Electronic Supplementary Material (ESI) for Polymer Chemistry.

Polyester synthesis based on 3-carene as renewable feedstock

Supporting Information

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1. GENERAL EXPERIMENTAL

All reactions and polymerizations involving air- and moisture-sensitive compounds were performed in a MBraun LabMaster120 glovebox filled with 4.6 argon purchased from Westfalen or using standard Schlenk techniques. Chemicals were purchased from Sigma-Aldrich, ABCR or TCI Europe and used without purification unless stated otherwise. Solvents were dried using an MBraun SPS-800 or by filtration over activated aluminium oxide and stored over 3 Å molecular sieve.

Nuclear magnetic resonance (NMR) spectra ($^{1}H/^{13}C$/2D-experiments) were recorded on a Bruker AV-400HD or a Brucker AV-500CR as indicated. The NMR spectroscopical shifts δ are reported in ppm relative to the residual carbon or proton signal of the deuterated solvent. $CDCl_3$ was purchased from Deutero and dried over 3 Å molecular sieve prior to use. Spectra interpretation was performed using MestreNova software.

Size-exclusion chromatography (SEC) was performed on a PL-GPC50 plus from Polymer Laboratories with THF (with 222 mg/L 3,5-di-*tert*-butyl-4-hydroxytoluol as stabilizing agent) as eluent at 30 °C. Size separation was done using two Polargel Mixed-C columns by Agilent Technologies with a polymer sample concentration of 2.0-3.0 mg/L. Molecular weight and polydispersity is measured via single RI-detection and reported against polystyrene standards.

Gas-chromatography mass spectrometry (GC-MS) measurements were performed on an Agilent GC-7890B equipped with a MSD 59771 mass detector, a 7693 automatic liquid sampler and a G4513A autoinjector. Sample separation is done using a HP-5MS UI column (30 m length, 0.25 mm diameter, 0.25 µm film) in a temperature range of 60-300 °C followed by mass spectrometry using full scan method in a mass range of 40-500 au. Samples are prepared by dissolving 1 mg/mL in HPLC grade dichloromethane prior to measurement.

Attenuated total reflection infrared spectroscopy (ATR-IR) spectra were recorded on a Bruker Vertex 70v ATR-IR spectrometer at room temperature under argon as inert gas.

Thermogravimetric analysis (TGA) is performed from 2 mg samples on a TGA Q5000 by TA Instruments. Samples are heated from room temperature to 1000 °C with a heat rate of 10 K/min under argon. Analysis of mass loss and determination of $T_{5\%}$ is done using TA Analysis software.

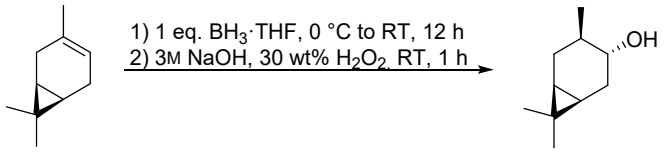
Differential scanning calorimetry (DSC) was measured using a DSC Q2000 by TA instruments in exo-down mode. Sample size is about 6 mg in non-hermetic aluminum pans in the range of -100 °C to 250 °C depending on the sample. Analysis is performed using TA Analysis.

Powder X-Ray diffractometry (pXRD) was performed using a PANalytical Empyrean diffractometer with a PANalytical PIXcel 1D detector in Bragg-Brentano geometry. Cu K_α radiation with a voltage of 45 kV (40 mA intensity) with λ_1 = 1.5406 Å / λ_2 = 1.5444 Å [I_1/I_2 = 0.5] was used for measurements in the 2θ of 5-60 ° (step size 0.01 °, measurement time 7 h). The obtained data was analysed using HighScore software, Cu K_α is stripped using the *Rachinger* method and the amorphous background is determined using the *Sonneveld* and *Visser* method with a granularity of 15 and a bending factor of 8 for the subsequent peak fit. The calculation of crystallinity fraction in the region of 5 – 27 ° is done by a peak deconvolution using OriginPro 2020 with 2 peaks for the amorphous backscattering of the polymer and 8 peaks for the crystalline diffraction peaks. The degree of crystallinity X_C is obtained by peak integration and the areas of the amorphous parts AA and crystalline parts AC via $X_C = A_C / (A_C + A_A)$.[4]

Electron-Spray Ionization Mass Spectrometry (ESI-MS) was measured on a Thermo Fisher Scientific Exactive Plus in negative mode in HPLC acetronitrile directly from the reaction mixture without purification. Oligomers were prepared using a 1:5 ratio of catalyst to monomer with the conditions reported in the manuscript.

2. MONOMER SYNTHESIS

2.1 Hydroboration of 3-carene[1]



136.24 g/mol 154.14 g/mol

Under inert conditions 260 mL 1M borane in tetrahydrofuran (260 mmol, 1.0 eq.) were cooled to 0 °C. Via addition funnel 37.0 g (272 mmol, 1.0 eq.) 3-carene dissolved in 100 mL tetrahydrofuran were added dropwise to the stirred borane solution. The mixture is stirred at 0 °C for one hour and additional 12 hours at room temperature. Subsequently, 40 mL water and 40 mL tetrahydrofuran are added, the mixture is stirred for additional two hours and 40 mL of a 3M aqueous sodium hydroxide solution are added. To complete the reaction, 40 mL 30 wt% $H_2O_{2(aq)}$ were added dropwise, keeping the temperature below 40 °C. The mixture is stirred for an additional hour before extracting with diethyl ether (3×300 mL). The combined organic phases are washed with water (3×200 mL) and brine (2×200 mL) before drying over magnesium sulphate. The solvent was removed in vacuo resulting in 40.1 g of crude 4-*iso*-caranol. Distillation under reduced pressure using a Vigreux column ($bp_{5\ mbar}$ = 76 °C) yielded 38.6 g (250 mmol, 92 %) 4-*iso*-caranol as colourless oil.

^{1}H-NMR spectrum (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 3.06 (td, $^3J_{H,H}$ = 9.8, 6.6 Hz, 1H), 2.08 (dd, $^3J_{H,H}$ = 14.1, 6.6 Hz, 1H), 2.02-1.89 (m, 1H), 1.65-1.48 (m, 1H), 1.30-1.15 (m, 1H), 0.97 (s, 3H), 0.92 (s, 3H), 0.90 (s, 3H), 0.85-0.75 (m, 1H), 0.74-0.64 (m, 2H).

^{13}C-NMR spectrum (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 74.8, 36.5, 30.5, 29.0, 28.6, 22.0, 20.3, 17.9, 17.8 16.1.

GC-MS: t_R = 8.13 min, m/z = 154.1 (M^+), 136.1 ($[M\text{-}OH]^+$).

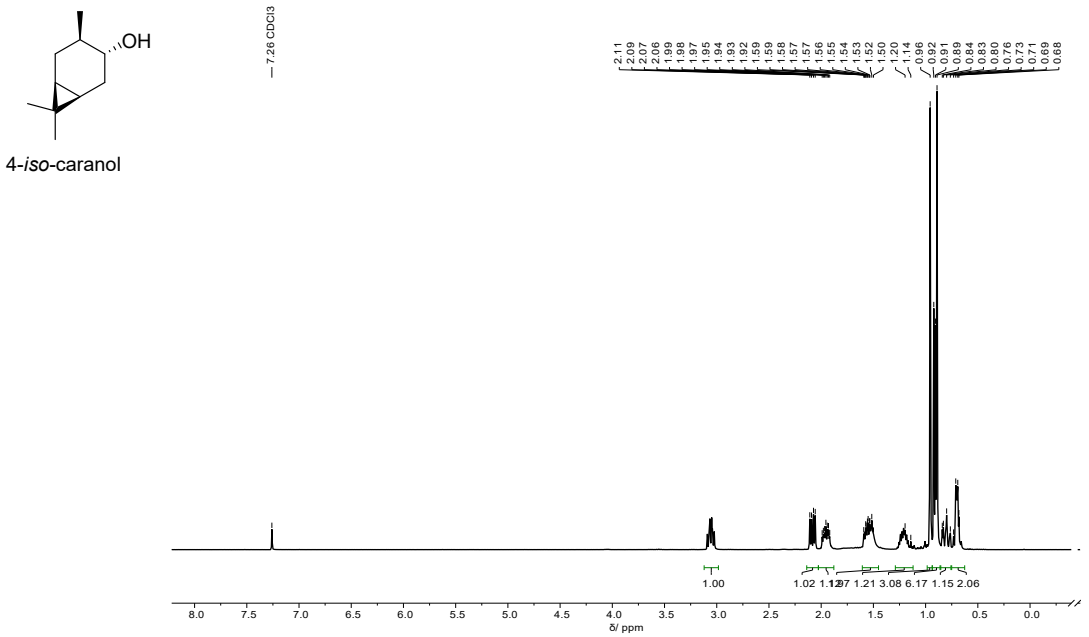


Figure S1: ^{1}H-NMR spectrum (400 MHz, $CDCl_3$, 300K) of 4-*iso*-caranol.

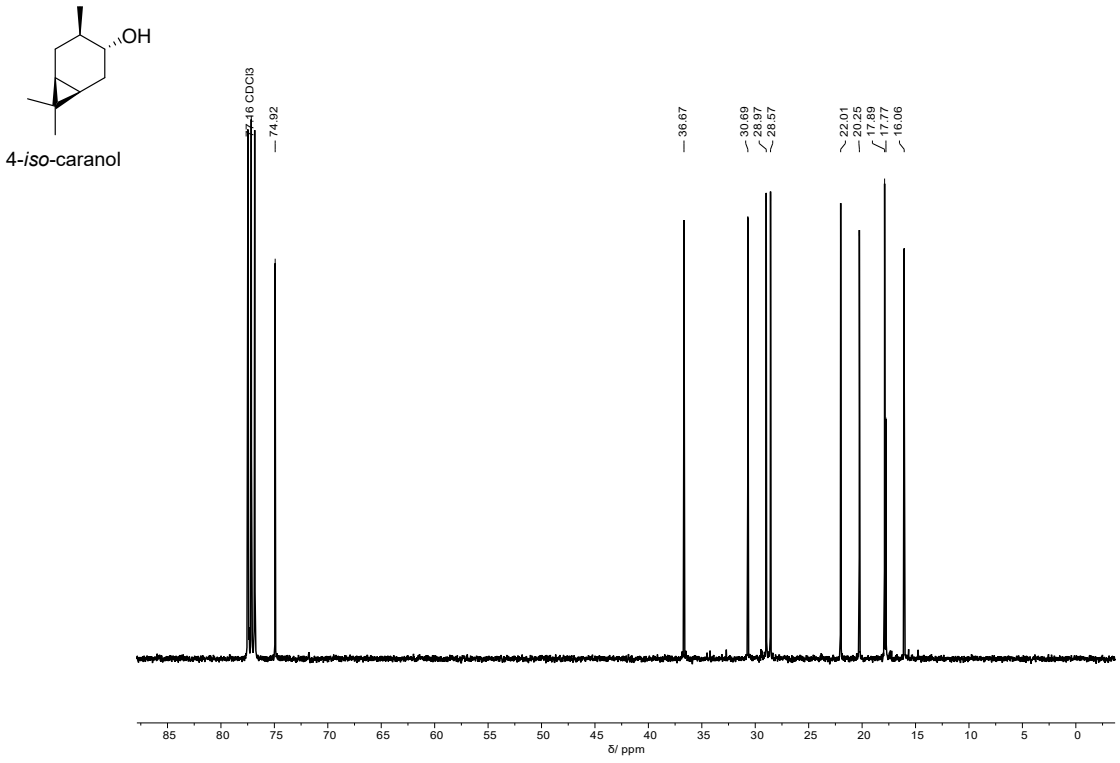
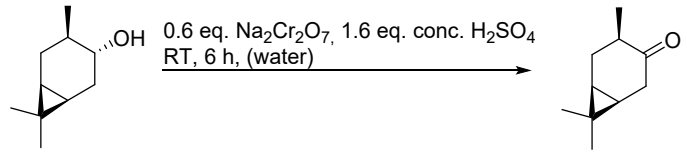


Figure S2: ^{13}C-NMR spectrum (125 MHz, $CDCl_3$, 300K) of 4-*iso*-caranol.

2.2 Oxidation of 4-*iso*-caranol[1]



154.14 g/mol 152.14 g/mol

For the oxidation of 4-*iso*-caranol to 4-*iso*-caranone, a chromic acid solution was prepared by adding 8.5 mL (15.6 g, 159 mmol, 1.6 eq.) concentrated sulfuric acid to 16.12 g (54 mmol, 0.6 eq.) sodium dichromate and 90 mL water were added for dilution. 15.0 g (97 mmol, 1.0 eq.) 4-*iso*-caranol were diluted in 50 mL diethyl ether and the chromic acid solution was added to the alcohol over 2 hours at room temperature. After complete addition, the remaining suspension is stirred for additional 4 hours at room temperature before separating the phases and extracting the aqueous phase with diethyl ether (2×50 mL). The combined organic phases were washed with water (2×60 mL) and brine (2×60 mL) before drying over magnesium sulphate. Afterwards the solvent was removed in vacuo and the crude product was purified via column chromatography (silica, *p*-anisaldehyde staining, hexanes/ethyl acetate = 1:20), yielding 7.65 g (50 mmol, 51%) 4-*iso*-caranone as colorless oil.

^{1}H-NMR spectrum (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 2.51 (dd, $^{3}J_{H,H}$ = 18.0, 8.4 Hz, 1H), 2.41-2.33 (m, 1H), 2.32-2.20 (m, 2H), 1.32-1.15 (m, 1H), 1.12-1.05 (m, 1H), 1.00 (s, 3H), 1.01-0.95 (m, 1H), 0.94 (d, $^{3}J_{H,H}$ = 6.4 Hz, 3H), 0.80 (s, 3H).

^{13}C-NMR spectrum (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 216.8, 42.1, 36.9, 29.9, 28.0, 22.9, 20.5, 19.6, 15.0, 14.2.

GC-MS: t_R = 8.15 min, m/z = 152.1 (M^+), 136.1 ([M-Me]$^+$).

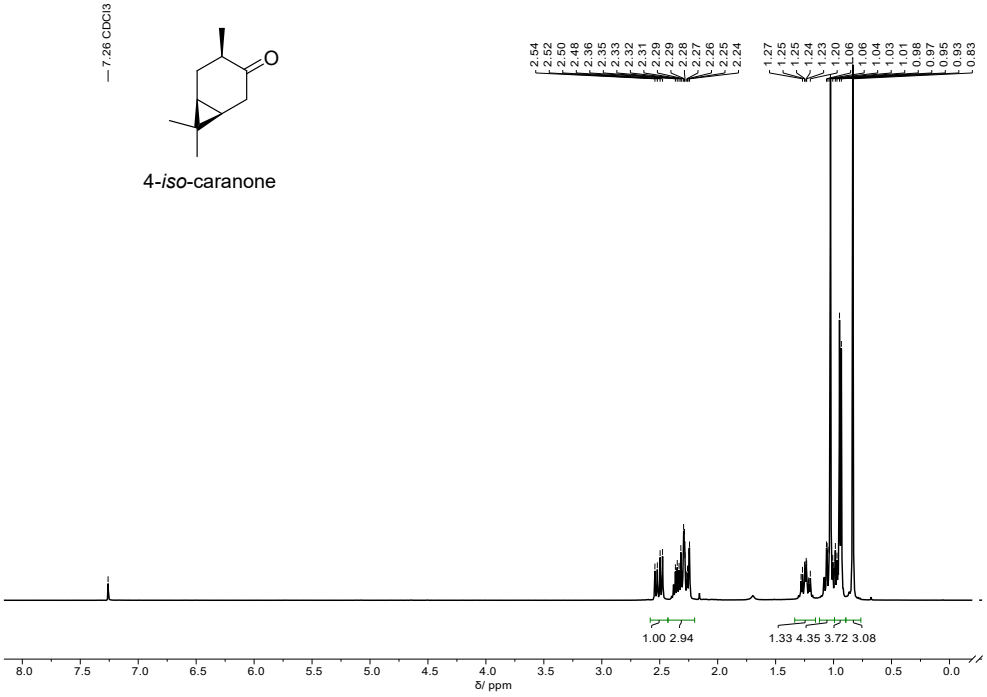


Figure S3: ^{1}H-NMR spectrum (400 MHz, $CDCl_3$, 300K) of 4-*iso*-caranone.

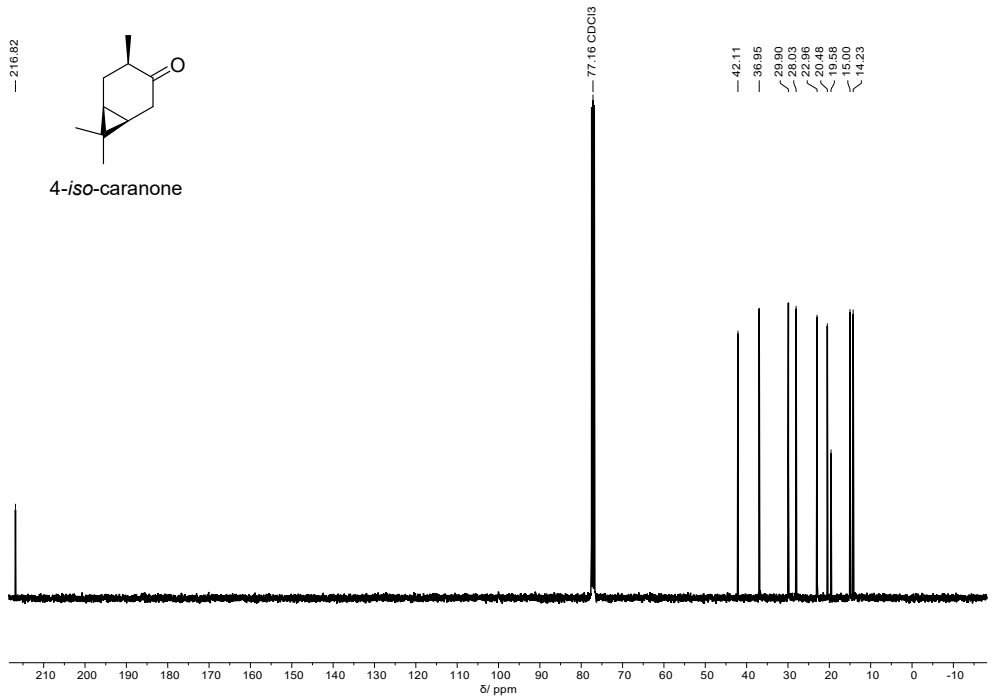
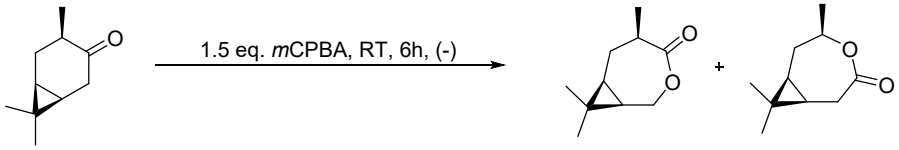


Figure S4: ^{13}C-NMR spectrum (125 MHz, $CDCl_3$, 300K) of 4-*iso*-caranone.

2.3 Baeyer-Villiger Oxidation of 4-*iso*-caranone[2]



152.14 g/mol 168.12 g/mol

For the lactone synthesis, 3.0 g (20.0 mmol, 1.0 eq.) 4-*iso*-caranone were put in a 50 mL flask with stirring bar and 5.03 g (29.0 mmol, 1.5 eq.) *meta*-chloroperbenzoic acid were added without solvent and a reflux condenser was attached. After stirring at room temperature for 6 hours, the mixture is diluted with 20 mL dichloromethane, 11.1 g (80 mmol, 4.0 eq.) potassium carbonate were added to remove residual *m*CPBA and 4-chlorobenzoic acid and the solution was filtered off. After solvent removal the crude product was dissolved in 40 mL diethyl ether and the organic phase was washed with saturated sodium sulfite solution (3×40 mL), water (2×40 mL) and brine (2x40 mL) and dried with magnesium sulphate. The solvent was removed to yield 1.66 g crude product. GC-MS analysis revealed a conversion of 65 % with regard to used 4-*iso*-caranone. Separation via column chromatography (silica, hexane/diethyl ether = 1:3, CAM staining) yielded 0.23 g α-carenelactone (0.8 mmol, 4 %) as yellow oil, 0.31 g ε-carenelactone (1.7 mmol, 8 %) as white crystals and a mixture of both lactones (0.31 g, 2.0 mmol, 10 %, αCarL:εCarL = 40:60). Non-converted 4-*iso*-caranone was isolated as separate fraction and reused for the BVO.

α-carenelactone:
^{1}H-NMR spectrum (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 4.45 (dd, $^{3}J_{H,H}$ = 13.1 Hz, $^{2}J_{H,H}$ = 3.7 Hz, 1H, OC*H*HCH), 4.30 (dd, $^{3}J_{H,H}$ = 13.1 Hz, $^{2}J_{H,H}$ = 3.7 Hz, 1H, OCH*H*CH), 3.00-2.84 (m, 1H, Me-C*H*-CH_2), 1.99-1.87 (m, 1H, Me-CH-CH*H*), 1.58-1.45 (m, 1H, Me-CH-C*H*H), 1.27 (d, $^{3}J_{H,H}$ = 7.1 Hz, 3H, Me), 1.10 (s, 3H, *gem*-Me), 1.05 (s, 3H, *gem*-Me), 1.04-0.98 (m, 2H, $CH_{cyclopropane}$).
^{13}C-NMR spectrum (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 177.3 (CO), 66.3 (CH2), 41.3 (CH), 27.4 (*gem*-CH_3), 27.4 (CH_2), 25.4 (CH), 24.9 (CH), 20.2 (C_{quart}), 19.7 (CH_3), 15.3 (*gem*-CH_3).
GC-MS: t_R = 10.2 min, m/z = 168.1 (M^+), 153.2 ($(M-Me)^+$).
ATR-IR: $\tilde{\nu}$ = 3440 cm^{-1}, 2940 cm^{-1}, 2866 cm^{-1}, 1722 cm^{-1}, 1470 cm^{-1}, 1286 cm^{-1}, 1276 cm^{-1}, 1193 cm^{-1}.

ε-carenelactone:
^{1}H-NMR spectrum (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 4.68-4.55 (m, 1H, O-CH-Me), 3.16 (dd, $^{3}J_{H,H}$ = 15.6 Hz, $^{2}J_{H,H}$ = 4.3 Hz, 1H, OCC*H*H) 2.96 (dd, $^{3}J_{H,H}$ = 15.6 Hz, $^{2}J_{H,H}$ = 4.3 Hz, OCCH*H*), 2.11 (dd, $^{3}J_{H,H}$ = 16.3, 10.0 Hz, 1H, CH_2), 1.78 (td, $^{3}J_{H,H}$ = 15.9, 10.2, $^{2}J_{H,H}$ = 5.1 Hz, 1H, CH_2), 1.30 (d, $^{3}J_{H,H}$ = 6.4 Hz, 3H, Me), 1.05 (s, 3H, *gem*-Me), 1.03 (s, 3H, *gem*-Me), 0.95-0.83 (m, 1H, C$H_{cyclopropane}$), 0.78-0.68 (m, 1H, C$H_{cyclopropane}$).

^{13}C-NMR spectrum (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 173.3 (CO), 77.06 (CH), 33.2 (CH_2), 30.8 (CH_2), 29.2 (CH_3), 22.2 (CH, CH_3), 20.9 (CH), 18.6 (C_{quart}), 15.0 (CH_3).
GC-MS: t_R = 10.2 min, m/z = 168.1 (M^+), 153.2 ($(M-Me)^+$).
ATR-IR: $\tilde{\nu}$ = 3440 cm^{-1}, 2940 cm^{-1}, 2866 cm^{-1}, 1722 cm^{-1}, 1470 cm^{-1}, 1286 cm^{-1}, 1276 cm^{-1}, 1193 cm^{-1}.

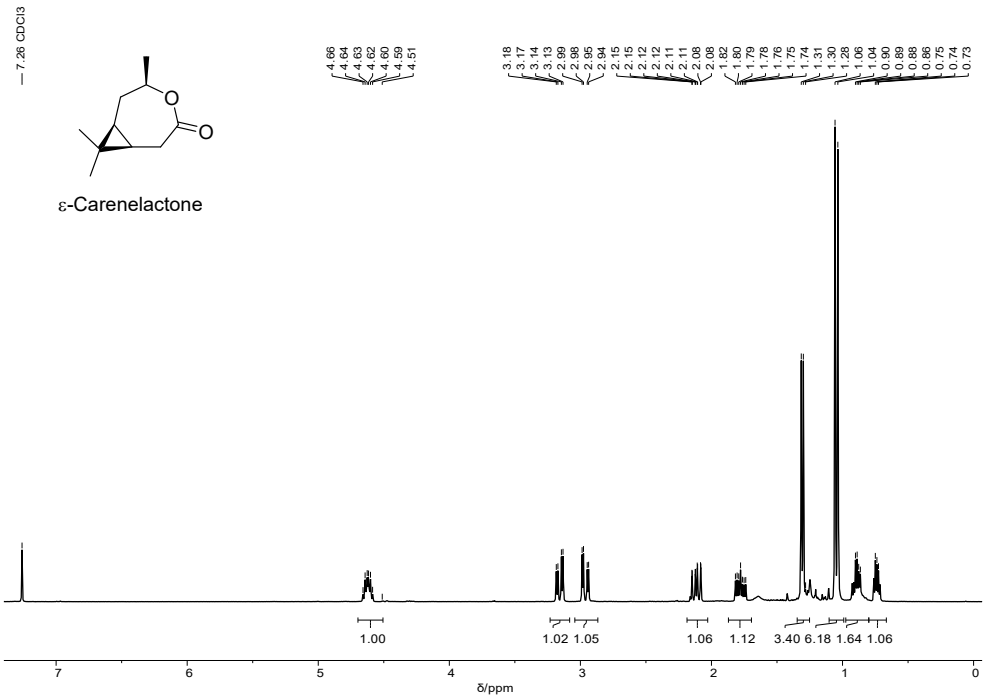


Figure S5: ^{1}H-NMR spectrum (400 MHz, $CDCl_3$, 300K) of ε-carenelactone.

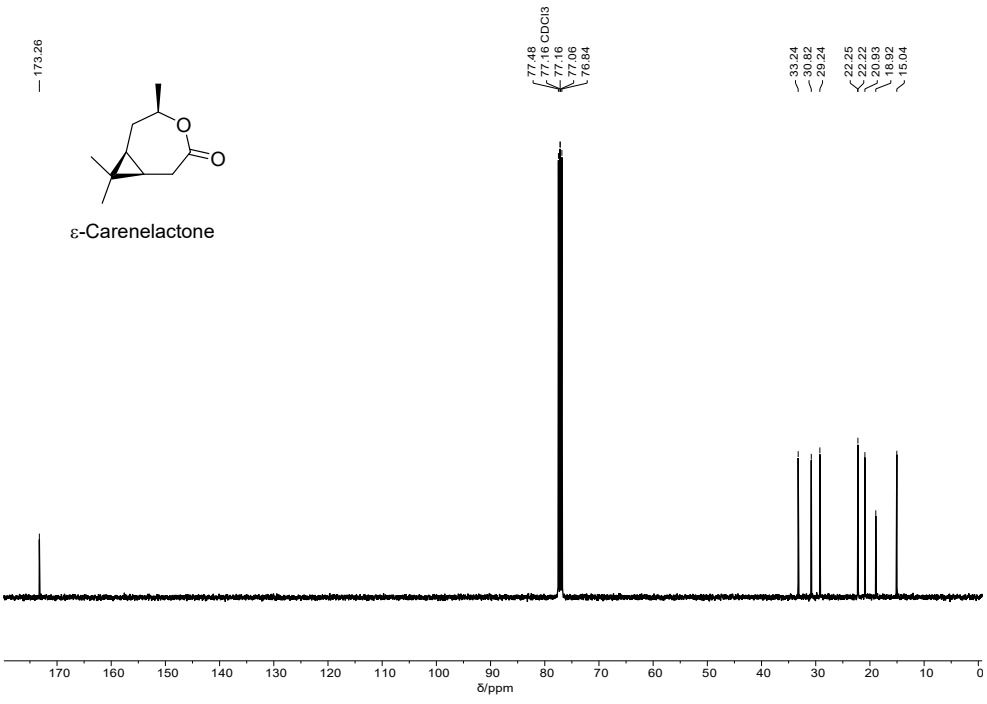


Figure S6: ^{13}C-NMR spectrum (400 MHz, $CDCl_3$, 300K) of ε-carenelactone.

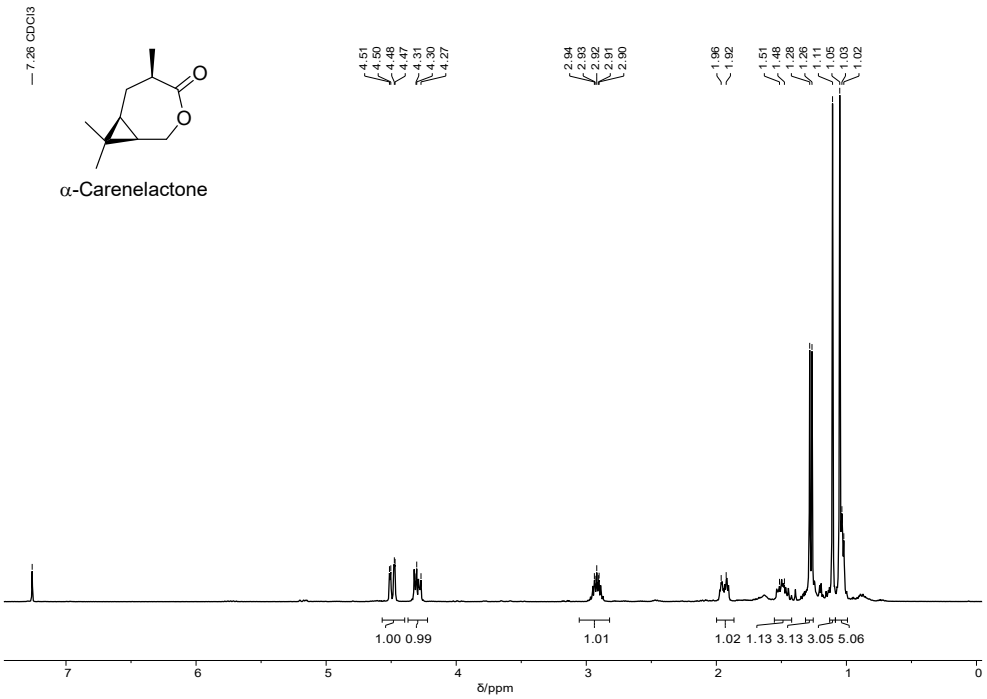


Figure S7: ^{1}H-NMR spectrum (400 MHz, $CDCl_3$, 300K) of α-carenelactone.

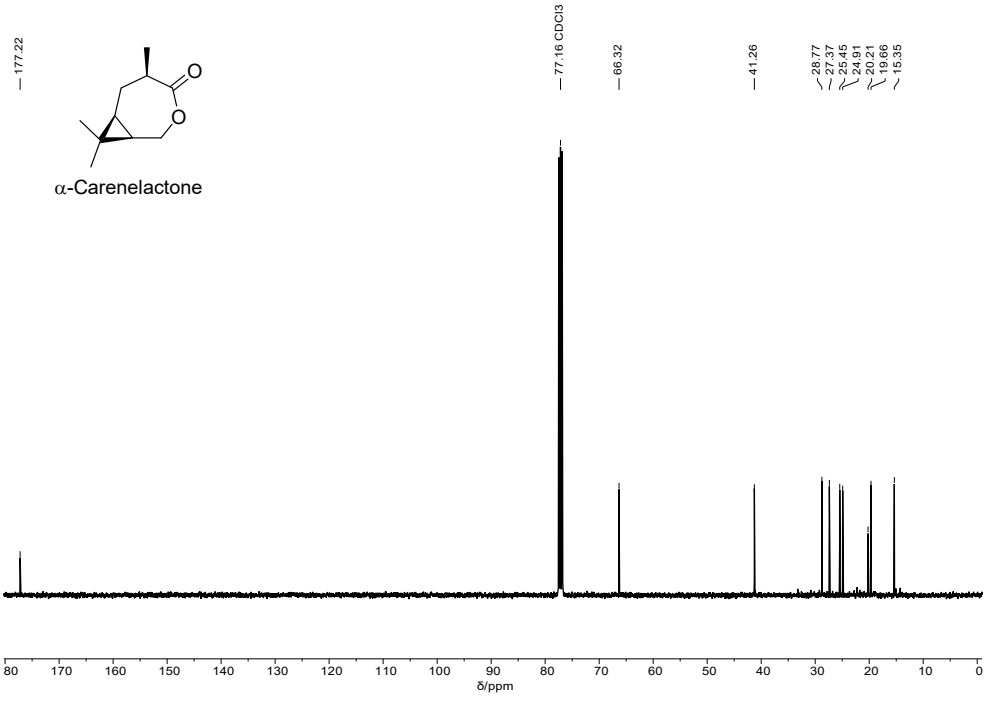
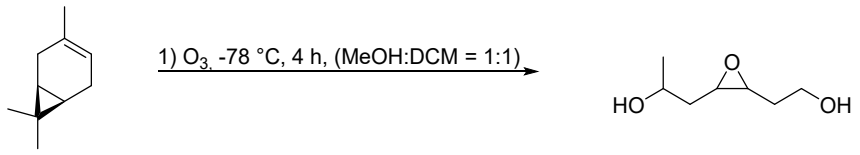


Figure S8: ^{13}C-NMR spectrum (125 MHz, $CDCl_3$, 300K) of α-carenelactone.

2.4 Reductive ozonolysis of 3-carene[3]



154.14 g/mol

172.15 g/mol

25.5 g (187 mmol, 1.0 eq.) 3-carene were dissolved in a 50:50 vol% mixture of dichloromethane and methanol, the reaction flask was cooled to -78 °C and a steady flow of ozone was bubbled through the mixture until a blue color occurred (approx. 4 h). To remove excess of ozone, the flask was purged with argon for 30 min. Subsequently, 7.5 g (198 mmol, 1.1 eq.) sodium borohydride were added stepwise, and the mixture was allowed to warm to room temperature overnight. 20 mL water and 20 mL 1M hydrochloric acid were added and a pH of 1 was adjusted. The reaction mixture was extracted with ethyl acetate (2×80 mL). Afterwards the organic phase was washed with water (2×200 mL) and brine (2×200 mL) before drying over magnesium sulphate. After solvent removal in vacuo, the crude product was distilled under reduced pressure (b_p = 150 °C, 7 mbar) to yield 19.8 g (115 mmol, 61 %) 3-carene diol as colorless oil.

^{1}H-NMR spectrum (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 3.97-3.81 (m, 1H, CH_2CHMe), 3.79-3.58 (m, 2H, CH_2OH), 1.67-1.48 (m, 2H, CH_2), 1.47-1.31 (m, 2H, CH_2), 1.27-1.19 (m, 3H, Me), 1.07 (d, $^3J_{H,H}$ = 3.1 Hz, *gem*-Me), 0.94 (d, $^3J_{H,H}$ = 12.9 Hz, 3H, *gem*-Me), 0.63-0.50 (m, 2H, $CH_{cyclopropane}$).
^{13}C-NMR spectrum (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 70.0, 68.4, 63.6, 63.5, 33.9, 33.8, 29.3, 28.0, 27.7, 23.7, 23.1, 16.8, 16.2, 15.4.
GC-MS: t_R = 9.86 min, m/z = 172.1 (M^+), 125.1 ($(M\text{-}Me\text{-}2\times OH)^+$)

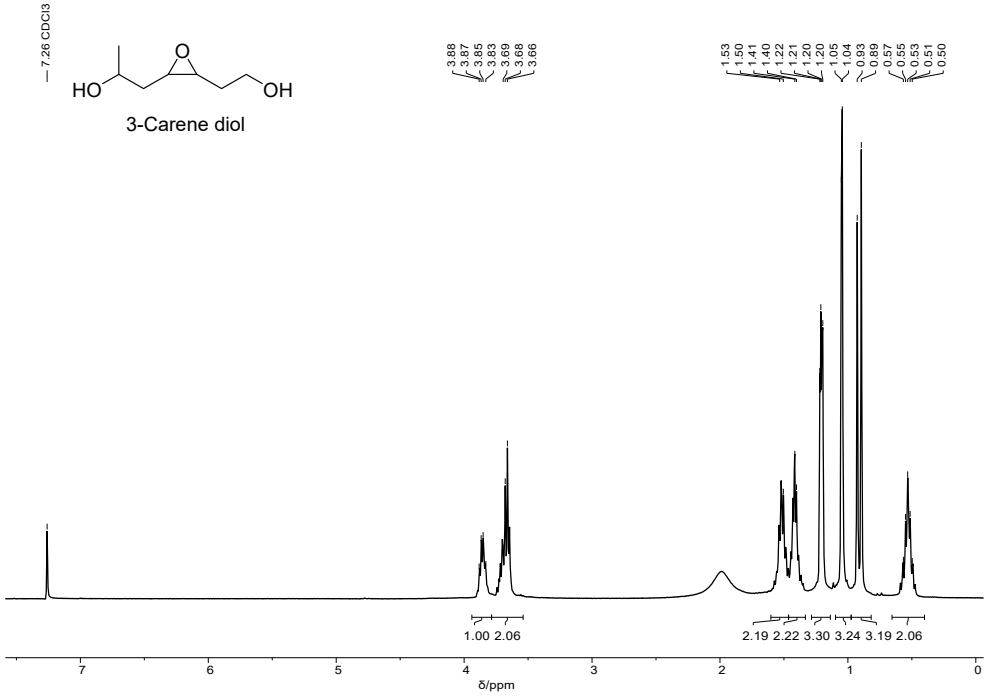


Figure S9: ^{1}H-NMR spectrum (400 MHz, $CDCl_3$, 300K) of 3-carene diol.

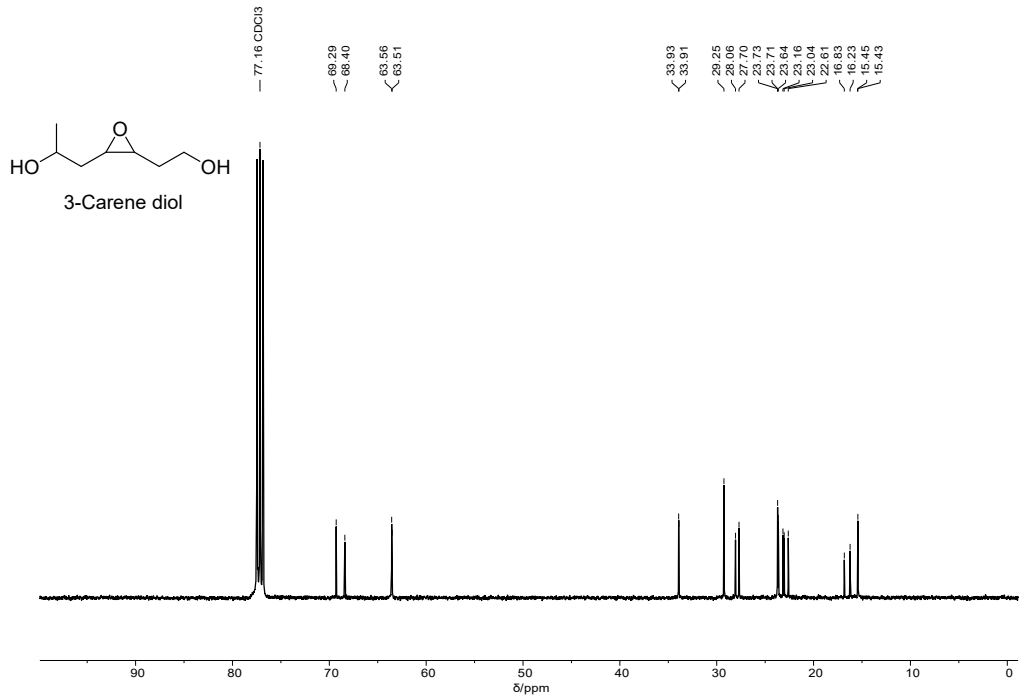


Figure S10: ^{13}C-NMR spectrum (125 MHz, $CDCl_3$, 300K) of 3-carene diol.

3. RING-OPENING POLYMERIZATION OF CARENLACTONES

3.1 Polymerization conversion determination

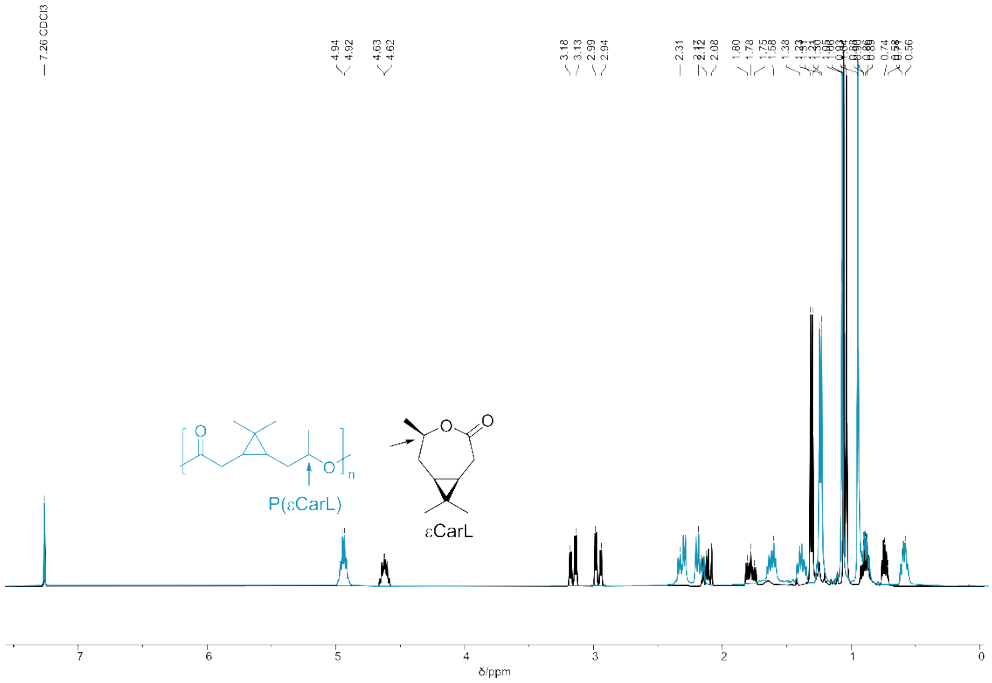


Figure S11: Conversion determination for the polymerization of εCarL (black) to P(εCarL) (blue) via integration of the methine proton as indicated by the arrow with $X = I_{Polymer}/(I_{Monomer}+I_{Polymer})$.

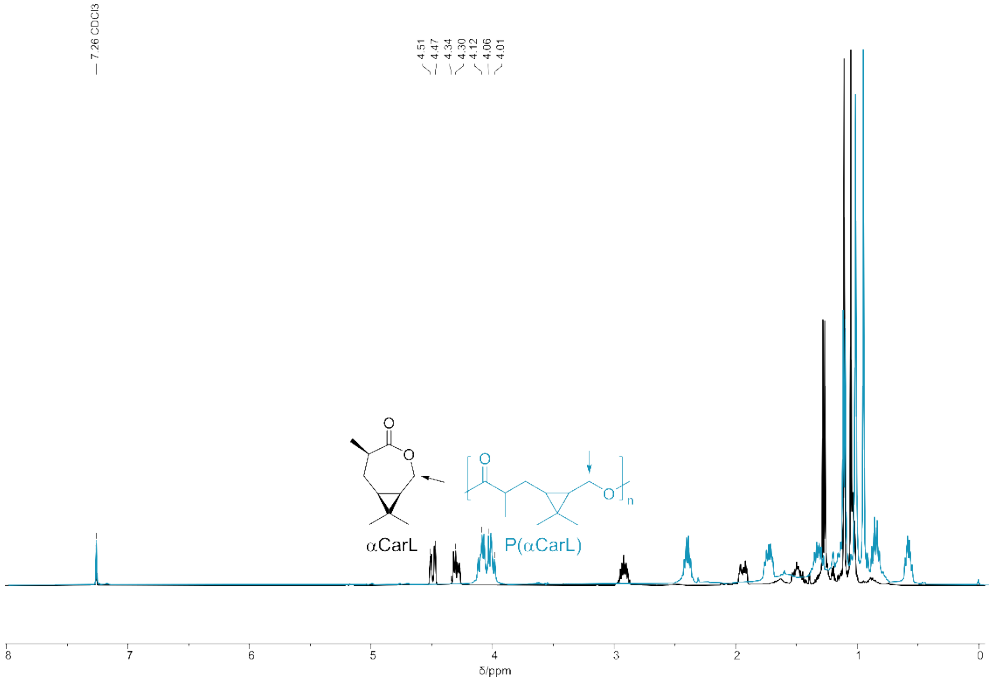


Figure S12: Conversion determination for the polymerization of αCarL (black) to P(αCarL) (blue) via integration of the CH_2-group in α-position to the main chain ester oxygen as indicated by the arrow with $X = I_{Polymer}/(I_{Monomer}+I_{Polymer})$.

3.2 Additional ^{13}C-NMR spectra

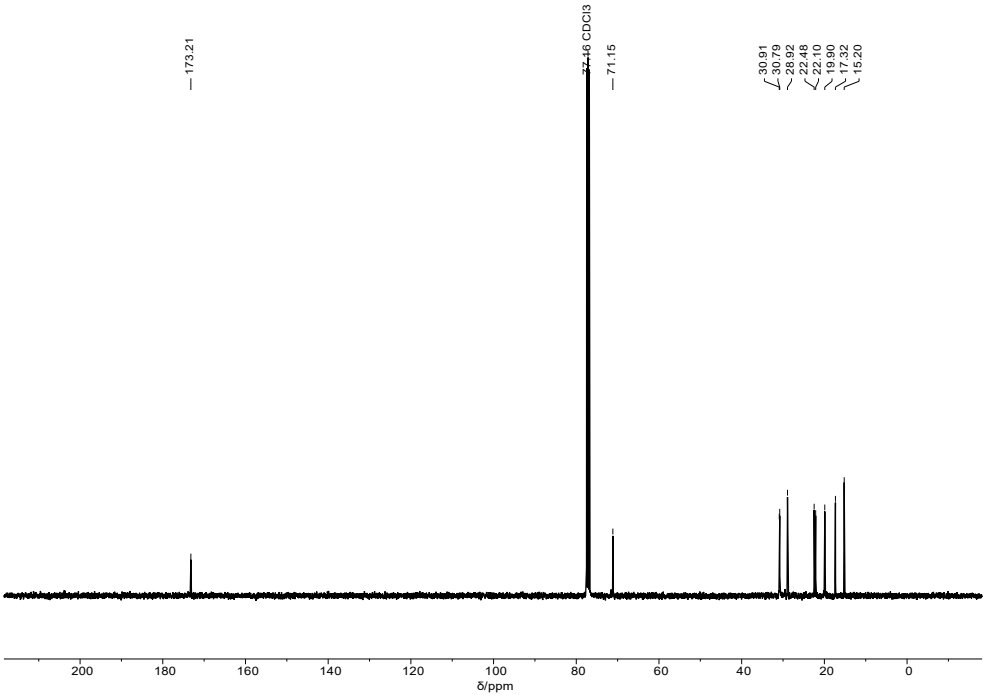


Figure S13: ^{13}C-NMR spectrum (125 MHz, $CDCl_3$, 300K) of P(εCarL).

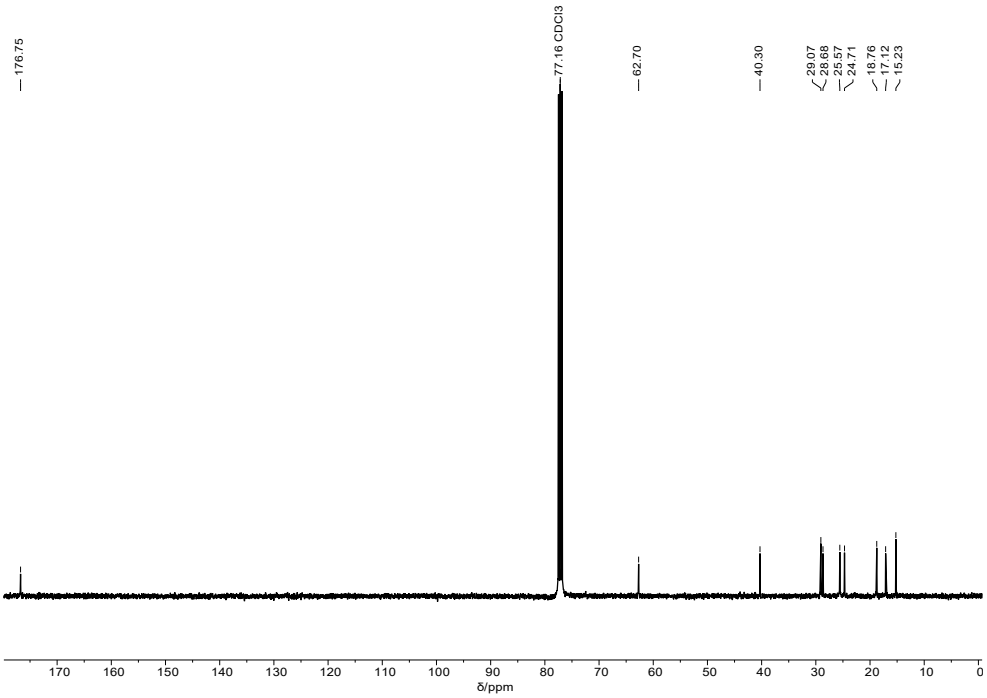


Figure S14: ^{13}C-NMR spectrum (125 MHz, $CDCl_3$, 300K) of P(αCarL).

3.3 Copolymer linkage analysis of P(αCarL-*co*-εCarL)$_{stat}$

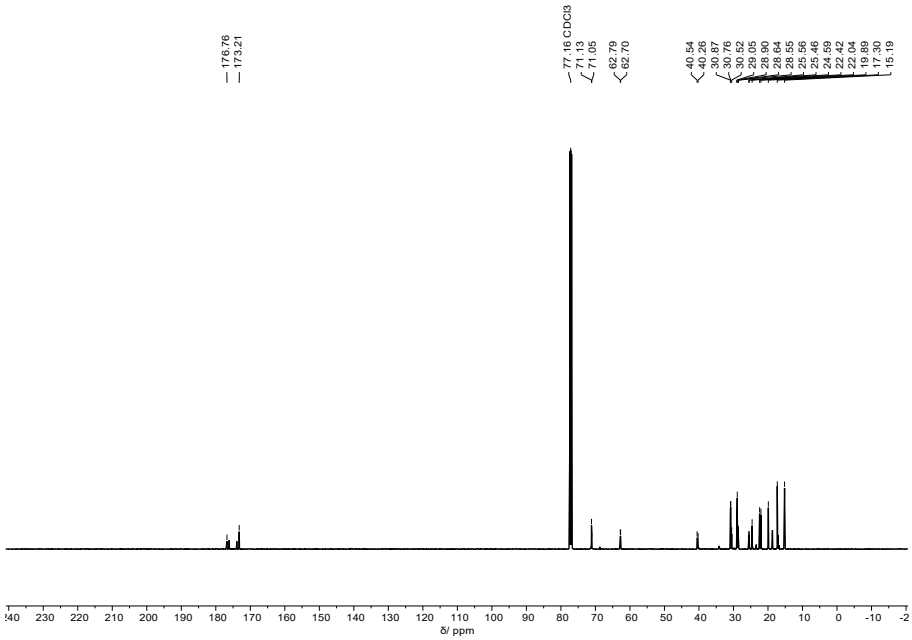


Figure S15: ^{13}C-NMR spectrum (125 MHz, $CDCl_3$, 300K) of P(αCarL-*co*-εCarL)$_{stat}$.

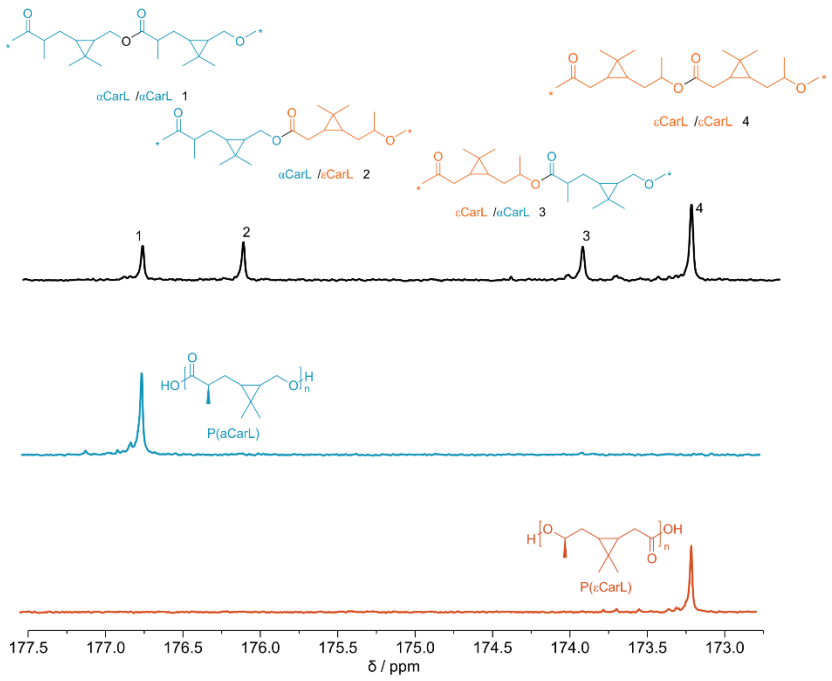


Figure S16: Close-up of the carbonyl region in the ^{13}C-NMR spectra (125 MHz, $CDCl_3$, 300 K) of P(εCarL) (orange, bottom), P(αCarL) (blue, middle) and P(αCarL-*co*-εCarL)$_{stat}$ (black, top) with the four different observable linkages of εCarL and αCarL.

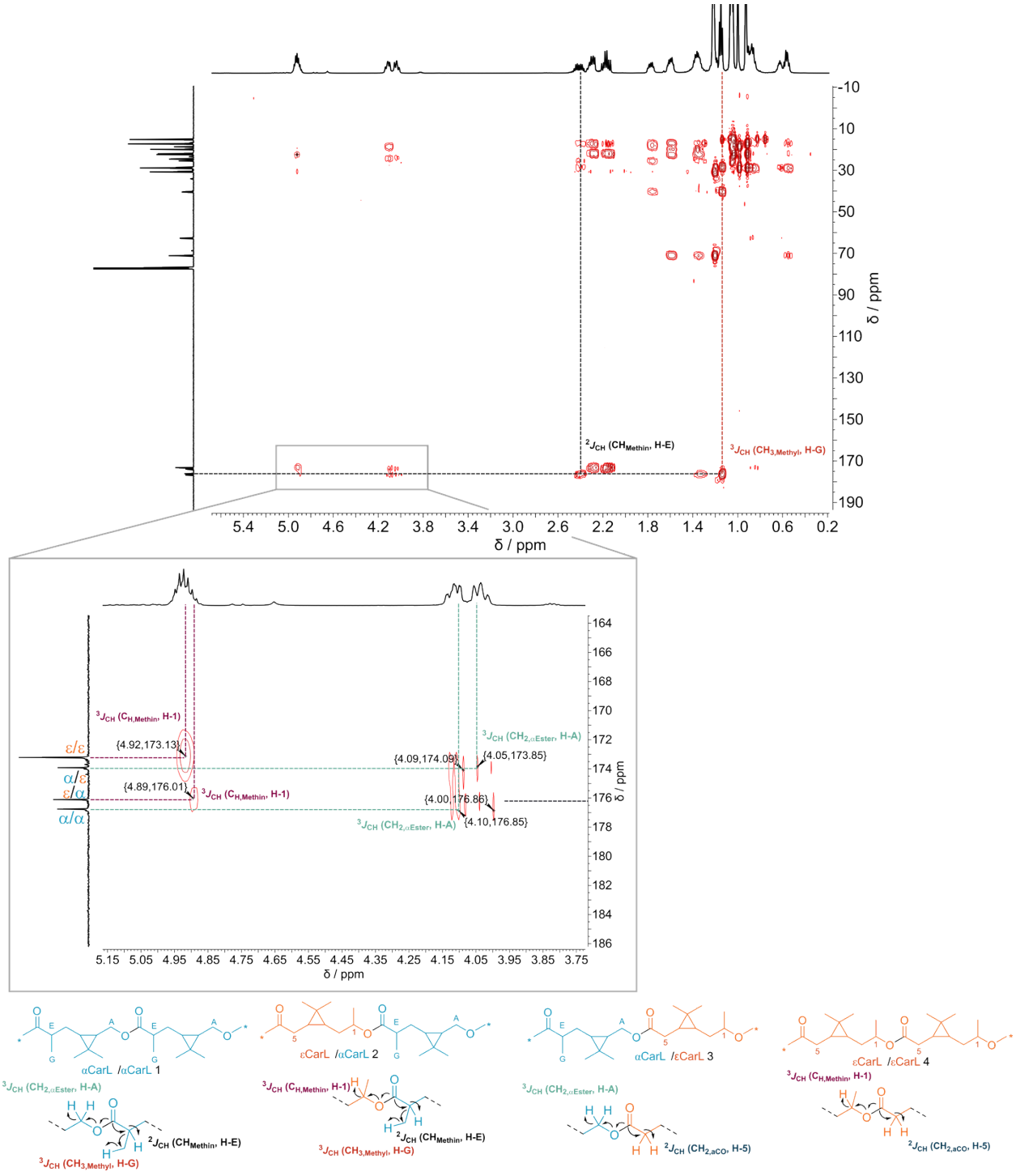


Figure S17: ^{1}H-^{13}C-HMBC (500 MHz, $CDCl_3$, 300K) peak assignment of the different carbonyl signals in the copolyesters P P(αCarL-*co*-εCarL)$_{stat}$.

3.4 SEC characterization of ROP polymers (Table 1)

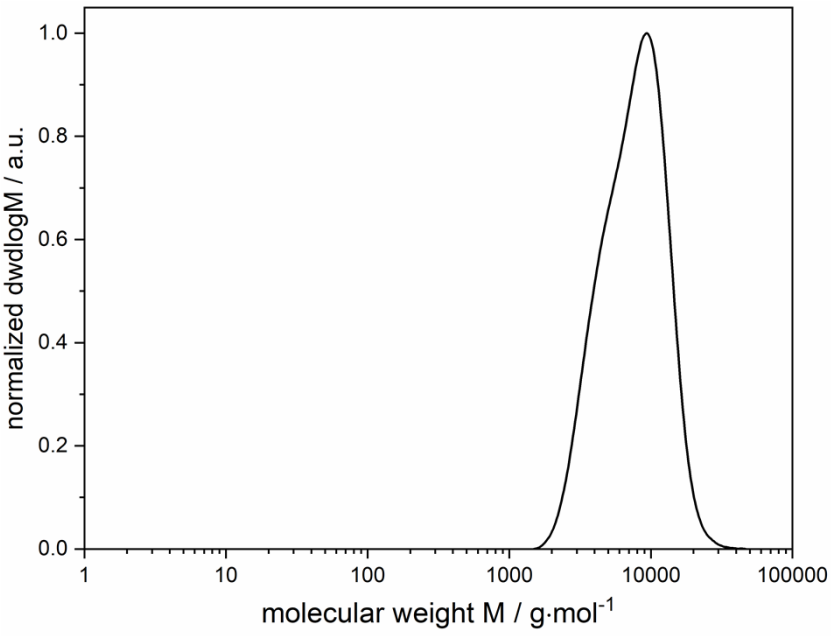


Figure S18: Molecular weight distribution of P(εCarL) (Table 2, entry 1) determined via SEC in THF at 30 °C using RI detection.

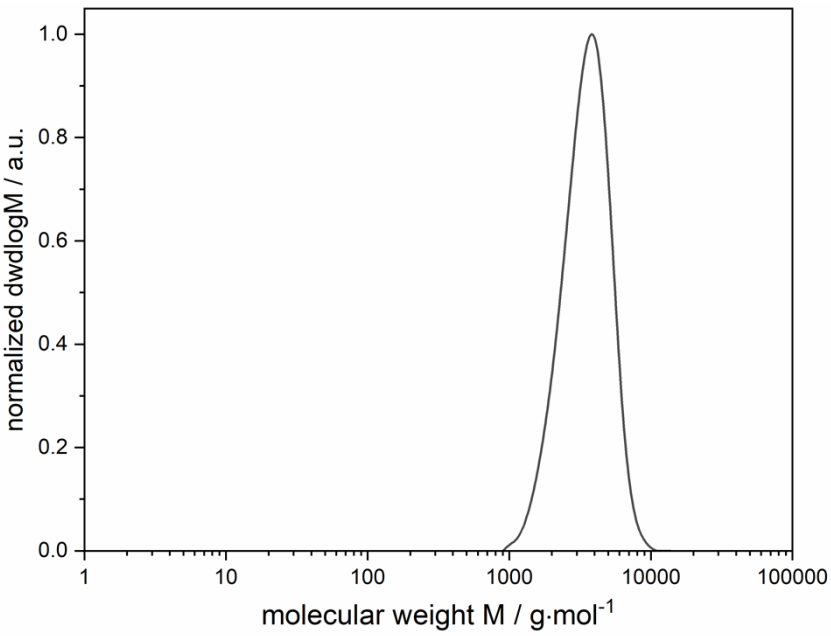


Figure S19: Molecular weight distribution of P(εCarL) (Table 2, entry 2) determined via SEC in THF at 30 °C using RI detection.

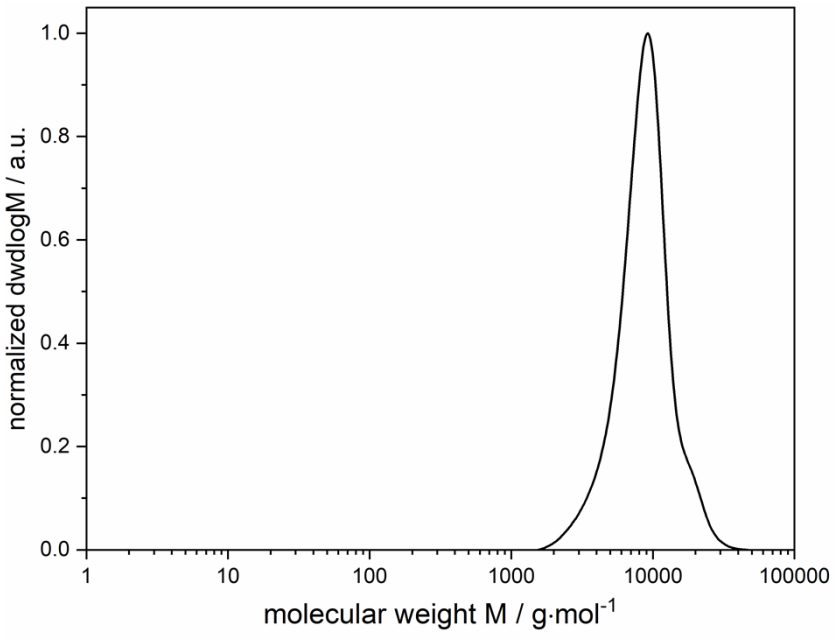


Figure S20: Molecular weight distribution of P(εCarL) (Table 2, entry 3) determined via SEC in THF at 30 °C using RI detection.

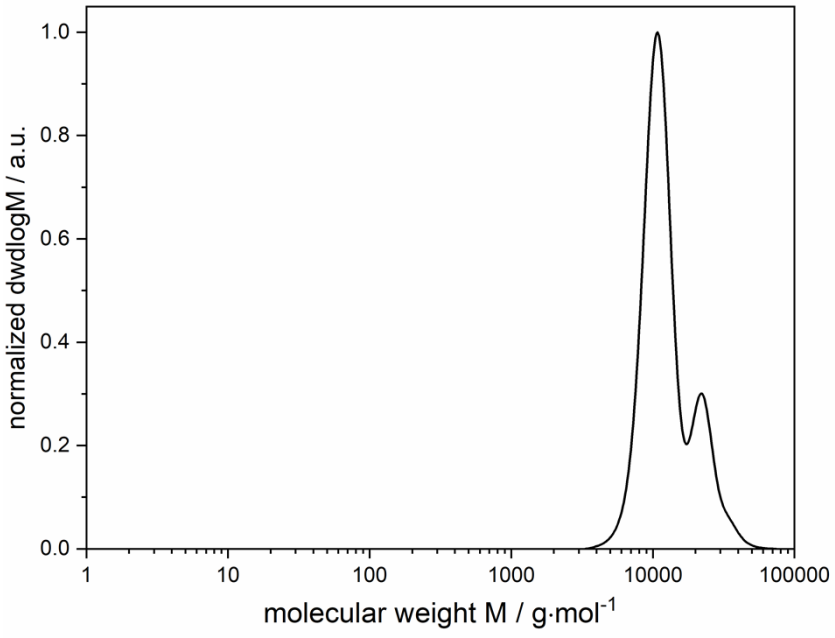


Figure S21: Molecular weight distribution of P(εCarL) (Table 2, entry 4) determined via SEC in THF at 30 °C using RI detection.

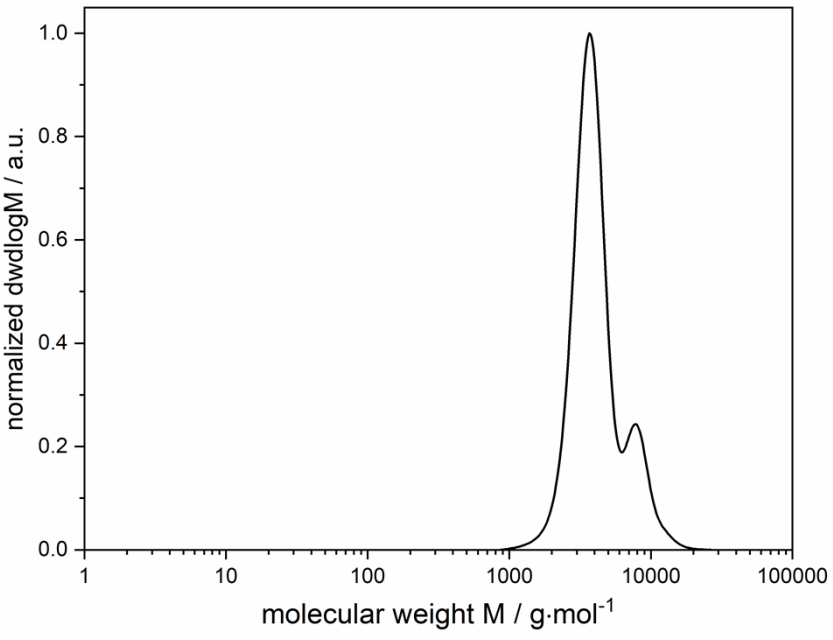


Figure S 22: Molecular weight distribution of P(εCarL) (Table 2, entry 5) determined via SEC in THF at 30 °C using RI detection.

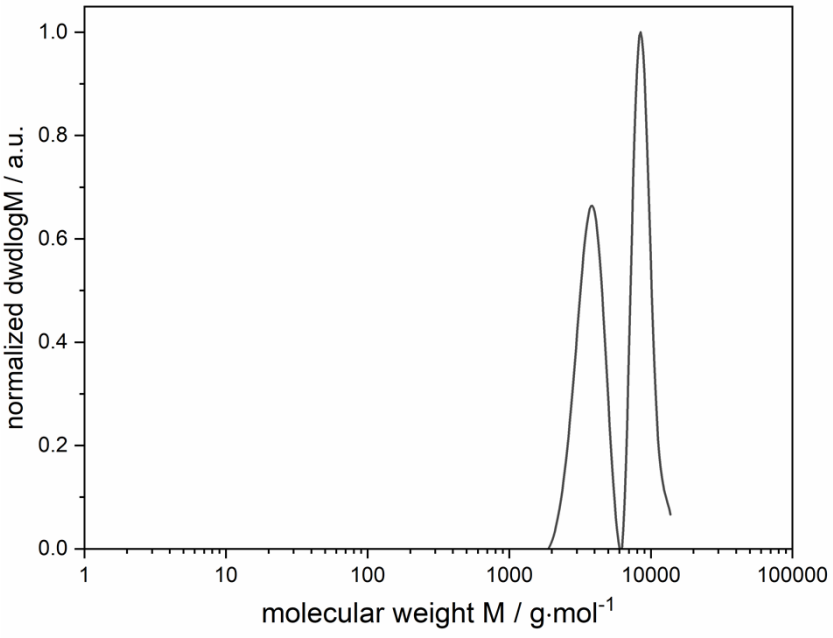


Figure S 23: Molecular weight distribution of P(εCarL) (Table 2, entry 6) determined via SEC in THF at 30 °C using RI detection.

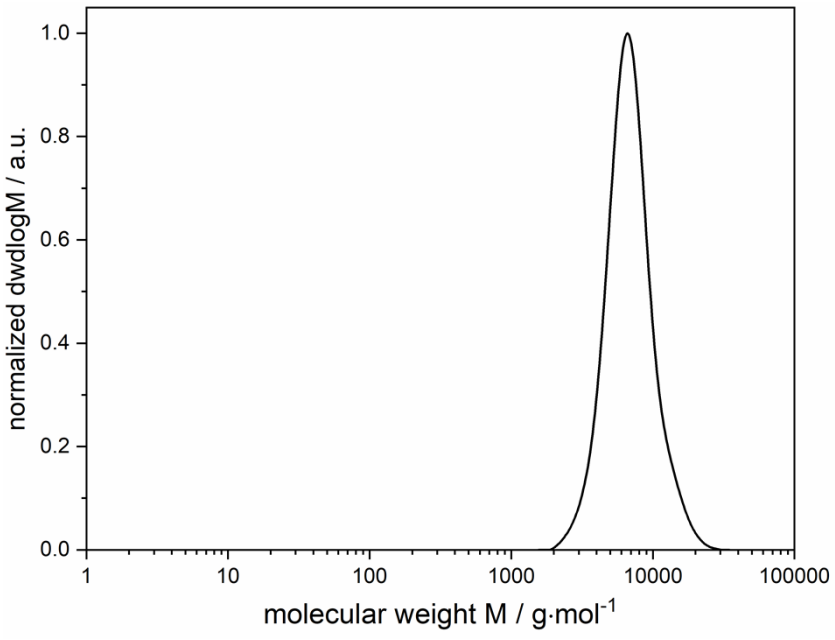


Figure S24: Molecular weight distribution of P(εCarL) (Table 2, entry 7) determined via SEC in THF at 30 °C using RI detection.

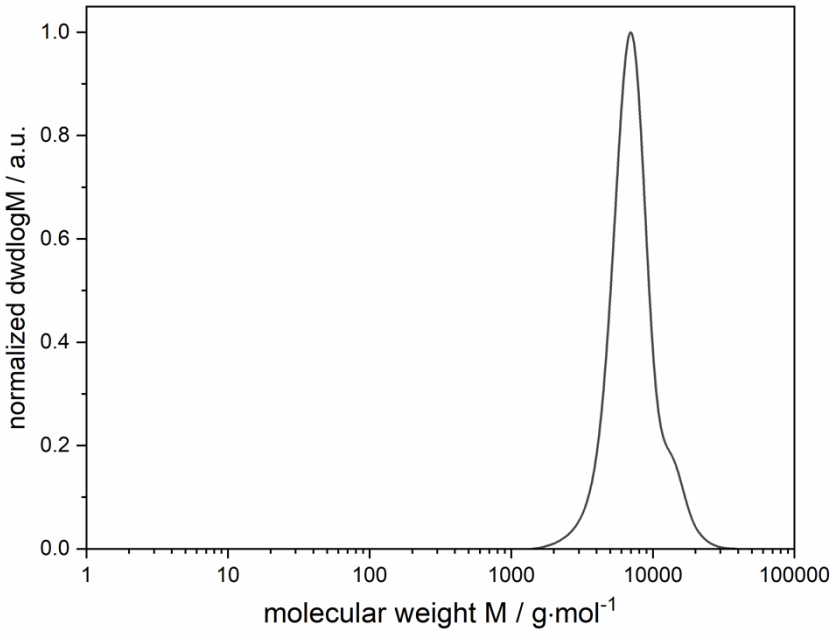


Figure S25: Molecular weight distribution of P(εCarL) (Table 2, entry 8) determined via SEC in THF at 30 °C using RI detection.

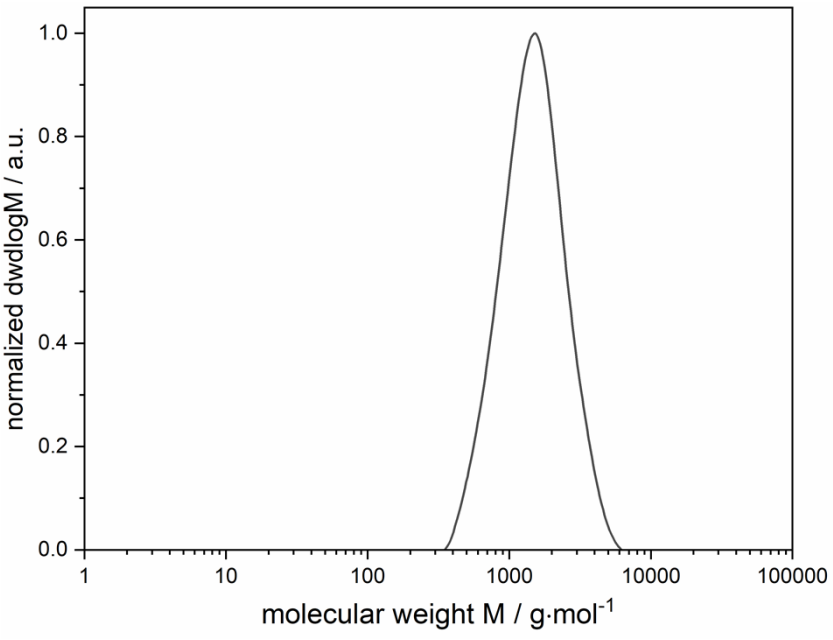


Figure S26: Molecular weight distribution of P(αCarL) (Table 2, entry 9) determined via SEC in THF at 30 °C using RI detection.

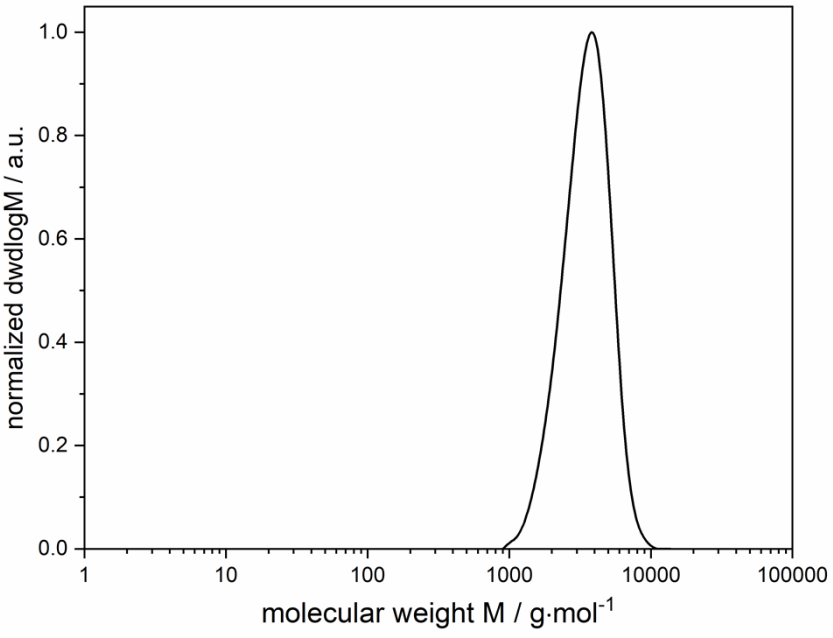


Figure S27: Molecular weight distribution of P(αCarL) (Table 2, entry 10) determined via SEC in THF at 30 °C using RI detection.

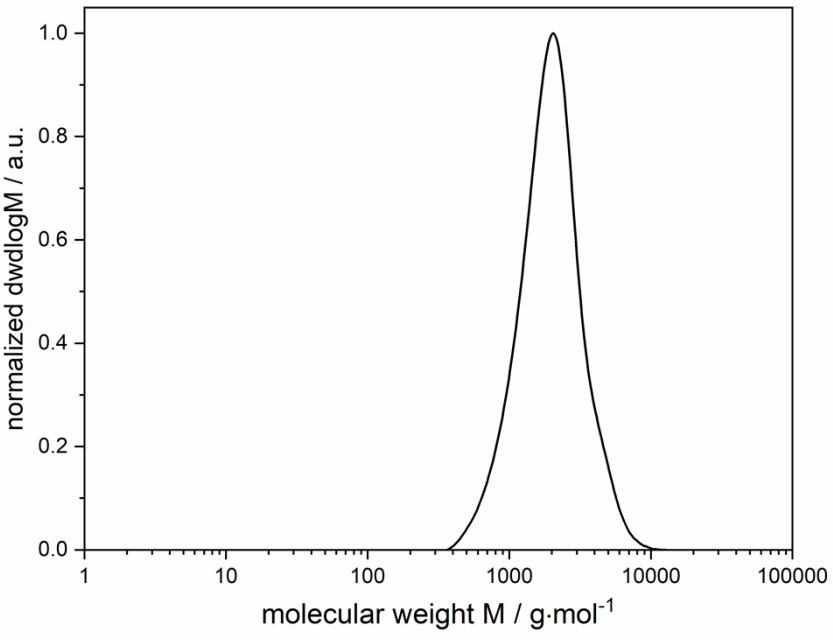


Figure S28: Molecular weight distribution of P(αCarL) (Table 2, entry 11) determined via SEC in THF at 30 °C using RI detection.

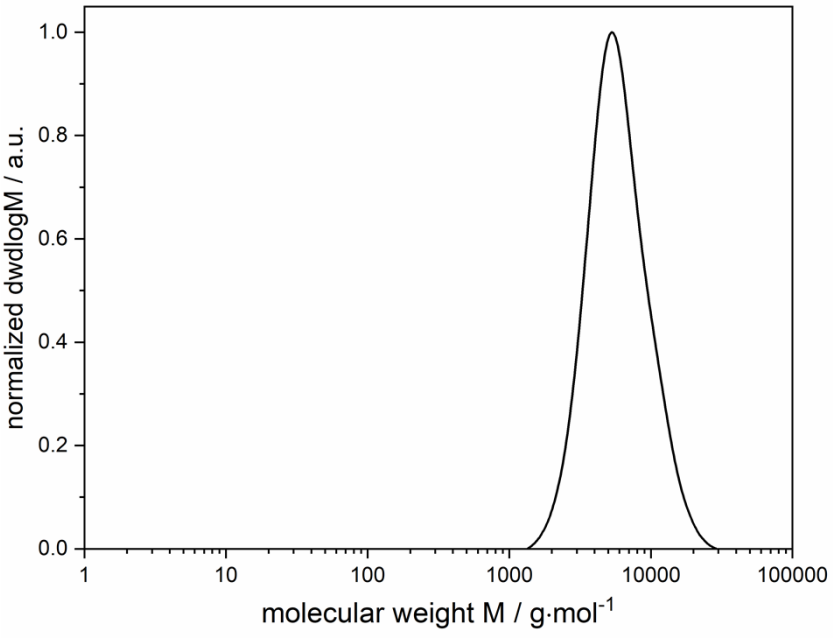


Figure S29: Molecular weight distribution of P(αCarL-*co*-εCarL)$_{stat}$ (Table 2, entry 12) determined via SEC in THF at 30 °C using RI detection.

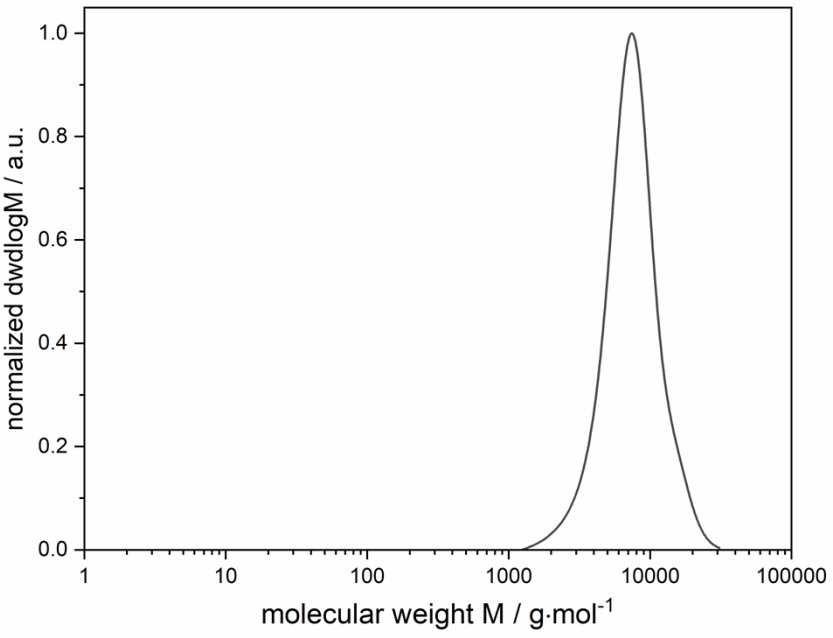


Figure S30: Molecular weight distribution of P(αCarL-*co*-εCarL)$_{stat}$ (Table 2, entry 13) determined via SEC in THF at 30 °C using RI detection.

4. POLYCONDENSATION OF 3-CARENE DIOL

Table S1: Reaction parameters and molecular weights for the polycondensation of 3-carene diol with DMT.

Entry	[3CarDiol]:[DMT]:[Cat][a]	Precondensation		Polycondensation		Method [b]	$M_{n,rel}$ [c]	$Đ$ [c]
	[mol]:[mol]:[mol]	p_1 [mbar]	T_1 [°C]	p_2 [mbar]	T_2 [°C]		[kg/mol]	[-]
1	200:100:1	1013	170	0.5	180	slow	6.4	1.5
2	200:100:1	1013	170	0.5	180	fast	12.8	2.0

[a] ratio of 3-carene diol to dimethyl terephthalate to catalyst titanium tetra-*n*-butanolate as weighed, 35 mmol of 3-carene diol; [b] heating method with heating to T_1 over time (slow) versus sudden increase in temperature (fast), [c] relative molecular weight and polydispersity measured in THF at 30 °C relative to polystyrene.

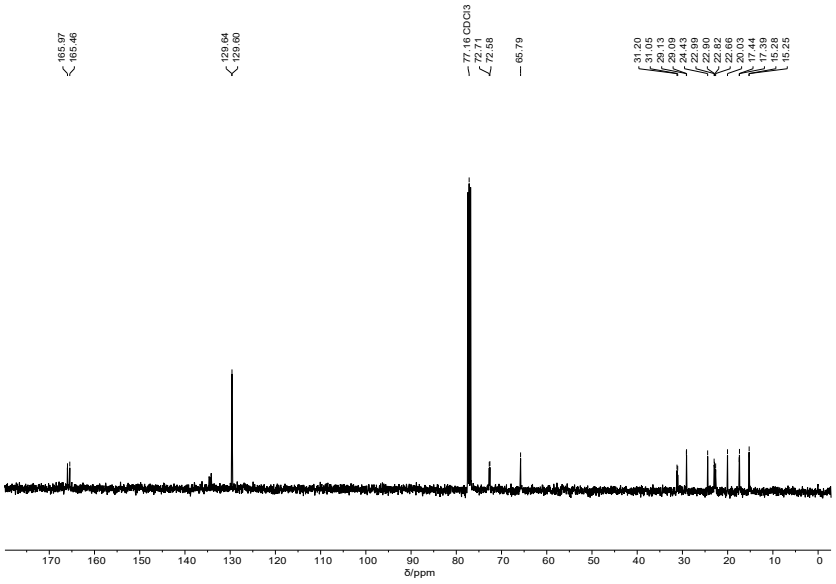


Figure S31: ^{13}C-NMR spectrum (125 MHz, $CDCl_3$, 300K) of P(3CarDiol-*co*-DMT).

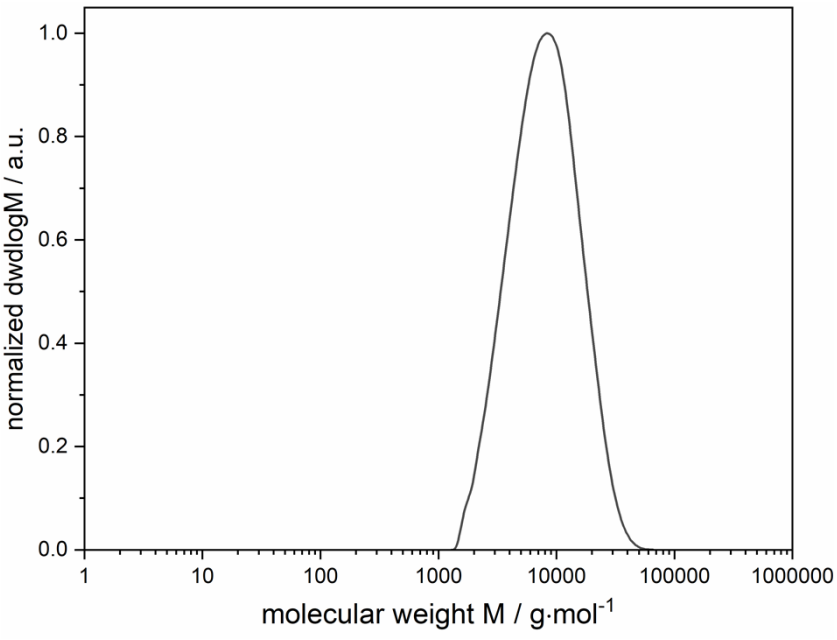


Figure S32: Molecular weight distribution of P(3CarDiol-*co*-DMT) (Table S1, entry 1) determined via SEC in THF at 30 °C using RI detection.

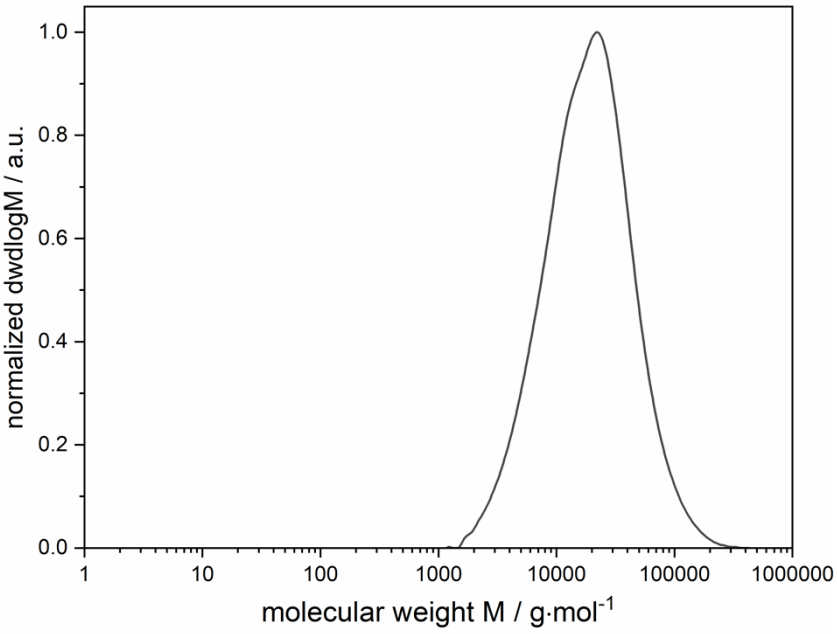


Figure S33: Molecular weight distribution of P(3CarDiol-*co*-DMT) (Table S1, entry 2) determined via SEC in THF at 30 °C using RI detection.

5. ADDITIONAL ANALYSIS

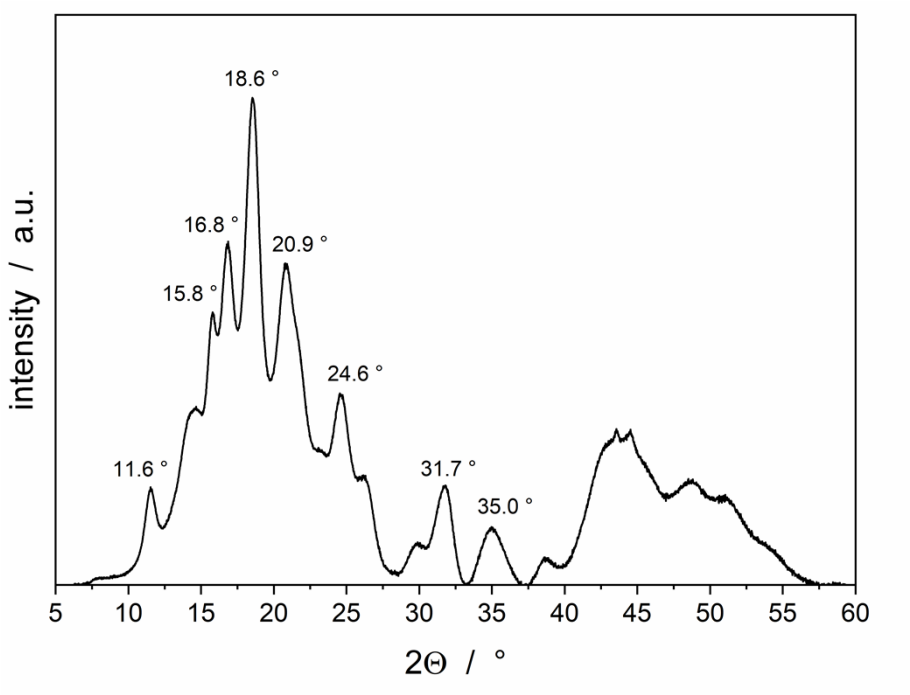


Figure S34: Powder X-Ray diffractogram of P(εCarL) (Table 2, entry 7).

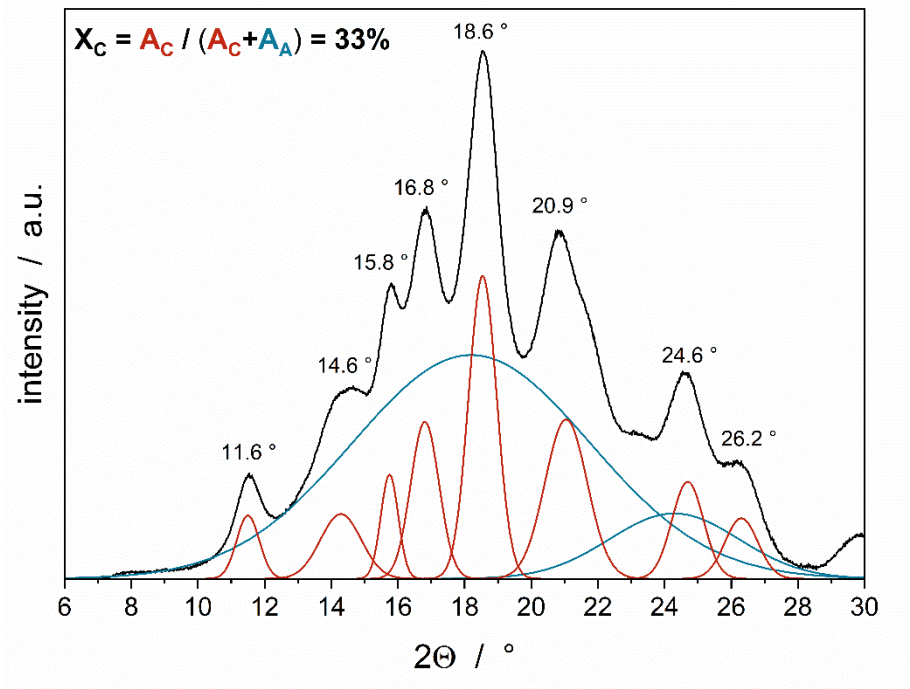


Figure S35: Peak deconvolution in the peak area between 7 – 28 ° (amorphous background blue, crystalline peaks red) for calculation of crystalline fraction X_C via area integration of the amorphous parts A_A and the crystalline parts A_C.[4]

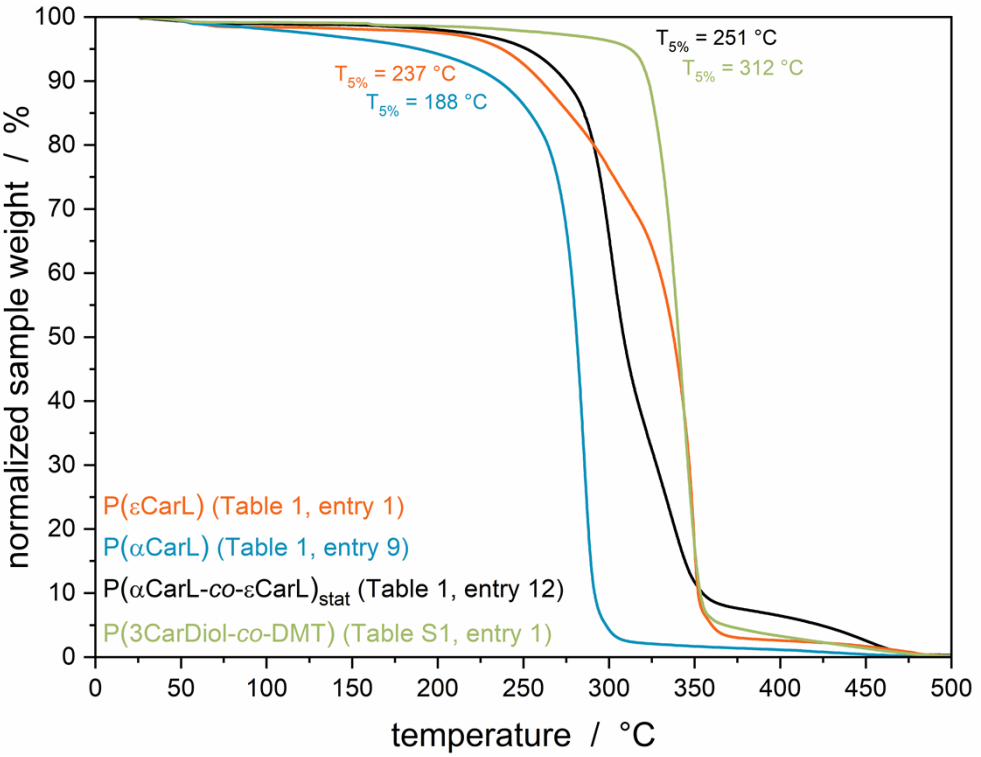


Figure S36: Thermogravimetric analysis of P(εCarL) (orange), P(αCarL) (blue), P(αCarL-*co*-εCarL)$_{stat}$ (black) and P(3CarDiol-*co*-DMT) (green).

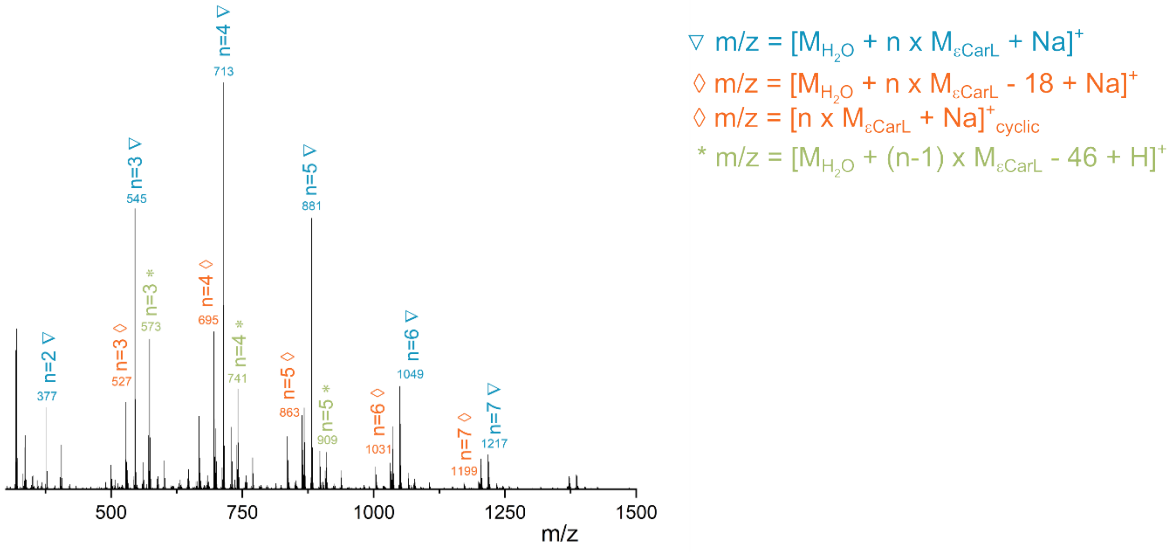


Figure S37: ESI-MS of P(εCarL) oligomers prepared with tin 2-ethylhexanoate SnOct$_2$ (M:Cat = 5:1, toluene, 110 °C, 20 min) and peak assignment.

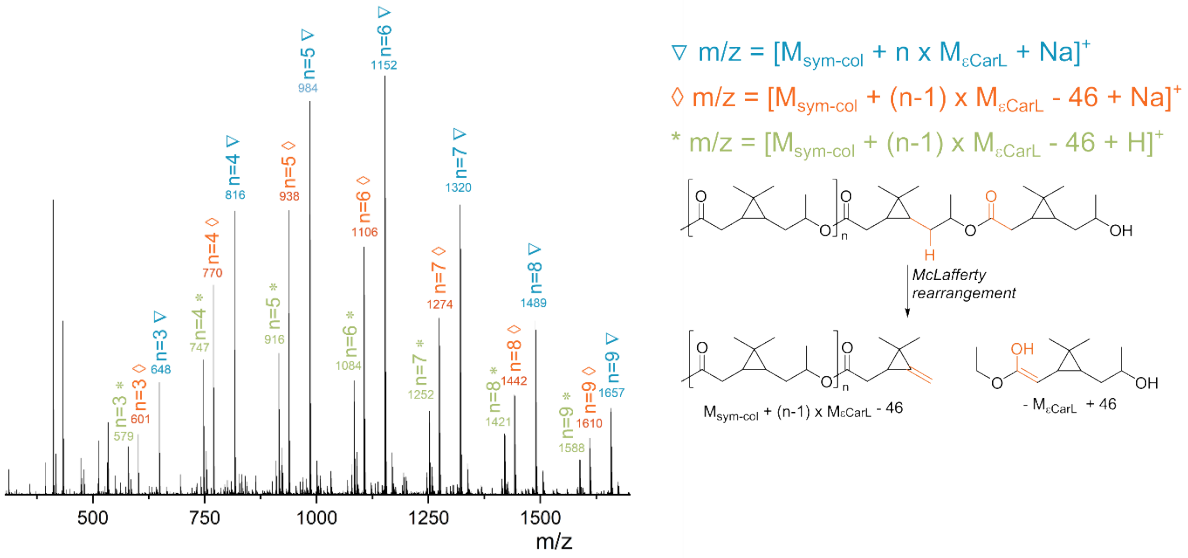


Figure S38: ESI-MS of P(εCarL) oligomers prepared with 2-methoxyethylamino-bisphenolate yttrium catalyst [(ONOO)$^{t\text{Bu}}$Y(*sym*-col)(thf)] (M:Cat = 5:1, toluene, rt , 10 min) and peak assignment.

6. REFERENCES

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