3e	82.14	80.38	83.21	83.84	82.9	82.37	83.39	82.60	1.14

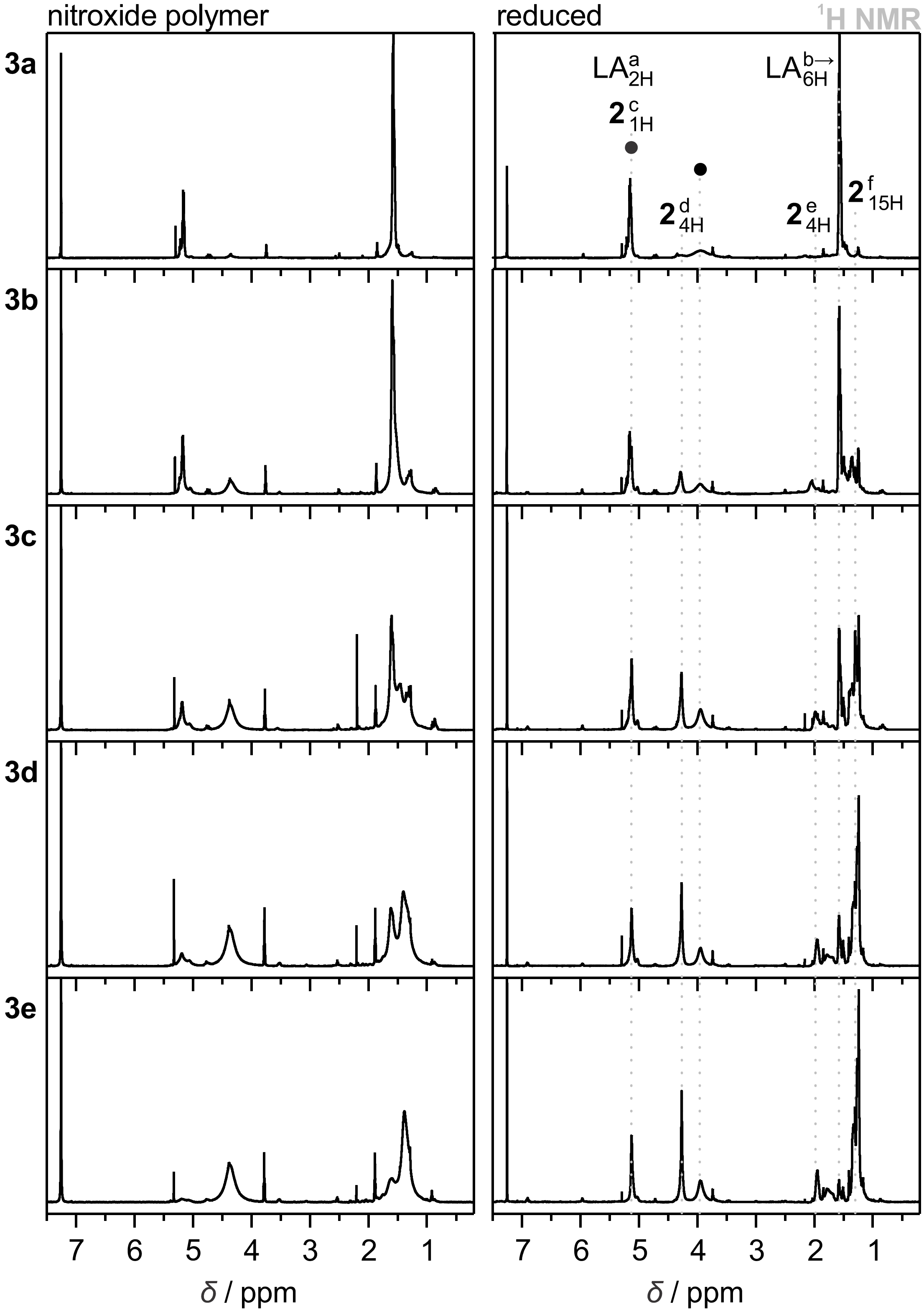


Figure S4. NMR spectra of the original polymers **3a-3e** (left) and respective spectra after addition of pentafluorophenyl hydrazine to reduce the free radical species (right). The signals are annotated according to the monomer they are assigned to (LA = lactide, **2** = nitroxide carbonate), the specific proton (a-f) as depicted in the structure in **Table S2**, as well as the number of protons expected for this signal. The signals induced by the pentafluorophenyl hydrazine are denoted with ●.

To determine the conversion of the polymerization, NMR spectra of the crude polymerization mixtures were recorded in $CDCl_3$ after reduction of the free radical moiety using pentafluorophenyl hydrazine. **Figure S5a** exemplarily shows an overview of the spectrum of **3c** (black line) in comparison to the NMR spectra of both monomers, lactide (dark grey) and the nitroxide carbonate **2** (dark grey line, after reduction with pentafluorophenyl hydrazine). **Figure S5b** depicts an enlarged view of the region between 5.4 ppm and 4.0 ppm. The chemical shifts of the ring protons in the monomers are different to the shifts of their respective ring-opened equivalents. However, the broadening of the polymer peaks leads to an overlay with the initial signals. Considering the signal at 4.65 ppm, the conversion in the nitroxide monomer seems to be close to quantitative. **Figure S5c** depicting the second region between 2.1 ppm and 0.9 ppm displays the same impedance.

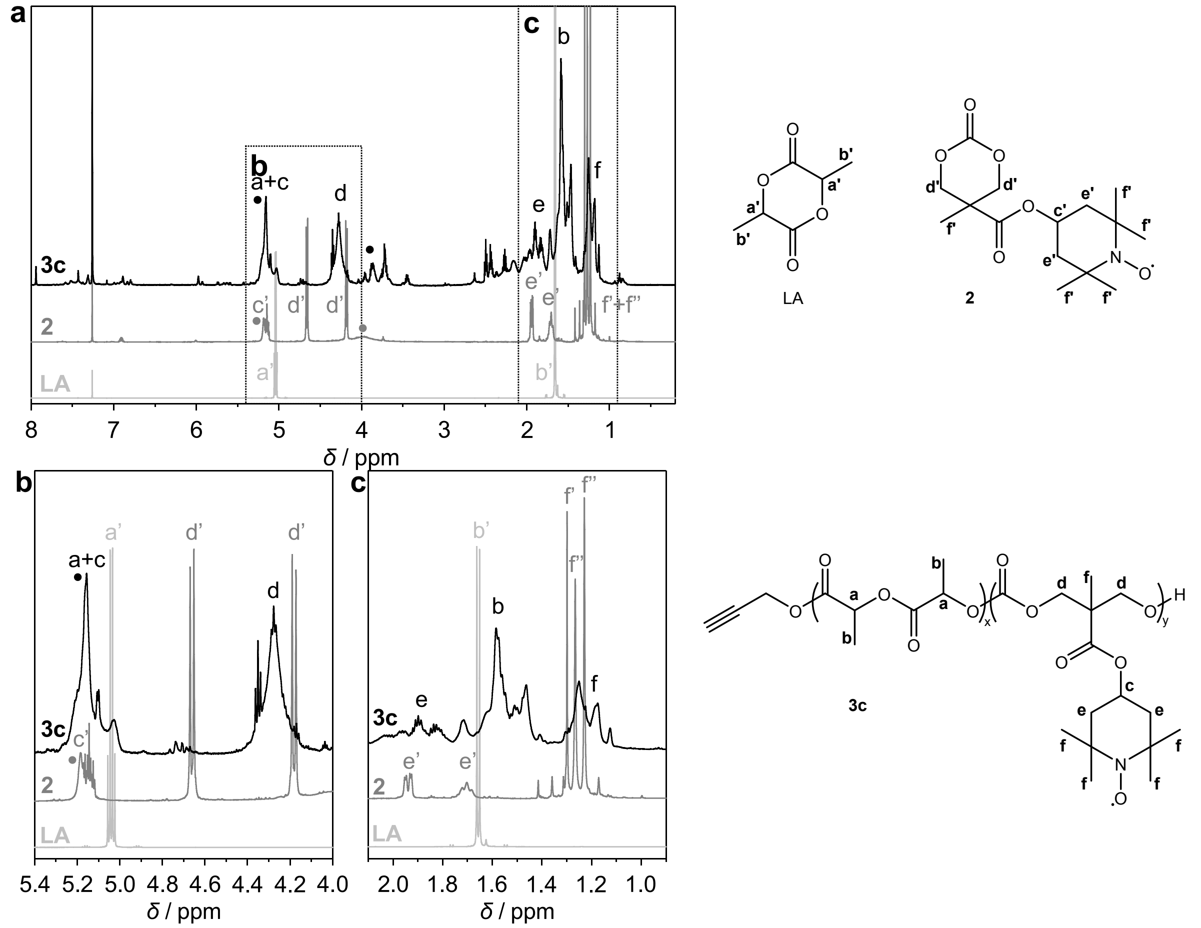


Figure S5. a Overview over the ^1H NMR spectrum of the crude polymerization mixture of **3c** after reduction with pentafluorophenyl hydrazine (black) in comparison to the two monomer spectra, lactide (LA, light grey) and nitroxide carbonate **2** (dark grey, reduced with pentafluorophenyl hydrazine). **b,c** enlarged views of the relevant regions as indicated in a. All spectra were recorded in $CDCl_3$. Please refer to the structures on the right for signal assignments.

Details of the SEC-ESI-MS analyses

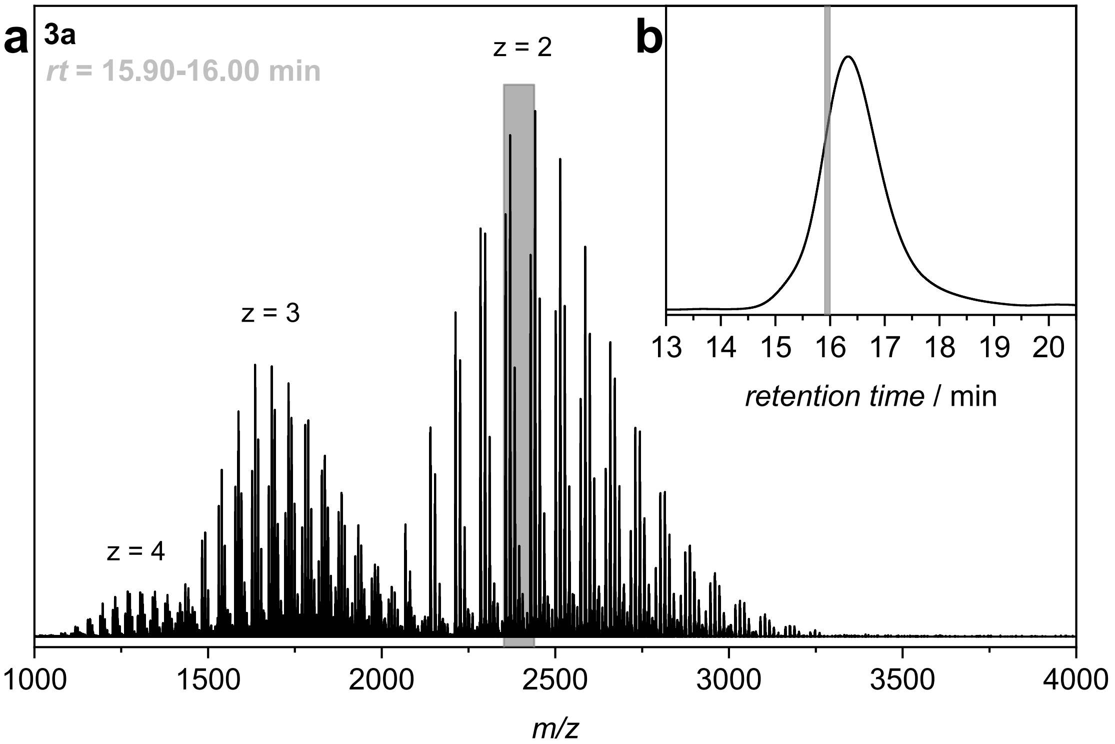


Figure S6. (**a**) Overview over the mass spectrum of polymer **3a** between *m/z* = 1000 and 4000 showing the polymer distribution for charge states *z* = 2 to 4. (**b**) The MS spectrum was derived from the spectra recorded 15.9 and 16.0 min of the SEC experiment, highlighted in grey.

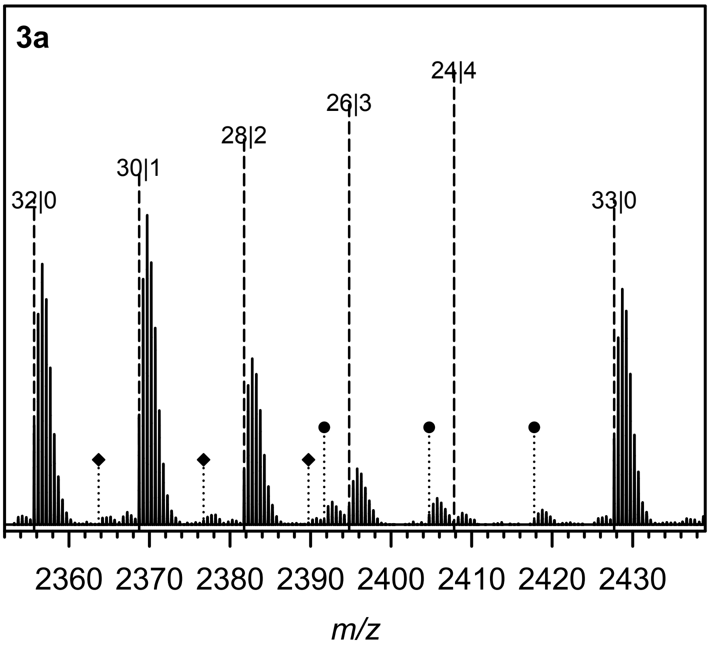


Figure S7. Representative detailed view of one lactide repeating unit in the MS spectrum of **3a** in the range of *m/z* = 2352 to 2439 (z = 2) as highlighted in **Figure S6a**. Please refer to **Table S4**Error! Reference source not found. for a comparison of the experimentally found m/z values with the theoretically expected values for the assigned compositions.

Table S4. Collation of observed signals in the mass spectrum of **3a** in the range of m/z = 2352 to 2439 (z = 2) and the theoretically expected values for the assigned compositions. The resolution was determined to be 43000.

Major Signals

Symbol	m/z^{exp}	m/z^{theor}	Δ_{ppm}	composition
32|0	2355.6819	2355.6790	1.21	[PgO-(lactide)$_{32}$-H +2Na]$^{2+}$
30|1	2368.7194	2368.7170	1.03	[PgO-(lactide)$_{30}$-(MTC-COO-TEMPO)$_{1}$-H +2Na]$^{2+}$
28|2	2381.7574	2381.7549	1.06	[PgO-(lactide)$_{28}$-(MTC-COO-TEMPO)$_{2}$-H +2Na]$^{2+}$
26|3	2394.7971	2394.7928	1.80	[PgO-(lactide)$_{26}$-(MTC-COO-TEMPO)$_{3}$-H +2Na]$^{2+}$
24|4	2407.8327	2407.8307	0.82	[PgO-(lactide)$_{24}$-(MTC-COO-TEMPO)$_{4}$-H +2Na]$^{2+}$
33|0	2427.7018	2427.7002	0.67	[PgO-(lactide)$_{33}$-H +2Na]$^{2+}$

Transesterified

Symbol	m/z^{exp}	m/z^{theor}	Δ_{ppm}	composition
●	2391.6901	2391.6896	0.21	[PgO-(lactide)$_{32}$-(halflactide)$_{1}$-H +2Na]$^{2+}$
●	2404.7266	2404.7275	0.38	[PgO-(lactide)$_{30}$-(halflactide)$_{1}$-(MTC-COO-TEMPO)$_{1}$-H +2Na]$^{2+}$
●	2417.7759	2417.7654	4.32	[PgO-(lactide)$_{28}$-(halflactide)$_{1}$-(MTC-COO-TEMPO)$_{2}$-H +2Na]$^{2+}$

Macrocycle

Symbol	m/z^{exp}	m/z^{theor}	Δ_{ppm}	composition
◆	2363.6796	2363.6765	1.31	[(lactide)$_{32}$-(halflactide)$_{1}$ +2Na]$^{2+}$
◆	2376.7118	2376.7144	1.10	[(lactide)$_{30}$-(halflactide)$_{1}$-(MTC-COO-TEMPO)$_{1}$ +2Na]$^{2+}$
◆	2389.7379	2389.7523	6.04	[(lactide)$_{28}$-(halflactide)$_{1}$-(MTC-COO-TEMPO)$_{2}$ +2Na]$^{2+}$

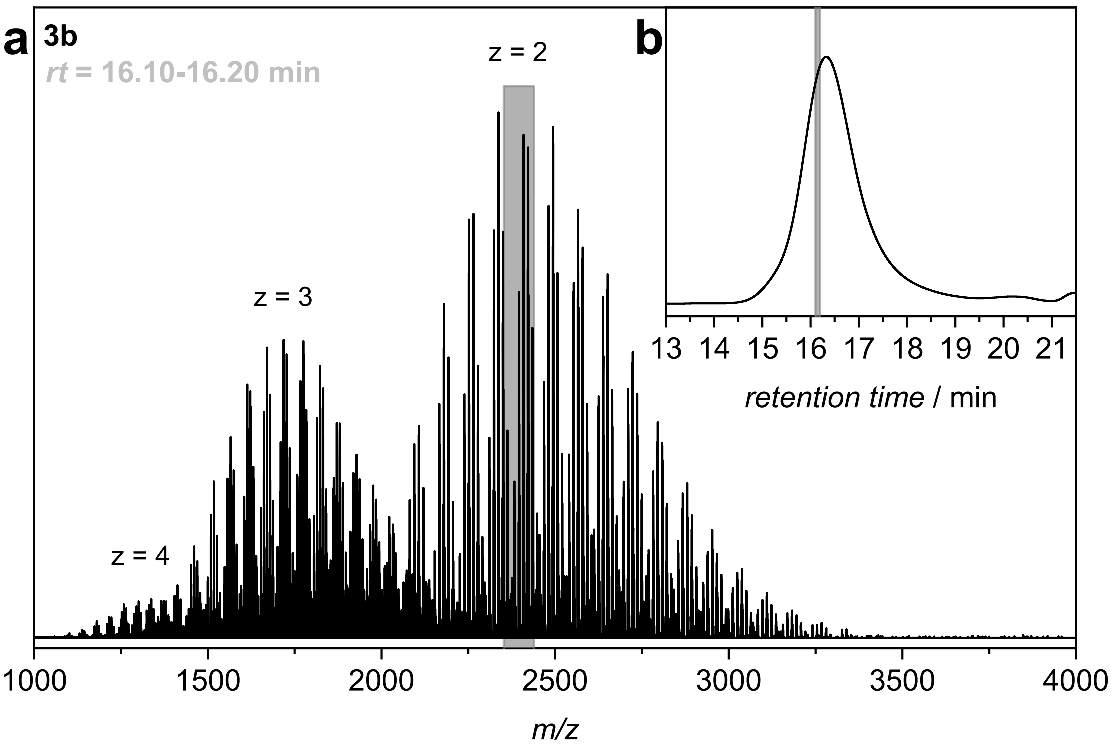


Figure S8. (**a**) Overview over the mass spectrum of polymer **3b** between *m/z* = 1000 and 4000 showing the polymer distribution for charge states *z* = 2 to 4. (**b**) The MS spectrum was derived from the spectra recorded 16.1 and 16.2 min of the SEC experiment, highlighted in grey.

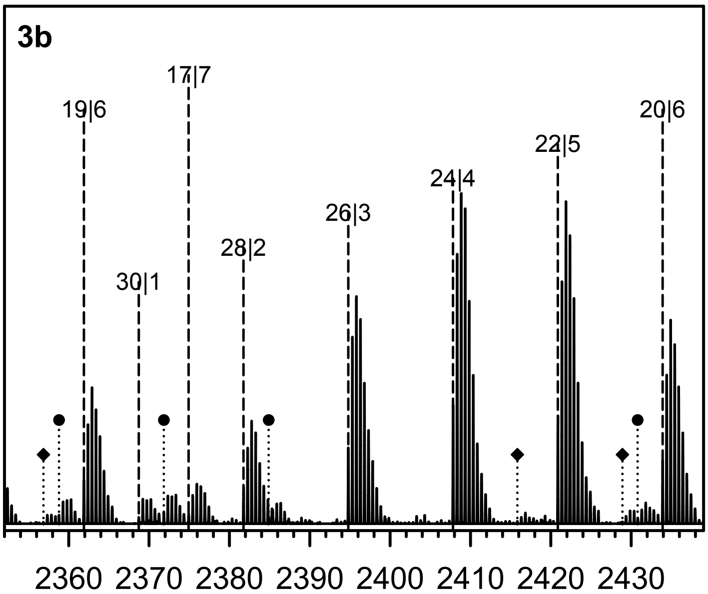


Figure S9. Representative detailed view of one lactide repeating unit in the MS spectrum of **3b** in the range of *m/z* = 2352 to 2439 (z = 2) as highlighted in **Figure S8a**. Please refer to **Table S5** for a comparison of the experimentally found m/z values with the theoretically expected values for the assigned compositions.

Table S5. Collation of observed signals in the mass spectrum of **3b** in the range of m/z = 2352 to 2439 (z = 2) and the theoretically expected values for the assigned compositions. The resolution was determined to be 43000.

Major Signals

Symbol	m/z^{exp}	m/z^{theor}	Δ_{ppm}	composition
19|6	2361.8950	2361.8854	4.05	$[\text{PgO-(lactide)}_{19}\text{-(MTC-COO-TEMPO)}_{6}\text{-H +2Na}]^{2+}$
30|1	2368.7244	2368.7170	3.14	$[\text{PgO-(lactide)}_{30}\text{-(MTC-COO-TEMPO)}_{1}\text{-H +2Na}]^{2+}$
17|7	2374.9348	2374.9234	4.82	$[\text{PgO-(lactide)}_{17}\text{-(MTC-COO-TEMPO)}_{7}\text{-H +2Na}]^{2+}$
28|2	2381.7601	2381.7549	2.19	$[\text{PgO-(lactide)}_{28}\text{-(MTC-COO-TEMPO)}_{2}\text{-H +2Na}]^{2+}$
26|3	2394.7972	2394.7928	1.84	$[\text{PgO-(lactide)}_{26}\text{-(MTC-COO-TEMPO)}_{3}\text{-H +2Na}]^{2+}$
24|4	2407.8378	2407.8307	2.94	$[\text{PgO-(lactide)}_{24}\text{-(MTC-COO-TEMPO)}_{4}\text{-H +2Na}]^{2+}$
22|5	2420.8761	2420.8686	3.08	$[\text{PgO-(lactide)}_{22}\text{-(MTC-COO-TEMPO)}_{5}\text{-H +2Na}]^{2+}$
20|6	2433.9177	2433.9066	4.58	$[\text{PgO-(lactide)}_{20}\text{-(MTC-COO-TEMPO)}_{6}\text{-H +2Na}]^{2+}$

Transesterified

Symbol	m/z^{exp}	m/z^{theor}	Δ_{ppm}	composition
●	2358.7899	2358.7822	3.25	$[\text{PgO-(lactide)}_{25}\text{-(halflactide}_{)1}\text{-(MTC-COO-TEMPO)}_{3}\text{-H +2Na}]^{2+}$
●	2371.8391	2371.8202	7.99	$[\text{PgO-(lactide)}_{23}\text{-(halflactide)}_{1}\text{-(MTC-COO-TEMPO)}_{4}\text{-H +2Na}]^{2+}$
●	2384.8863	2384.8581	11.84	$[\text{PgO-(lactide)}_{21}\text{-(halflactide)}_{1}\text{-(MTC-COO-TEMPO)}_{5}\text{-H +2Na}]^{2+}$
●	2430.8034	2430.8034	0.01	$[\text{PgO-(lactide)}_{26}\text{-(halflactide)}_{1}\text{-(MTC-COO-TEMPO)}_{3}\text{-H +2Na}]^{2+}$

Macrocycle

Symbol	m/z^{exp}	m/z^{theor}	Δ_{ppm}	composition
◆	2356.8523	2356.8450	3.11	$[\text{(lactide)}_{21}\text{-(halflactide)}_{1}\text{-(MTC-COO-TEMPO)}_{5}\text{ +2Na}]^{2+}$
◆	2415.8281	2415.8282	0.03	$[\text{(lactide)}_{24}\text{-(halflactide)}_{1}\text{-(MTC-COO-TEMPO)}_{4}\text{ +2Na}]^{2+}$
◆	2428.9147	2428.8661	20.01	$[\text{(lactide)}_{22}\text{-(halflactide)}_{1}\text{-(MTC-COO-TEMPO)}_{5}\text{ +2Na}]^{2+}$

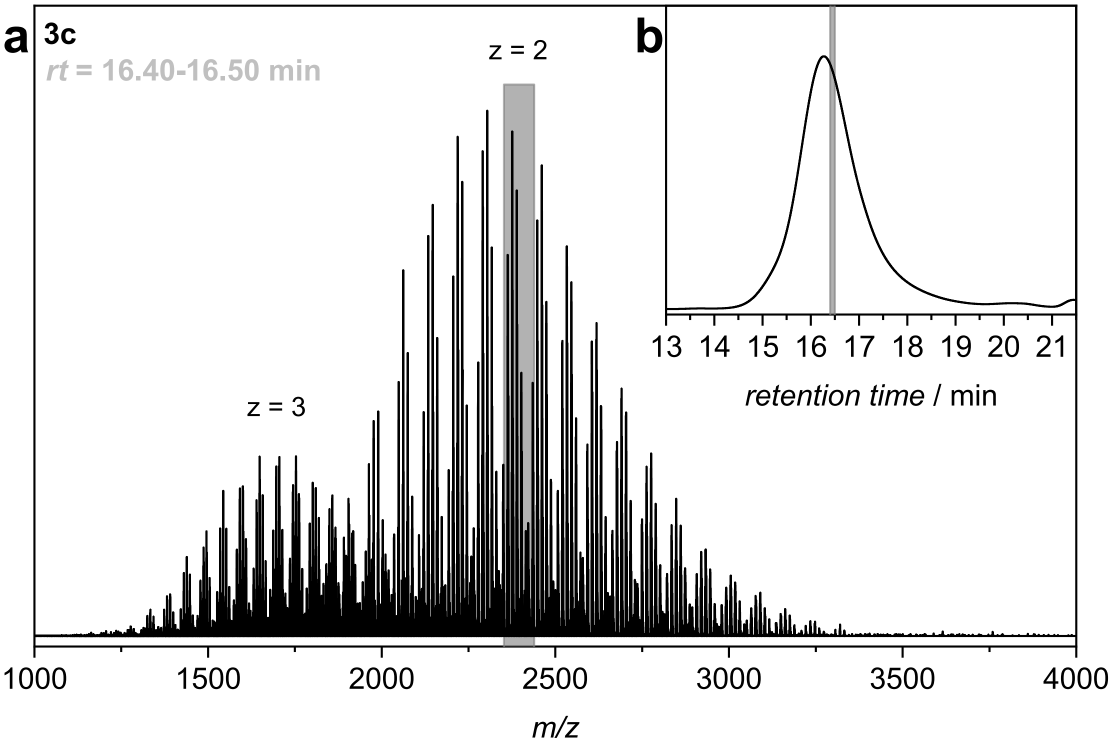


Figure S10. (**a**) Overview over the mass spectrum of polymer **3c** between *m/z* = 1000 and 4000 showing the polymer distribution for charge states *z* = 2 and 3. (**b**) The MS spectrum was derived from the spectra recorded 16.4 and 16.5 min of the SEC experiment, highlighted in grey.

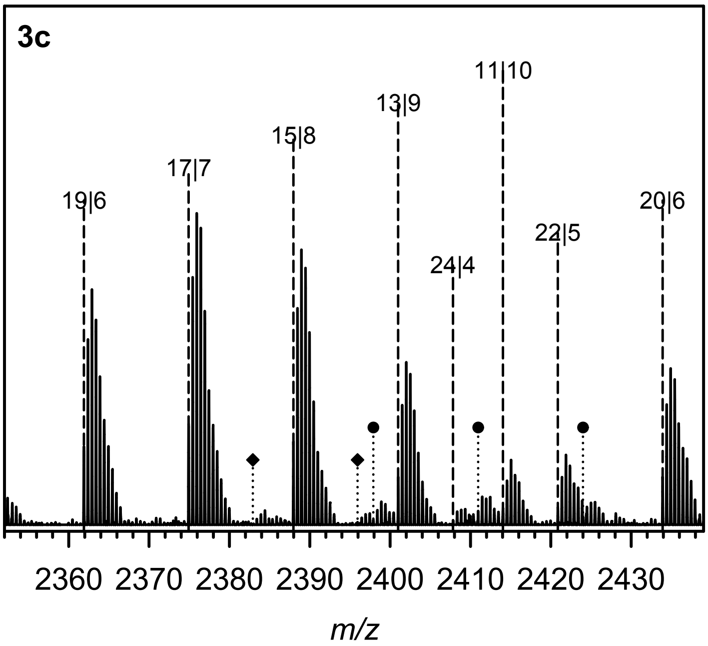


Figure S11. Representative detailed view of one lactide repeating unit in the MS spectrum of **3c** in the range of *m/z* = 2352 to 2439 (z = 2) as highlighted in **Figure S10a**. Please refer to **Table S6** for a comparison of the experimentally found m/z values with the theoretically expected values for the assigned compositions.

Table S6. Collation of observed signals in the mass spectrum of **3c** in the range of m/z = 2352 to 2439 (z = 2) and the theoretically expected values for the assigned compositions. The resolution was determined to be 43000.

Major Signals

Symbol	m/z$^{\text{exp}}$	m/z$^{\text{theor}}$	Δ$_{\text{ppm}}$	composition
16|6	2361.8904	2361.8854	2.10	[PgO-(lactide)$_{16}$-(MTC-COO-TEMPO)$_{6}$-H +2Na]$^{2+}$
17|7	2374.9296	2374.9234	2.63	[PgO-(lactide)$_{17}$-(MTC-COO-TEMPO)$_{7}$-H +2Na]$^{2+}$
15|8	2387.9693	2387.9613	3.36	[PgO-(lactide)$_{15}$-(MTC-COO-TEMPO)$_{8}$-H +2Na]$^{2+}$
13|9	2401.0115	2400.9992	5.13	[PgO-(lactide)$_{13}$-(MTC-COO-TEMPO)$_{9}$-H +2Na]$^{2+}$
24|4	2407.8371	2407.8307	2.65	[PgO-(lactide)$_{24}$-(MTC-COO-TEMPO)$_{4}$-H +2Na]$^{2+}$
11|10	2414.0445	2414.0371	3.06	[PgO-(lactide)$_{11}$-(MTC-COO-TEMPO)$_{10}$-H +2Na]$^{2+}$
22|5	2420.8728	2420.8686	1.72	[PgO-(lactide)$_{22}$-(MTC-COO-TEMPO)$_{5}$-H +2Na]$^{2+}$
20|6	2433.9108	2433.9066	1.74	[PgO-(lactide)$_{20}$-(MTC-COO-TEMPO)$_{6}$-H +2Na]$^{2+}$

Transesterified

Symbol	m/z$^{\text{exp}}$	m/z$^{\text{theor}}$	Δ$_{\text{ppm}}$	composition
●	2397.9101	2397.8960	5.88	[PgO-(lactide)$_{19}$-(halflactide)$_{1}$-(MTC-COO-TEMPO)$_{6}$-H +2Na]$^{2+}$
●	2410.9527	2410.9339	7.79	[PgO-(lactide)$_{17}$-(halflactide)$_{1}$-(MTC-COO-TEMPO)$_{7}$-H +2Na]$^{2+}$
●	2424.0002	2423.9718	11.70	[PgO-(lactide)$_{15}$-(halflactide)$_{1}$-(MTC-COO-TEMPO)$_{8}$-H +2Na]$^{2+}$

Macrocycle

Symbol	m/z$^{\text{exp}}$	m/z$^{\text{theor}}$	Δ$_{\text{ppm}}$	composition
◆	2382.9225	2382.9208	0.71	[(lactide)$_{17}$-(halflactide)$_{1}$-(MTC-COO-TEMPO)$_{7}$ +2Na]$^{2+}$
◆	2395.9512	2395.9587	3.14	[(lactide)$_{15}$-(halflactide)$_{1}$-(MTC-COO-TEMPO)$_{8}$ +2Na]$^{2+}$

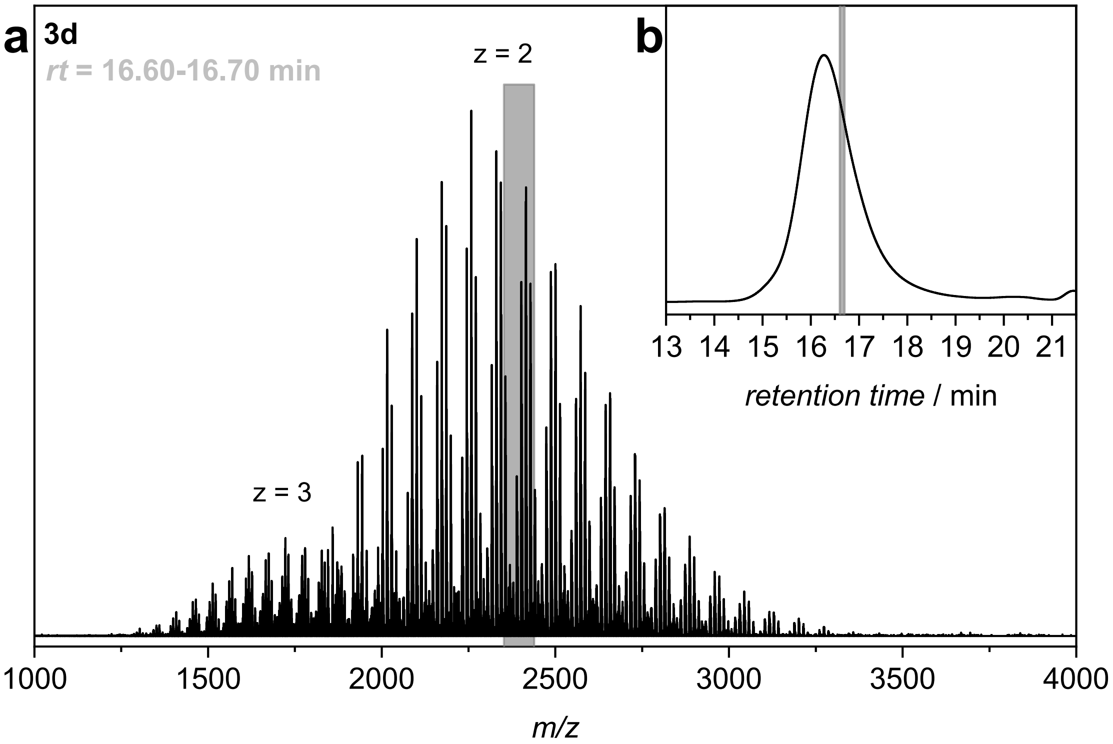


Figure S12. (**a**) Overview over the mass spectrum of polymer **3d** between *m/z* = 1000 and 4000 showing the polymer distribution for charge states *z* = 2 and 3. (**b**) The MS spectrum was derived from the spectra recorded 16.6 and 16.7 min of the SEC experiment, highlighted in grey.

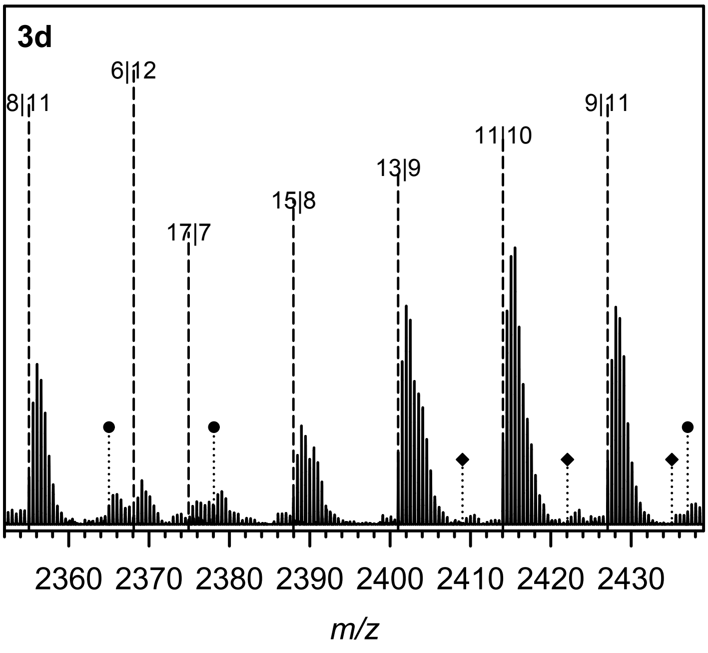


Figure S13. Representative detailed view of one lactide repeating unit in the MS spectrum of **3d** in the range of *m/z* = 2352 to 2439 (z = 2) as highlighted in **Figure S12a**. Please refer to **Table S7** for a comparison of the experimentally found m/z values with the theoretically expected values for the assigned compositions.

Table S7. Collation of observed signals in the mass spectrum of **3d** in the range of m/z = 2352 to 2439 showing one lactide repeating unit and the theoretically expected values for the assigned compositions. The resolution was determined to be 43000.

Major Signals

Symbol	m/z^{exp}	m/z^{theor}	Δ_{ppm}	composition
8|11	2355.0679	2355.0539	5.94	[PgO-(lactide)$_8$-(MTC-COO-TEMPO)$_{11}$-H +2Na]$^{2+}$
6|12	2368.0949	2368.0918	1.30	[PgO-(lactide)$_6$-(MTC-COO-TEMPO)$_{12}$-H +2Na]$^{2+}$
17|7	2374.9275	2374.9234	1.75	[PgO-(lactide)$_{17}$-(MTC-COO-TEMPO)$_7$-H +2Na]$^{2+}$
15|8	2387.9686	2387.9613	3.07	[PgO-(lactide)$_{15}$-(MTC-COO-TEMPO)$_8$-H +2Na]$^{2+}$
13|9	2401.0057	2400.9992	2.71	[PgO-(lactide)$_{13}$-(MTC-COO-TEMPO)$_9$-H +2Na]$^{2+}$
11|10	2414.0446	2414.0371	3.10	[PgO-(lactide)$_{11}$-(MTC-COO-TEMPO)$_{10}$-H +2Na]$^{2+}$
9|11	2427.0862	2427.0750	4.60	[PgO-(lactide)$_9$-(MTC-COO-TEMPO)$_{11}$-H +2Na]$^{2+}$

Transesterified

Symbol	m/z^{exp}	m/z^{theor}	Δ_{ppm}	composition
●	2365.0072	2364.9886	7.85	[PgO-(lactide)$_{12}$-(halflactide)$_1$-(MTC-COO-TEMPO)$_9$-H +2Na]$^{2+}$
●	2378.0586	2378.0265	13.48	[PgO-(lactide)$_{10}$-(halflactide)$_1$-(MTC-COO-TEMPO)$_{10}$-H +2Na]$^{2+}$
●	2437.0272	2437.0098	7.16	[PgO-(lactide)$_{13}$-(halflactide)$_1$-(MTC-COO-TEMPO)$_9$-H +2Na]$^{2+}$

Macrocycle

Symbol	m/z^{exp}	m/z^{theor}	Δ_{ppm}	composition
◆	2409.0078	2408.9966	4.63	[(lactide)$_{13}$-(halflactide)$_1$-(MTC-COO-TEMPO)$_9$ +2Na]$^{2+}$
◆	2422.0709	2422.0346	15.00	[(lactide)$_{11}$-(halflactide)$_1$-(MTC-COO-TEMPO)$_{10}$ +2Na]$^{2+}$
◆	2435.0585	2435.0725	5.74	[(lactide)$_9$-(halflactide)$_1$-(MTC-COO-TEMPO)$_{11}$ +2Na]$^{2+}$

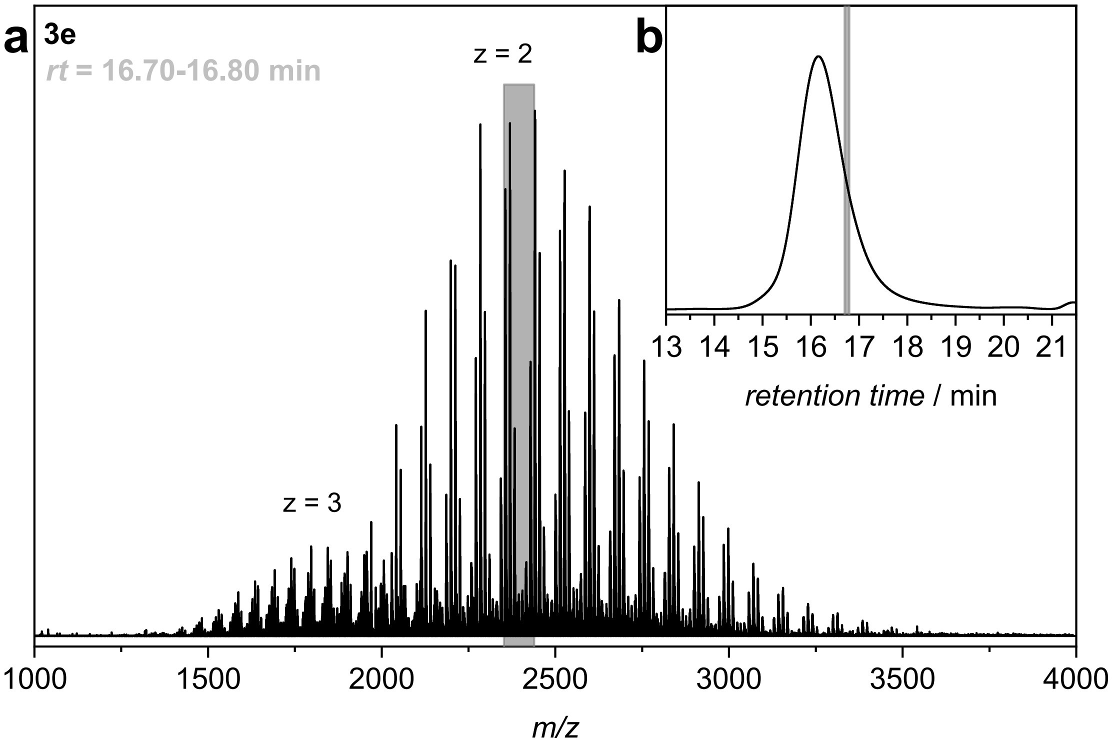


Figure S14. (**a**) Overview over the mass spectrum of polymer **3e** between *m/z* = 1000 and 4000 showing the polymer distribution for charge states *z* = 2 and 3. (**b**) The MS spectrum was derived from the spectra recorded 16.7 and 16.8 min of the SEC experiment, highlighted in grey.

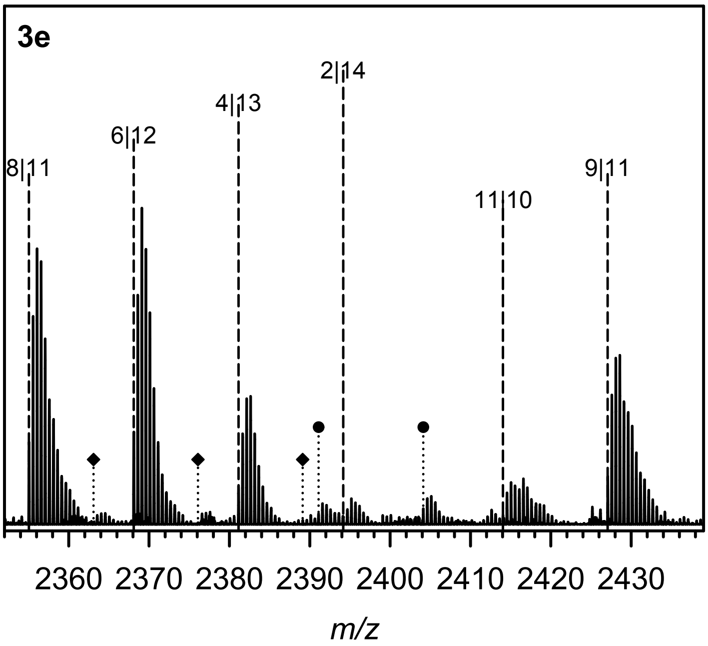


Figure S15. Representative detailed view of one lactide repeating unit in the MS spectrum of **3e** in the range of *m/z* = 2352 to 2439 (z = 2) as highlighted in **Figure S14a**. Please refer to **Table S8** for a comparison of the experimentally found m/z values with the theoretically expected values for the assigned compositions.

Table S8. Collation of observed signals in the mass spectrum of **3e** in the range of m/z = 2352 to 2439 showing one lactide repeating unit and the theoretically expected values for the assigned compositions. The resolution was determined to be 43000.

Major Signals

Symbol	m/z^{exp}	m/z^{theor}	Δ_{ppm}	composition
8|11	2355.0636	2355.0539	4.12	[PgO-(lactide)$_8$-(MTC-COO-TEMPO)$_{11}$-H +2Na]$^{2+}$
6|12	2368.1034	2368.09182	4.89	[PgO-(lactide)$_6$-(MTC-COO-TEMPO)$_{12}$-H +2Na]$^{2+}$
4|13	2381.1436	2381.12974	5.82	[PgO-(lactide)$_4$-(MTC-COO-TEMPO)$_{13}$-H +2Na]$^{2+}$
2|14	2394.17	2394.16766	0.98	[PgO-(lactide)$_2$-(MTC-COO-TEMPO)$_{14}$-H +2Na]$^{2+}$
11|10	2414.0457	2414.03711	3.56	[PgO-(lactide)$_{11}$-(MTC-COO-TEMPO)$_{10}$-H +2Na]$^{2+}$
9|11	2427.0849	2427.07503	4.07	[PgO-(lactide)$_9$-(MTC-COO-TEMPO)$_{11}$-H +2Na]$^{2+}$
8|11	2355.0636	2355.0539	4.12	[PgO-(lactide)$_8$-(MTC-COO-TEMPO)$_{11}$-H +2Na]$^{2+}$

Transesterified

Symbol	m/z^{exp}	m/z^{theor}	Δ_{ppm}	composition
●	2391.0888	2391.064465	10.18	[PgO-(lactide)$_8$-(halflactide)$_1$-(MTC-COO-TEMPO)$_{11}$-H +2Na]$^{2+}$
●	2404.1301	2404.102385	11.53	[PgO-(lactide)$_6$-(halflactide)$_1$-(MTC-COO-TEMPO)$_{12}$-H +2Na]$^{2+}$

Macrocycle

Symbol	m/z^{exp}	m/z^{theor}	Δ_{ppm}	composition
◆	2363.0844	2363.051355	13.98	[(lactide)$_8$-(halflactide)$_1$-(MTC-COO-TEMPO)$_{11}$ +2Na]$^{2+}$
◆	2376.0841	2376.089275	2.18	[(lactide)$_6$-(halflactide)$_1$-(MTC-COO-TEMPO)$_{12}$ +2Na]$^{2+}$
◆	2389.1186	2389.127195	3.60	[(lactide)$_4$-(halflactide)$_1$-(MTC-COO-TEMPO)$_{13}$ +2Na]$^{2+}$

References

1. R. C. Pratt, B. G. G. Lohmeijer, D. A. Long, P. N. P. Lundberg, A. P. Dove, H. Li, C. G. Wade, R. M. Waymouth and J. L. Hedrick, *Macromolecules*, 2006, **39**, 7863-7871.
2. T. Gruendling, M. Guilhaus and C. Barner-Kowollik, *Macromolecules*, 2009, **42**, 6366-6374.