



Supporting Information

Master of Chaos and Order: Opposite Microstructures of PCL-*co*-PGA-*co*-PLA Accessible by a Single Catalyst

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1. Experimental Section

1.1. General

All steps were performed under nitrogen (99.996%), which was dried with P₄O₁₀ granulate, using Schlenk techniques. Solvents were dried according to literature and stored under nitrogen.^[1] All chemicals were purchased from Sigma-Aldrich GmbH, TCI GmbH, Thermo Fisher (Kandel) GmbH and ABCR GmbH and were used without further purification. L-lactide was donated by Corbion and was recrystallized once from dried toluene and subsequently sublimed under vacuo. It was stored at -35 °C in a nitrogen filled glovebox. The ligand Methyl 2-((bis(dimethylamino)methylene)amino)-5-(dimethylamino)benzoate (TMG5NMe₂asme) and the referring complex with FeCl₂ (FeCl₂(TMG5NMe₂asme), **1**) were synthesized after known procedures from literature.^[2]

1.2. NMR spectroscopy

NMR spectra were recorded at room temperature on a Bruker Avance II (400 MHz) or a Bruker Avance III (400 MHz). The NMR signals were calibrated to the residual signals of the deuterated solvent [$\delta_{\text{H}}(\text{CDCl}_3) = 7.26 \text{ ppm}$, $\delta_{\text{C}}(\text{CDCl}_3) = 77.16 \text{ ppm}$] Data for ¹H NMR are reported as follows: chemical shift (δ ppm) (multiplicity, coupling constants (Hz), integration). Couplings are expressed by: s = singlet, d = doublet, m = multiplet or combinations thereof. ¹³C{¹H} NMR spectra are also expressed in parts per million (ppm) and reported as aforementioned. Various 2D NMR experiments (COSY, HSQC, HMBC, DEPT135) were used to assign the ¹H and ¹³C{¹H} NMR spectra.

1.3. Gel permeation chromatography (GPC)

The average molecular masses and the mass distributions of the obtained polylactide samples were determined by GPC in THF as the mobile phase at a flow rate of 1 mL min⁻¹. The utilized GPCmax VE-2001 from Viscotek was a combination of an HPLC pump, two Malvern Viscotek T columns (porous styrene divinylbenzene copolymer) with a maximum pore size of 500 and 5000 Å, a refractive index detector (VE-3580), and a viscometer (Viscotek 270 Dual Detector). Polystyrene standards were used for calibration. The evaluation of the molar masses were carried out with an universal method or with a conventional method in combination with multiplying a factor of 0.58 for PLA, 0.56 for PCL or an approximated factor of 0.57 for copolymers.^[3]

1.4. MALDI-ToF-MS

The end group analysis was performed by MALDI-TOF on a Bruker ultrafleXtreme equipped with a 337 nm smartbeam laser in the reflective mode. THF solutions of trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malonitrile (DCTB) (5 μL of a 20 mg/mL solution), sodium trifluoroacetate (0.1 μL of a 10 mg/mL solution), and analyte (5 μL of a 10 mg/mL) were mixed and a droplet thereof applied on the sample target. Protein 1 calibration standard is the name of the protein mixture used for calibration. For spectra 4000 laser shots with 24 % laser power were collected. The laser repetition rate was 1000 Hz. The homopolymer analysis was performed using Polymerix software (Sierra Analytics).

1.5. DSC of the polymers

DSC was performed with a Perkin Elmer DSC 8500. Samples were weighted with a Sartorius CP2P balance and encapsulated in a 50 μL aluminium pan with three punctures (0.2 mm) cover. The encapsulated pans were weighted before and after DSC runs, the mass loss was calculated and the final sample masses were used in DSC analysis. Method: heating – cooling – heating, 20 – 180 °C with a heating rate of 10 K min⁻¹, a nitrogen flow of 20 mL min⁻¹ and a cooling system at -50 °C.

1.6. Polymerization in Schlenk tubes

In a nitrogen filled glove box, the monomers (LL, Cap and/or GG, ratios referring to 2.0 g, 13.9 mmol lactide in a homopolymerization), the catalyst and the co-initiator benzyl alcohol (BnOH) were weighted in if solid or added with an Eppendorf pipette if liquid. The solid components were mixed in a mortar and filled in a Schlenk tube with stirring bar. The liquid components were mixed in a glass vial and added to the Schlenk tube. The Schlenk tube was removed from the glovebox and placed in a preheated oil bath. The reaction time was adjusted to the monomers and M/I ratio. The reaction mixture was dissolved in an appropriate amount of DCM and an aliquot was taken to determine the conversion by ¹H NMR spectroscopy in CDCl₃. The polymer was precipitated in methanol at room temperature, dried under vacuum and characterized via GPC and ¹³C{¹H}v NMR spectroscopy. Exemplary ¹H and ¹³C{¹H} NMR spectra of a random terpolymer are shown in Figure SI2.

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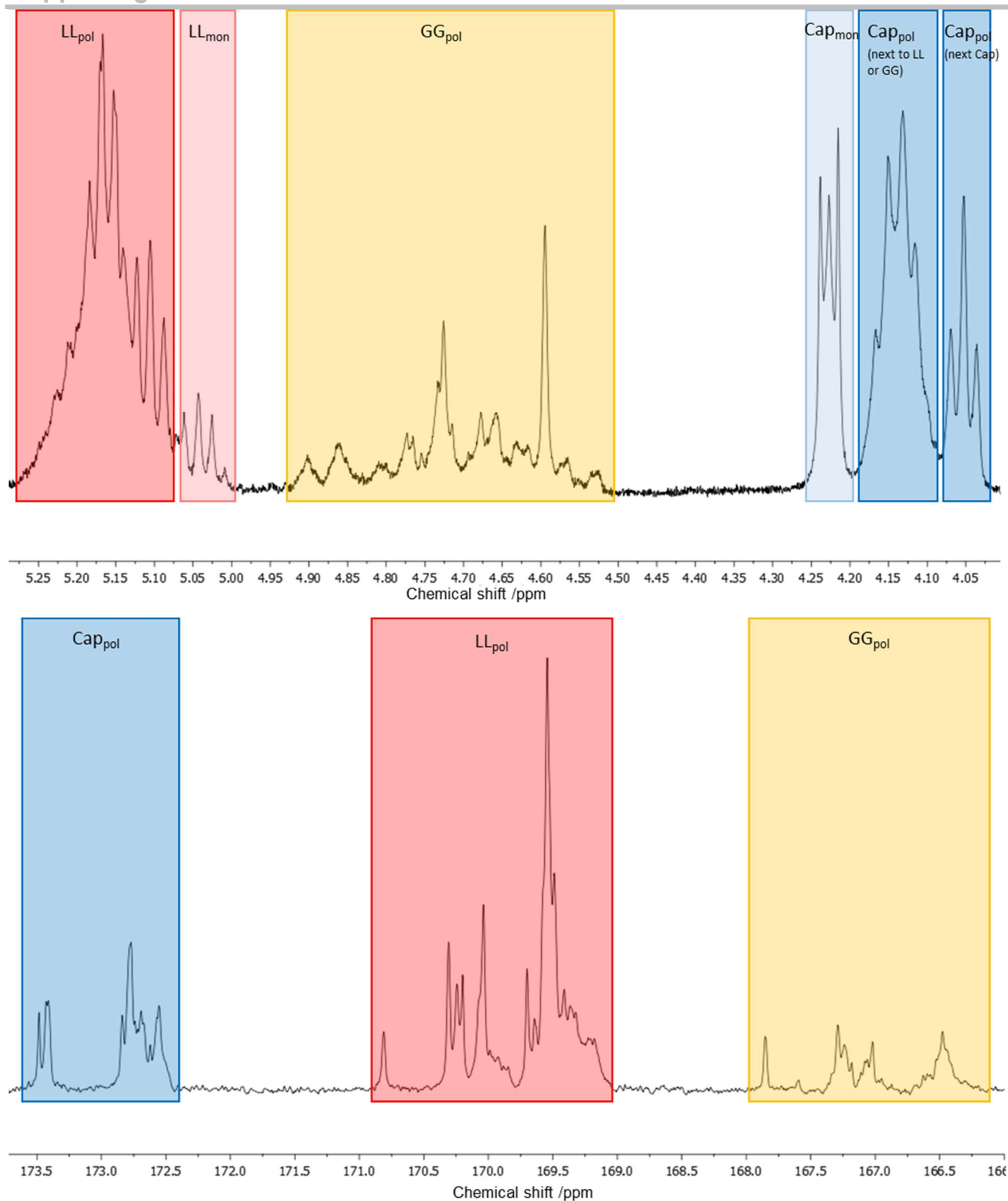


Figure S1. Example of ^1H (top, crude polymer) and $^{13}\text{C}\{^1\text{H}\}$ (bottom, precipitated polymer) NMR spectra of a random terpolymer of LL, Cap and GG. The conversions of LL and Cap were determined by $p = \frac{f_{\text{pol}}}{f_{\text{pol}} + f_{\text{mon}}}$. Since GG monomer is not soluble in CDCl_3 , the conversion of GG is determined by the ratio of GG in polymer referring to the total amount of LL present taking the M/I ratio into account.

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1.7. Polymerization monitored by *in situ* Raman spectroscopy

In a nitrogen filled glove box, the monomers (LL, Cap and/or GG, ratios referring to 8.0 g, 55.5 mmol lactide in a homopolymerization), the catalyst and the co-initiator benzyl alcohol (BnOH) were weighted in if solid or added with an Eppendorf pipette if liquid. For a simultaneous copolymerization the solid components were mixed in a mortar and filled in a glass vial. The liquid components were mixed in a separate glass vial. Both glass vials were removed from the glovebox. The reactor was heated to the desired temperature under vacuum and flashed three times with argon. The liquid reactants were added first directly followed by the solid ones during argon flow. For the sequential addition approach the catalyst and the co-initiator was only mixed with the first monomer while the other monomers were kept in different glass vials. Only the first monomer was added before the start of the reaction, after full conversion the second monomer was added to the reactor in an inert gas flow and so forth. The reaction was conducted under argon atmosphere and sample collection started after the reaction mixture insertion as soon as the reactor was closed. The spectra were measured with a RXN1 spectrometer of Kaiser Optical Systems. The laser was used at a wavelength of 785 nm and with a power of 450 mW through a probe head with sapphire lenses ($d = 0.1$ mm). The reaction time was adjusted to the monomers and M/I ratio. The reaction mixture was removed from the reactor and a $^1\text{H-NMR}$ spectrum in CDCl_3 was collected to determine the conversion. The reaction mixture was dissolved in an appropriate amount of DCM, the polymer was precipitated in methanol at room temperature, dried under vacuum and characterized via GPC and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy. Kinetic data were obtained by integration of the Raman spectrum with *Peaxact 4*, boundaries were $627 - 674$ cm^{-1} for lactide, $674 - 718$ cm^{-1} for Cap and $760 - 810$ cm^{-1} for GG.

1.8. Estimation of the copolymerization reactivity ratios *via* the Mayo-Lewis plot

The reactivity ratios r_{LL} and r_{Cap} are defined as the ratio of the reaction rate constants referring to the incorporation of the same monomer or the opposite one (see Equation 1). With r_{LL} and r_{Cap} both close to 1, the incorporation of both monomers is equally likely. If one of the parameters is substantially larger than 1, the incorporation of that monomer is preferred and only after the that monomer is completely consumed, the other monomer is incorporated.^[4]

$$r_{\text{LL}} = \frac{k_{\text{LL,LL}}}{k_{\text{LL,Cap}}} \quad r_{\text{Cap}} = \frac{k_{\text{Cap,Cap}}}{k_{\text{Cap,LL}}}$$

Equation 1.

The reactivity ratios for the copolymerization of LL and Cap was conducted graphically in a plot following the Mayo-Lewis Equation displayed in Equation 2. It contains the concentration of the monomer in the beginning of the polymerization ($[\text{LL}]$, $[\text{Cap}]$) and the molar ratio of the monomer in the resulting polymer $m_{\text{LL}}/m_{\text{Cap}}$.^[4]

$$r_{\text{LL}} = \frac{[\text{Cap}]}{[\text{LL}]} \left[\frac{m_{\text{LL}}}{m_{\text{Cap}}} \left(1 + \frac{[\text{Cap}]}{[\text{LL}]} r_{\text{Cap}} \right) - 1 \right]$$

Equation 2.

The necessary data are obtained by polymerization experiments with a M/I ratio of 500:1 and monomer-to-monomer ratios (LL/Cap ratios) between 1:1 and 1:6 in Schlenk tubes. The initial monomer concentrations $[\text{LL}]$ and $[\text{Cap}]$ were known from the experimental set up. The ratio of the incorporated monomers m_{LL} and m_{Cap} was determined by analyzing the resulting copolymers with ^1H NMR spectroscopy. The molar ratio of the monomer incorporated in the polymer can be calculated by the sum of the polymer signals, respectively. With the derived information, the Mayo-Lewis Equation can be plotted with chosen values r_{LL} versus r_{Cap} , the reactivity ratios for the given reaction system can then be found at the intercept of the lines.

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2. Polymerizations

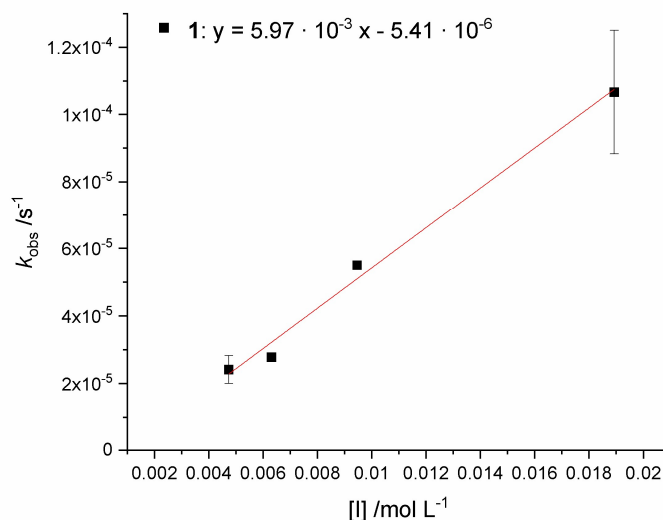
2.1. k_p determination of the polymerization of ϵ -caprolactone

Figure S2. k_p determination by plotting k_{obs} versus the initiator concentration $[I]$ with M/I ratios between 500:1 and 2000:1. $k_p(\text{Cap})=0.00597\pm 0.00155 \text{ L mol}^{-1} \text{ s}^{-1}$.

Table S1: Details of the polymerizations of Cap for the k_p determination.^[a]

Run	M/I ratio	Time /min	$p^{[b]}$	$k_{\text{obs}} \cdot 10^{-4} / \text{s}^{-1} \text{ [c]}$	$M_{n,\text{theo}} / \text{kgmol}^{-1} \text{ [d]}$	$M_n / \text{kgmol}^{-1} \text{ [e]}$	$\mathcal{D}^{[f]}$
1	500:1	135	0,44	1,250	25.1	16.1	1,7
2	500:1	120	0,67	3,430	48.2	36.2	1,6
3	1000:1	90	0,24	0,550	27.1	35.4	1,4
4	1500:1	160	0,26	0,278	44.5	37.7	1,5
5	2000:1	160	0,14	0,200	32.0	n.d. ^[f]	n.d. ^[f]
6	2000:1	90	0,19	0,283	43.4	n.d. ^[f]	n.d. ^[f]

[a] Polymerization in bulk at 150 °C. [b] Conversion of Cap determined by ^1H NMR spectroscopy. [c] Determined by plotting $\ln(1/1-p)$ vs. time. [d] Calculated by molar mass x conversion x M/I ratio. [e] Determined by GPC in THF. [f] Not determined due to unsuccessful precipitation.

2.2. Immortal polymerizations of L-lactide

Table S2: Details of polymerizations of LL under immortal conditions.^[a]

Run	M/Col/Cat ratio	Time /min	$p^{[b]}$	$M_{n,\text{theo}} \text{ [c]} / \text{kgmol}^{-1}$	$M_n \text{ [d]} / \text{kgmol}^{-1}$	$\mathcal{D}^{[d]}$
1	5000:100:1	20 min	0,90	6.5	4.7	1,05
2	10000:100:1	90 min	0,85	12.3	6.6	1,05
3	10000:200:1	90 min	0,89	6.4	4.5	1,03
4	10000:500:1	20 min	0,94	2.7	2.9	1,02

[a] Polymerization in bulk at 150 °C. [b] Conversion of LL determined by ^1H NMR spectroscopy. [c] Calculated by molar mass x conversion x M/Col ratio. [d] Determined by GPC in THF.

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2.3. Mayo-Lewis plot for estimation of the reactivity ratios of Cap and LL

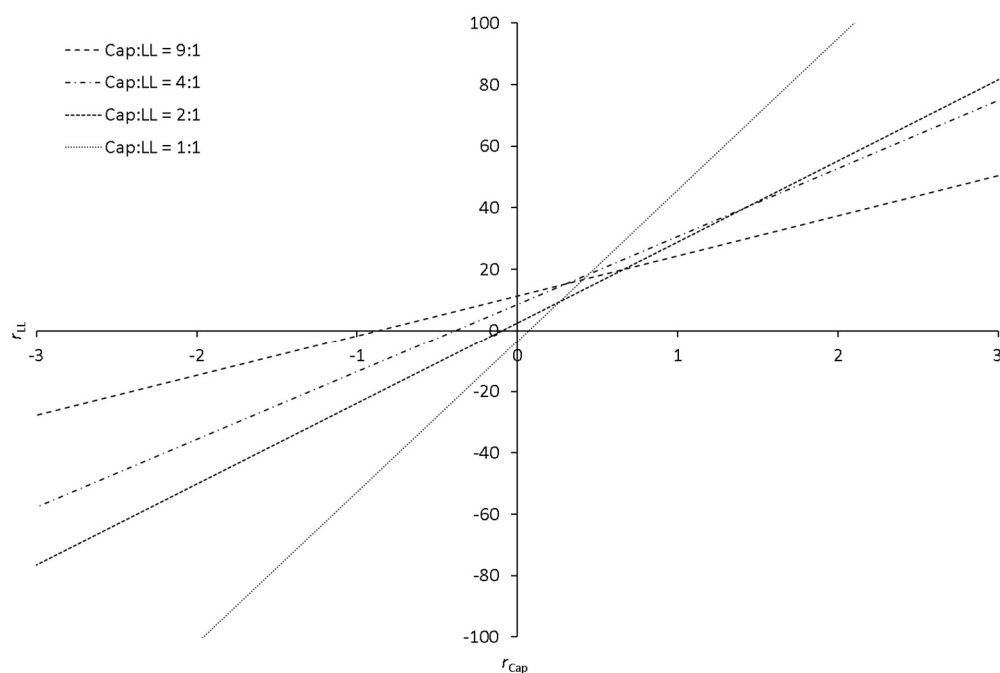


Figure S3. Mayo-Lewis plot for the estimation of reactivity ratios of Cap and LL with ratios between 1:1 and 9:1. $r_{LL} >> 1$, $r_{Cap} < 1$.

2.4. Additional copolymerizations

Table S3. Block and random copolymers synthesized under varied conditions.

Run	Monomers	M/Col/Cat ratio ^[a]	Temperature	Time	p_{LL} ^[b]	p_{Cap} ^[b]	feed	incorp. ^[c]
1 ^[d]	LL + Cap	500+500:1:1	150 °C	4h+4h	0,88	0,79	1:1	1.00:0.84
2 ^[e]	LL + Cap	500+500:1:1	150 °C	15min + 24h	0,95	0,34	1:1	1.00:0.25
3 ^[f]	LL + Cap	500+500:1:1	150 °C	24h	0,95	0,45	1:1	1.00:0.33
4 ^[f]	LL + Cap	500+500:5:1	180 °C	24h	0,87	0,88	1:1	1.05:1.00
5 ^[f]	LL + Cap	750+250:5:1	180 °C	24h	0,93	0,67	3:1	4.12:1.00
6 ^[f]	LL + Cap	250+750:5:1	180 °C	24h	0,59	0,94	1:3	1.00:3.24

[a] Benzyl alcohol as co-initiator. [b] Conversion of the individual monomers determined by ¹H NMR spectroscopy of the crude polymer. [c] Determined by ¹H NMR spectroscopy of the precipitated polymer. [d] Monomers were added sequentially with Cap as first monomer; $M_n=76400 \text{ g mol}^{-1}$, $D=1.34$. [e] Monomers were added sequentially with LL as first monomer. [f] Polymerization of a monomer mixture.

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2.5. Transesterification of a beforehand prepared block copolymer

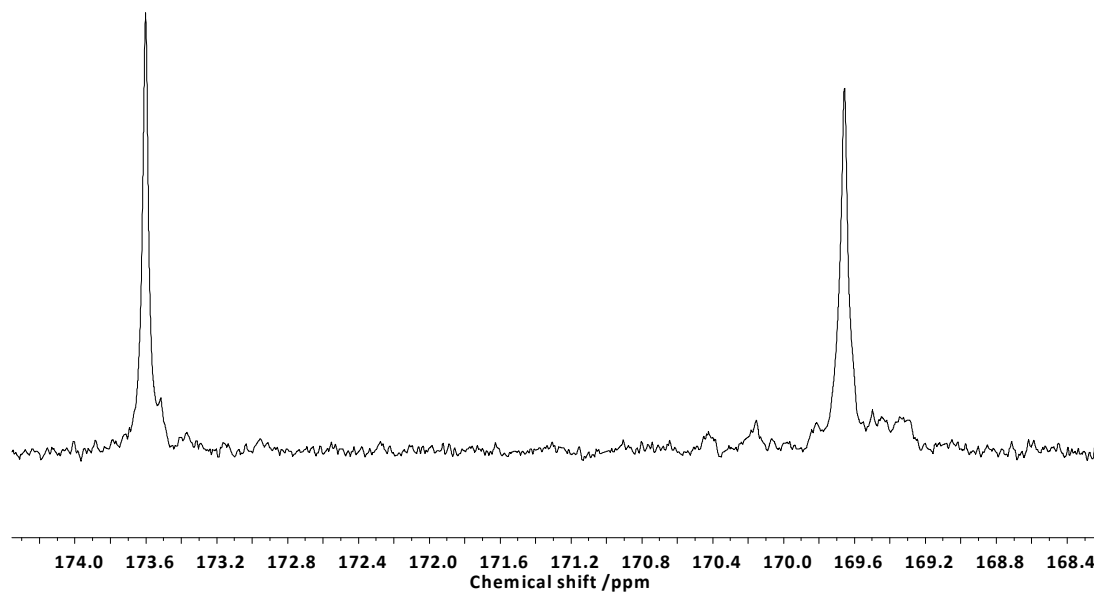


Figure S4. Carbonyl region of the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101MHz, CDCl_3) of PCL-*block*-PLA (Table 1, run 1) heated with freshly added catalyst (1000:1) for 24 h at 180 °C.

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3. Polymer Characterization

3.1. Block Copolymers

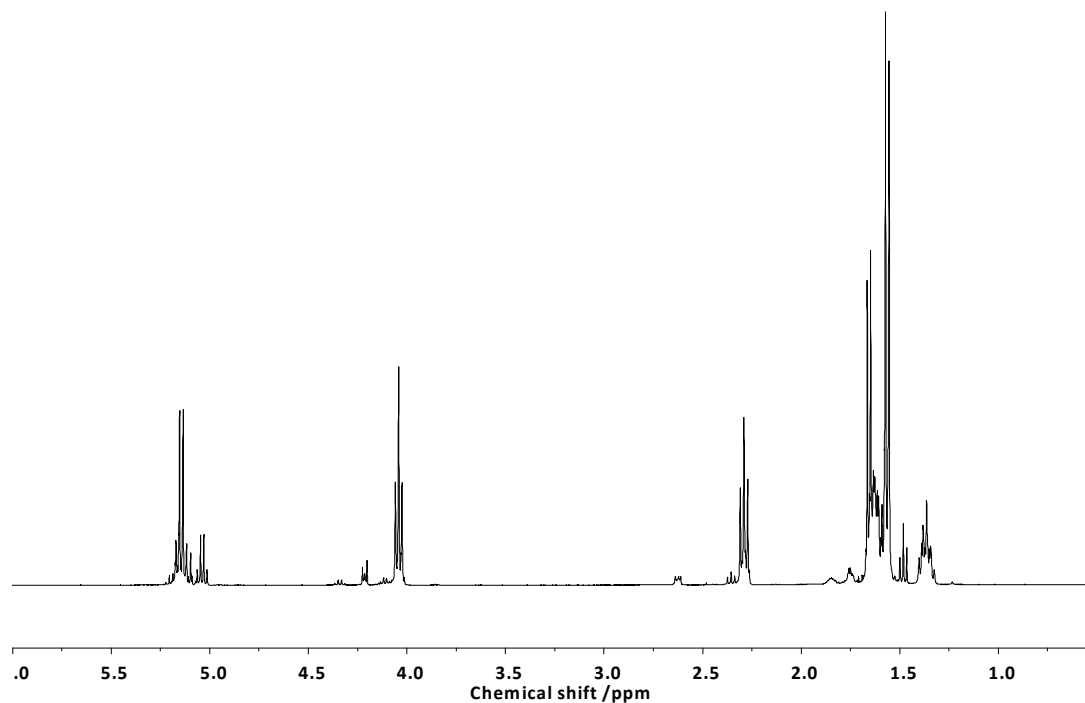


Figure S5. ^1H NMR spectrum (400 MHz, CDCl_3) of the crude polymerization mixture (Table 1, run 1).

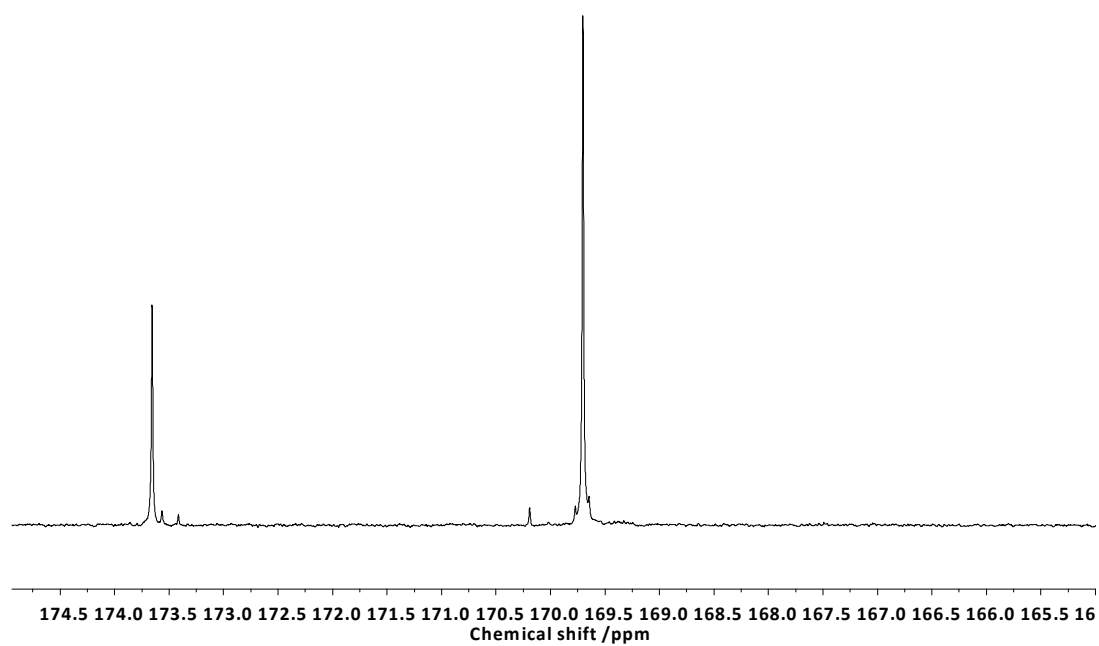


Figure S6. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, CDCl_3) of the isolated polymer (Table 1, run 1).

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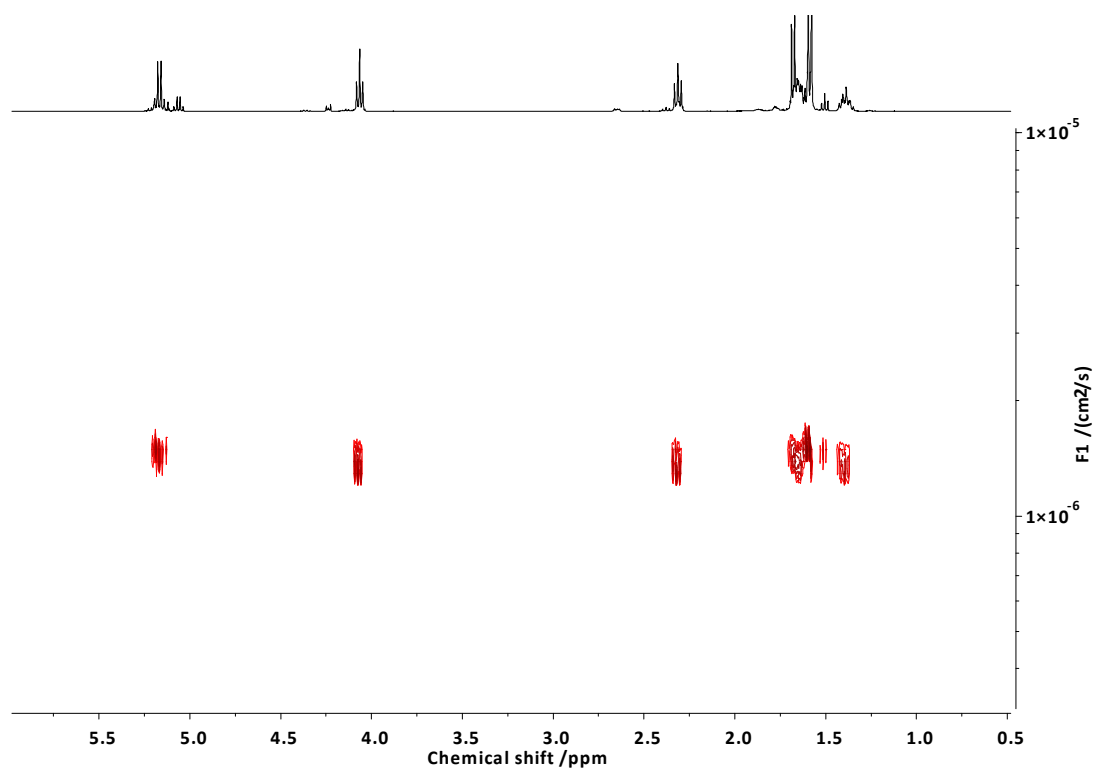


Figure S7. DOSY data (400 MHz, CDCl_3) of the isolated polymer (Table 1, run 1).

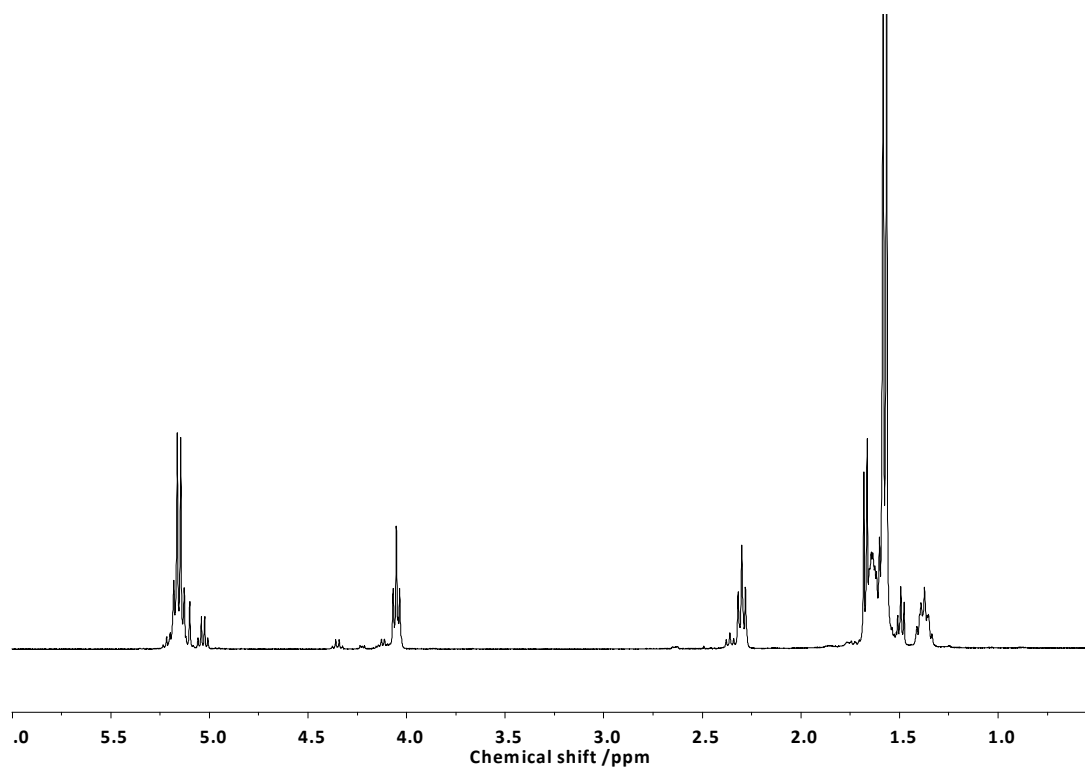


Figure S8. ^1H NMR spectrum (400 MHz, CDCl_3) of the crude polymerization mixture (Table 1, run 2). $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the isolated polymer see Figure 3.

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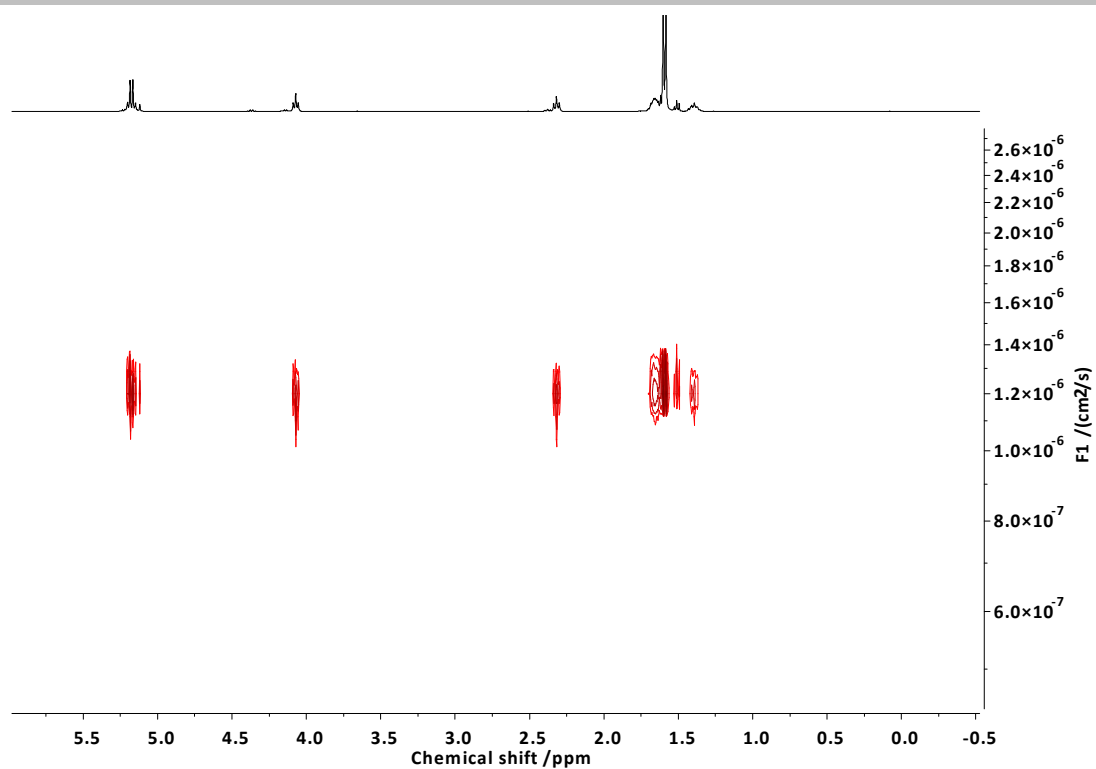


Figure S9. DOSY data (400 MHz, CDCl_3) of the isolated polymer (Table 1, run 2).

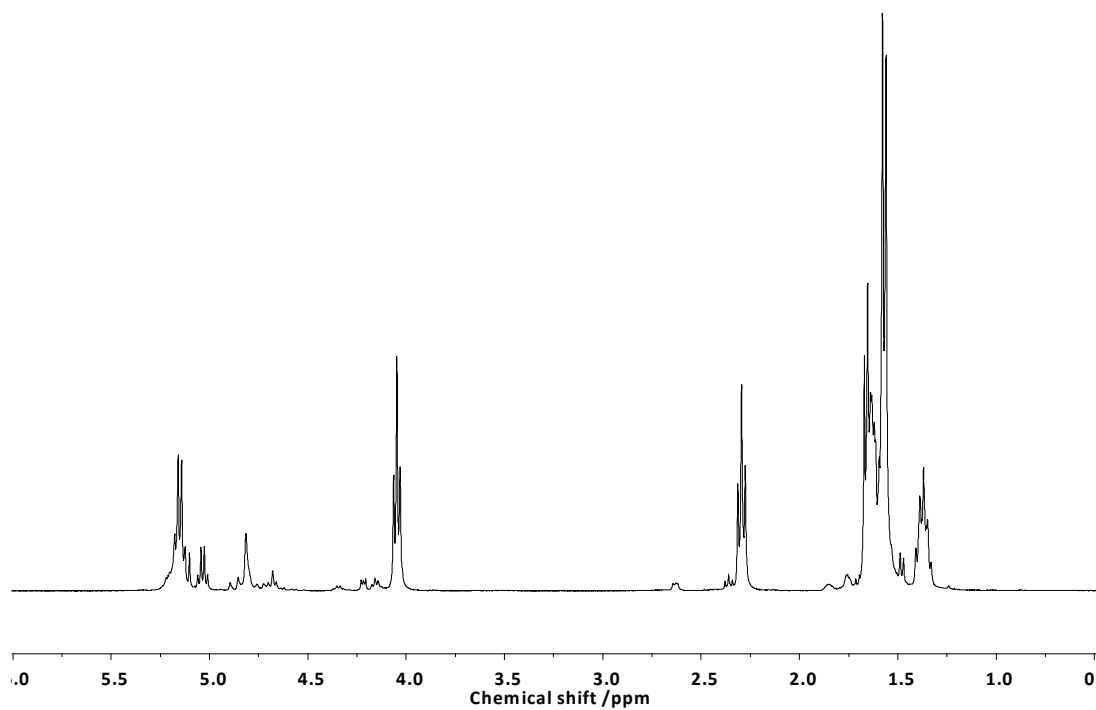


Figure S10. ^1H NMR spectrum (400 MHz, CDCl_3) of the crude polymerization mixture (Table 1, run 3).

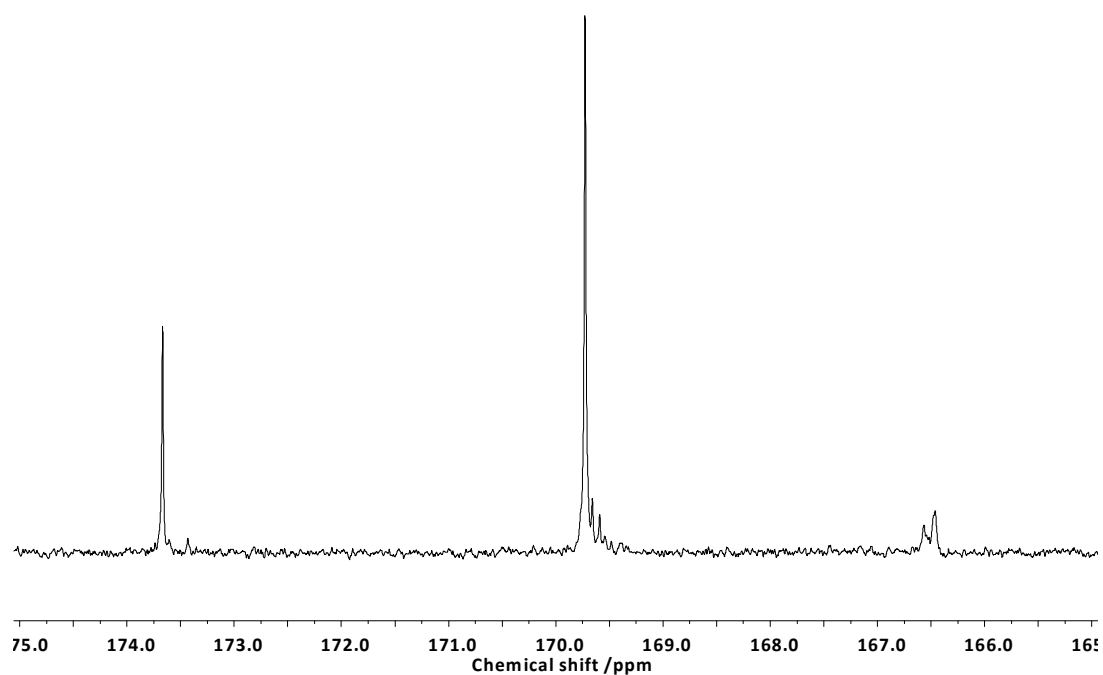


Figure S11. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, CDCl_3) of the isolated polymer (Table 1, run 3).

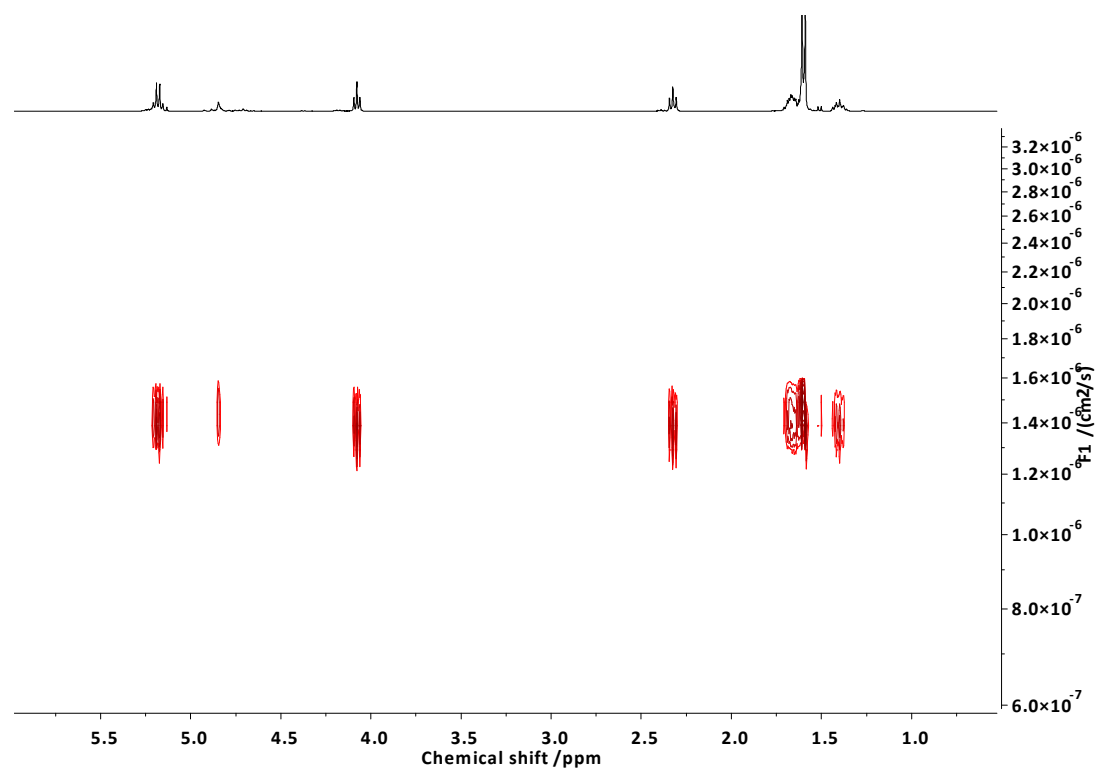


Figure S12. DOSY data (400 MHz, CDCl_3) of the isolated polymer (Table 1, run 3).

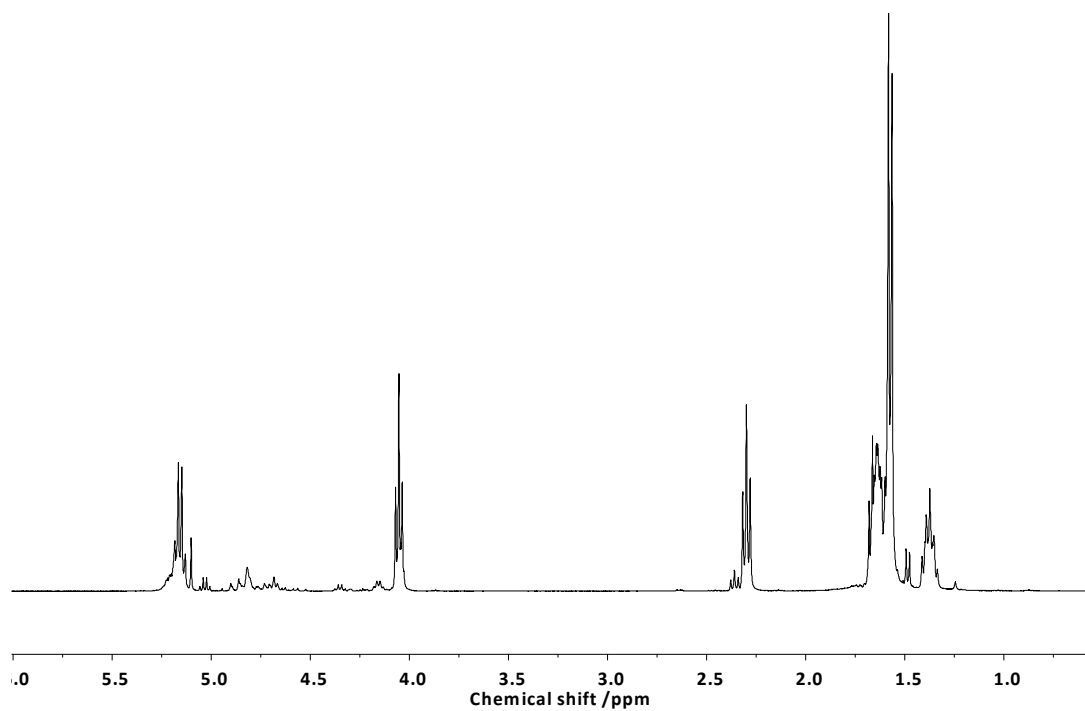


Figure S13. ^1H NMR spectrum (400 MHz, CDCl_3) of the crude polymerization mixture (Table 1, run 4). $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the isolated polymer see Figure 3.

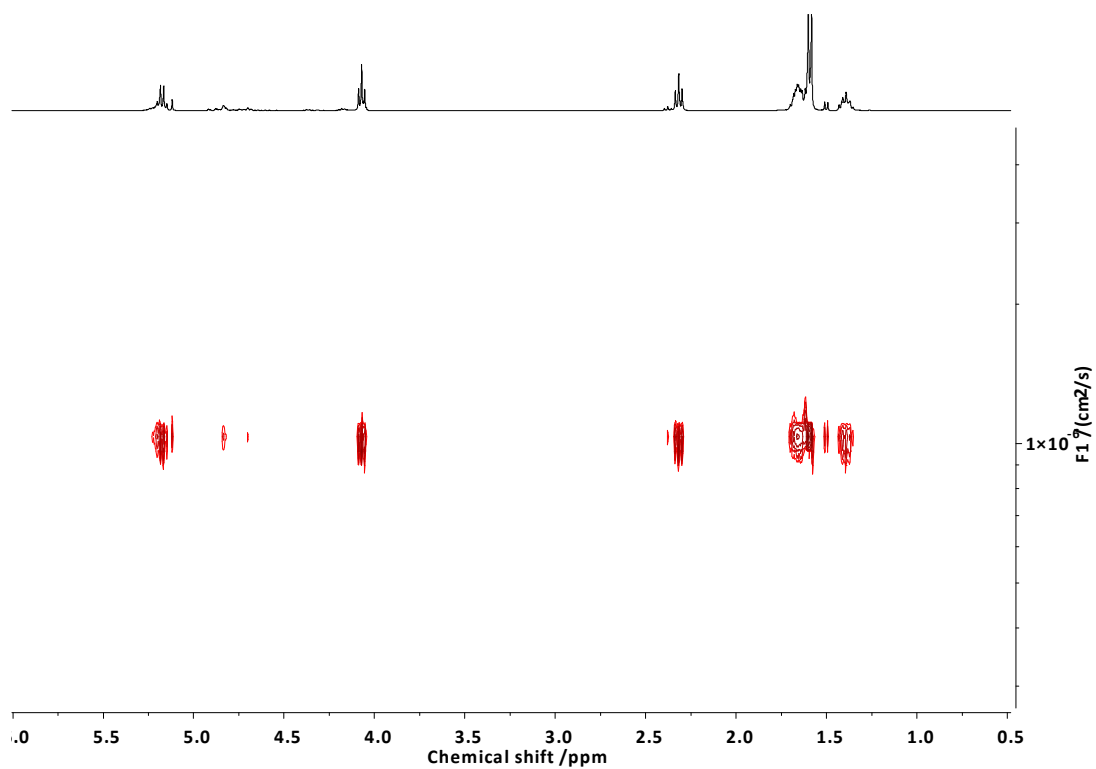


Figure S14. DOSY data (400 MHz, CDCl_3) of the isolated polymer (Table 1, run 4).

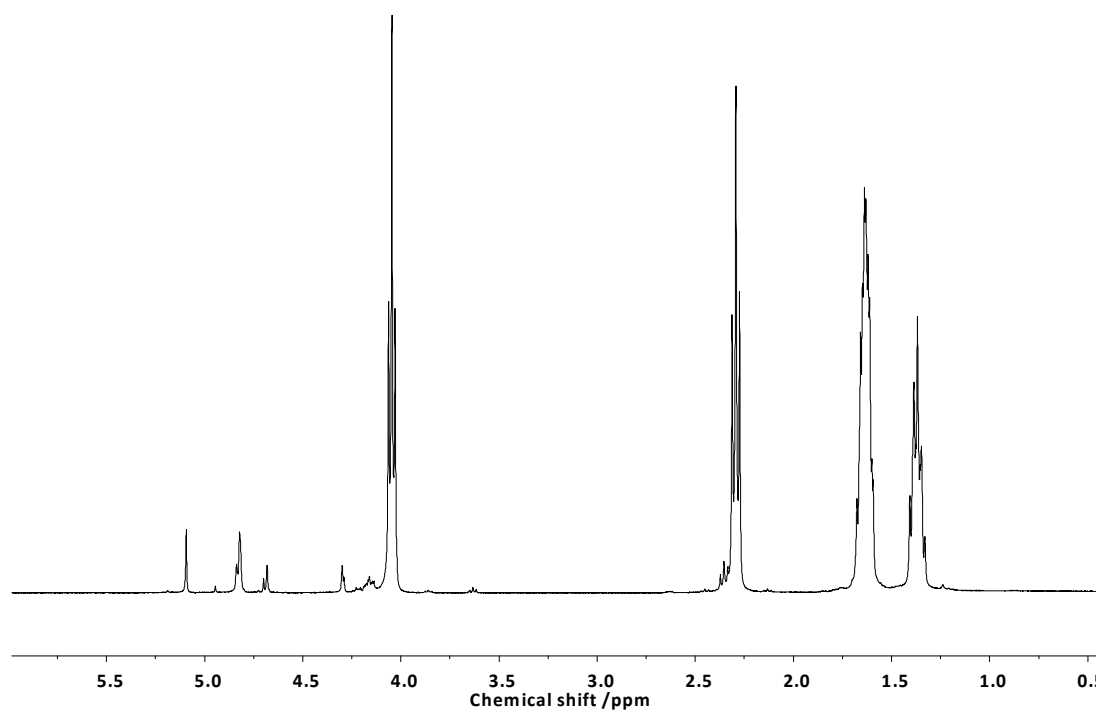


Figure S15. ^1H NMR spectrum (400 MHz, CDCl_3) of the crude polymerization mixture (Table 1, run 5).

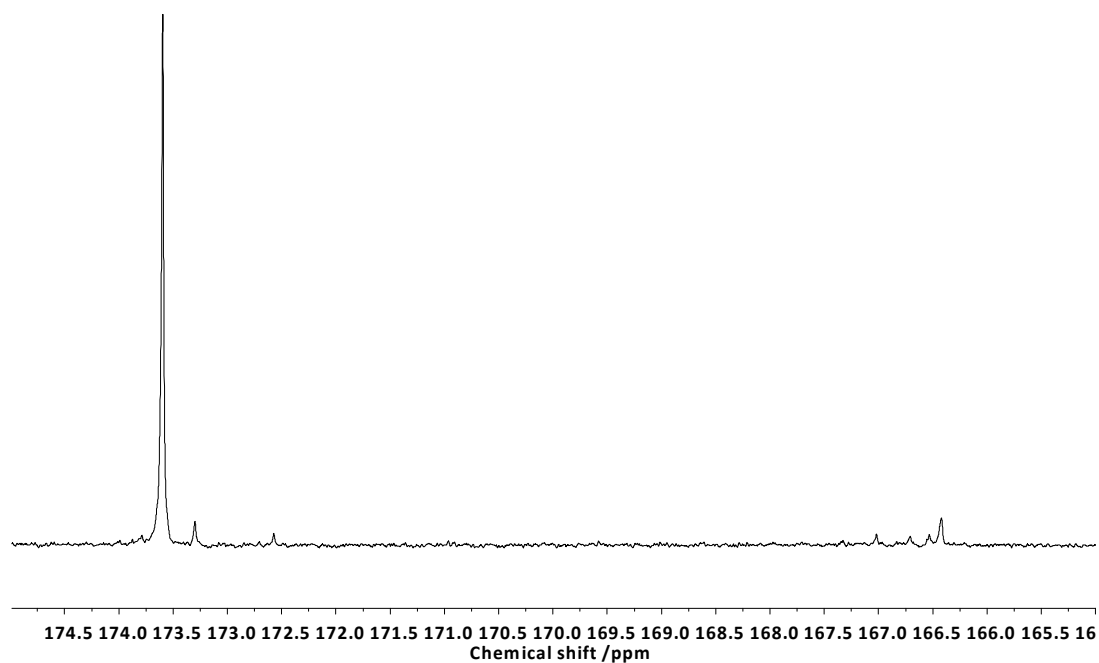


Figure S16. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, CDCl_3) of the isolated polymer (Table 1, run 5).

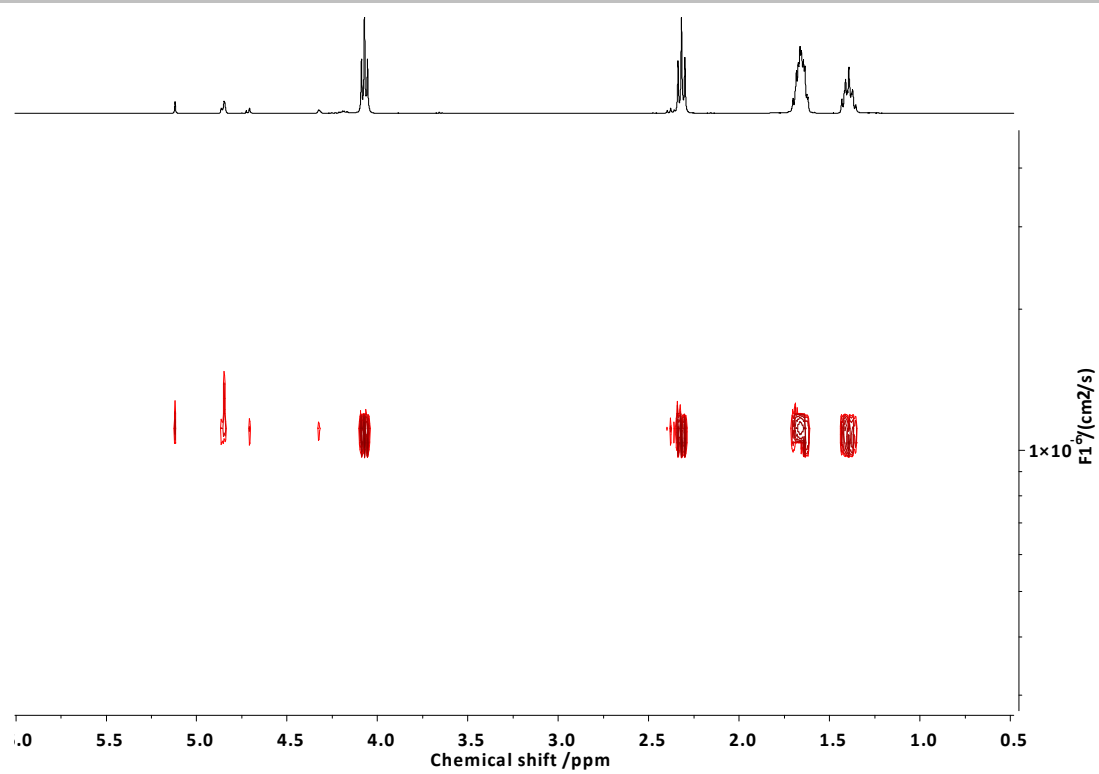


Figure S17. DOSY data (400 MHz, CDCl₃) of the isolated polymer (Table 1, run 5).

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3.2. Statistical Copolymers

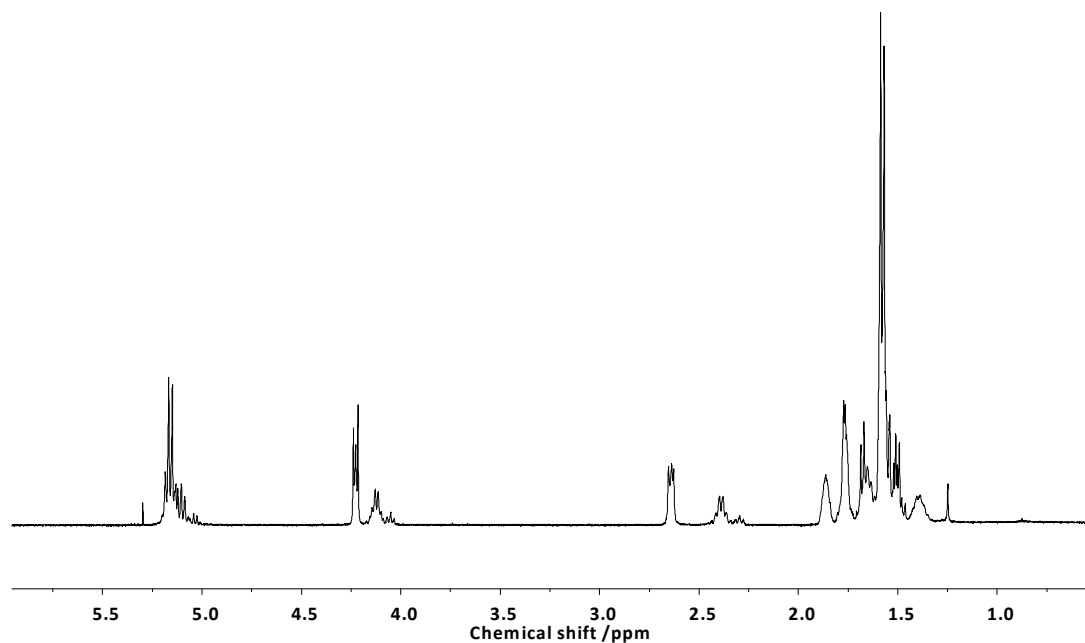


Figure S18. ^1H NMR spectrum (400 MHz, CDCl_3) of the crude polymerization mixture (Table S3, run 3).

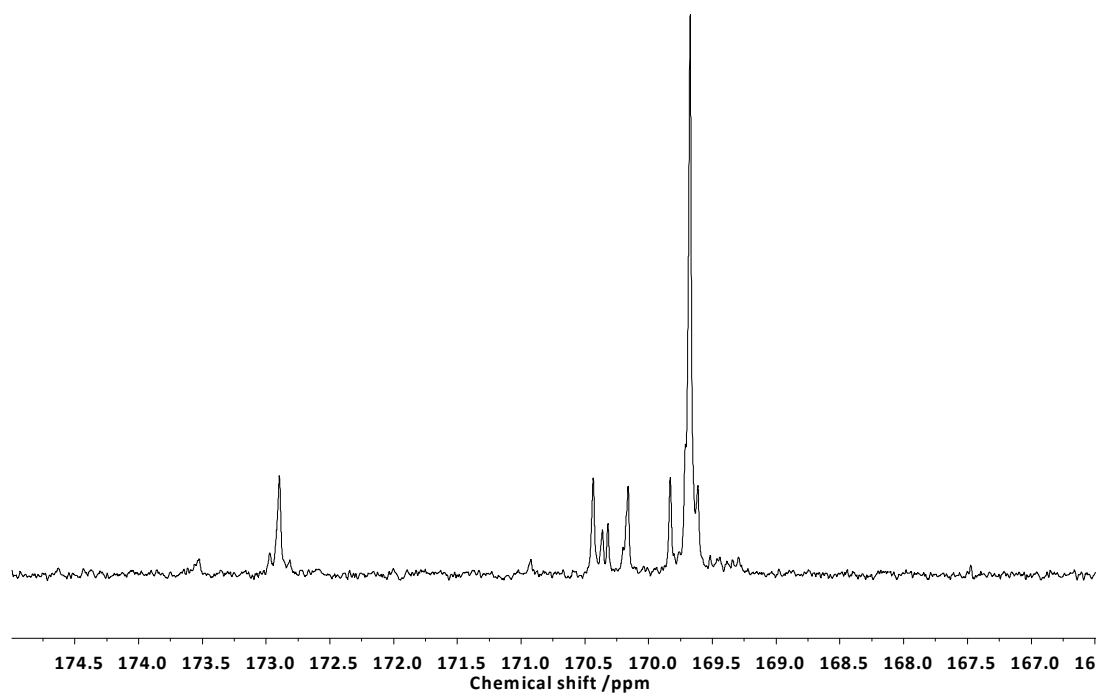


Figure S19. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, CDCl_3) of the isolated polymer (Table S3, run 3).

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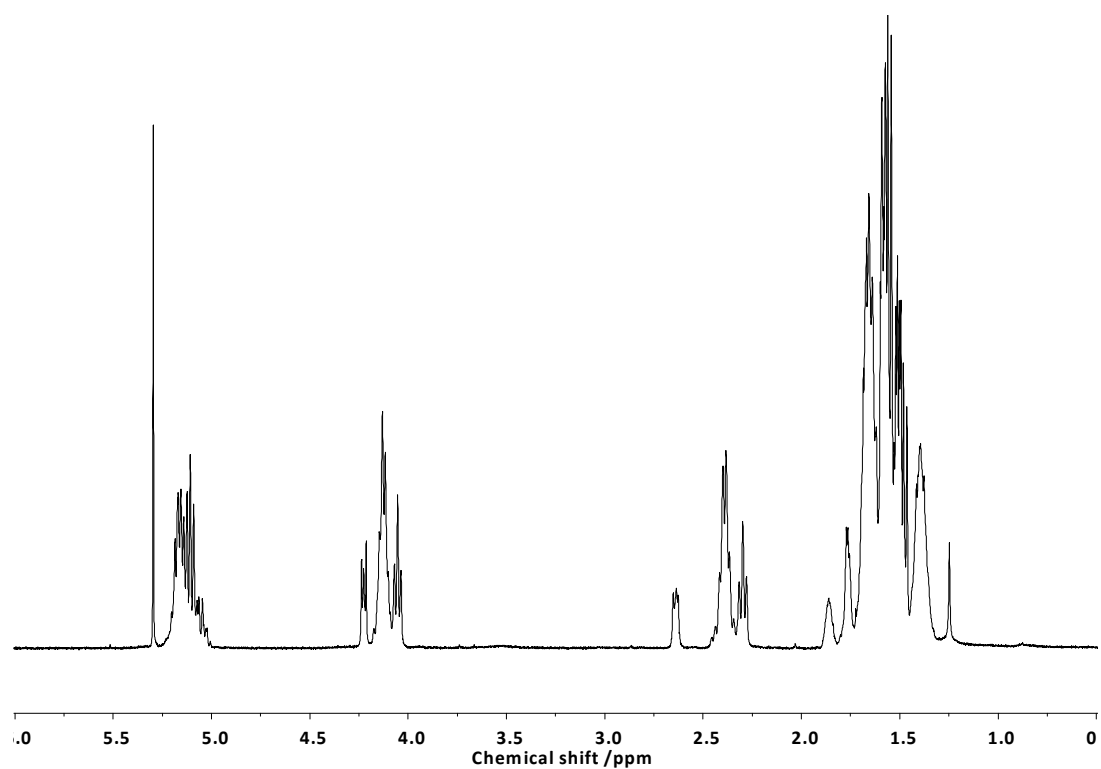


Figure S20. ^1H NMR spectrum (400 MHz, CDCl_3) of the crude polymerization mixture (Table 2, run 1).

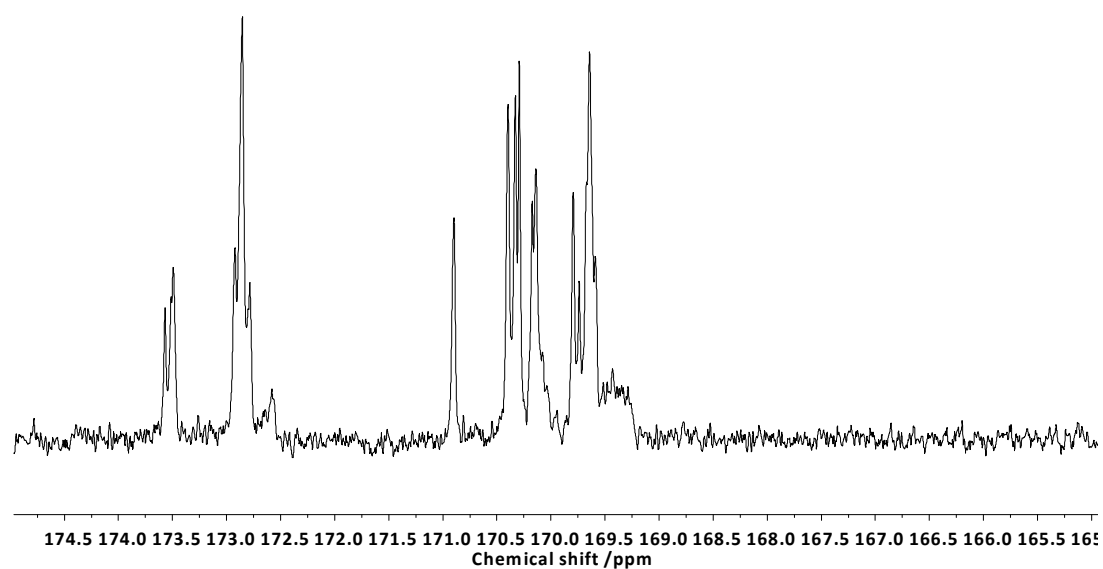


Figure S21. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, CDCl_3) of the isolated polymer (Table 2, run 1).

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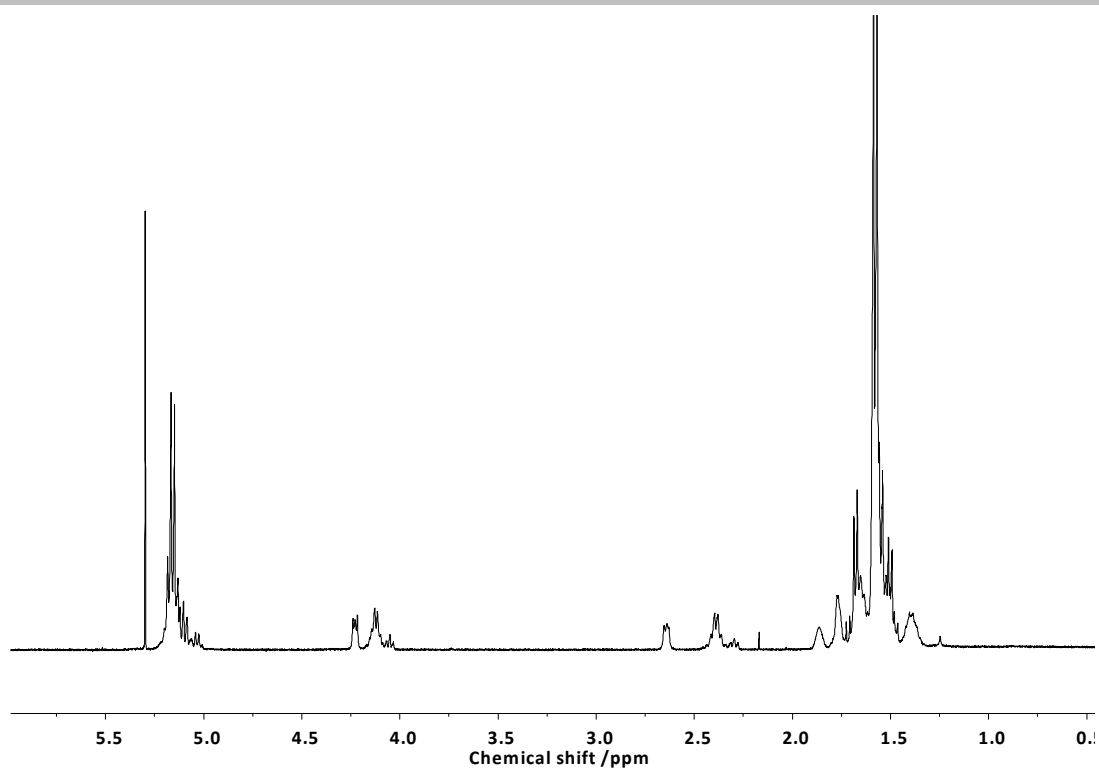


Figure S22. ^1H NMR spectrum (400 MHz, CDCl_3) of the crude polymerization mixture (Table 2, run 2).

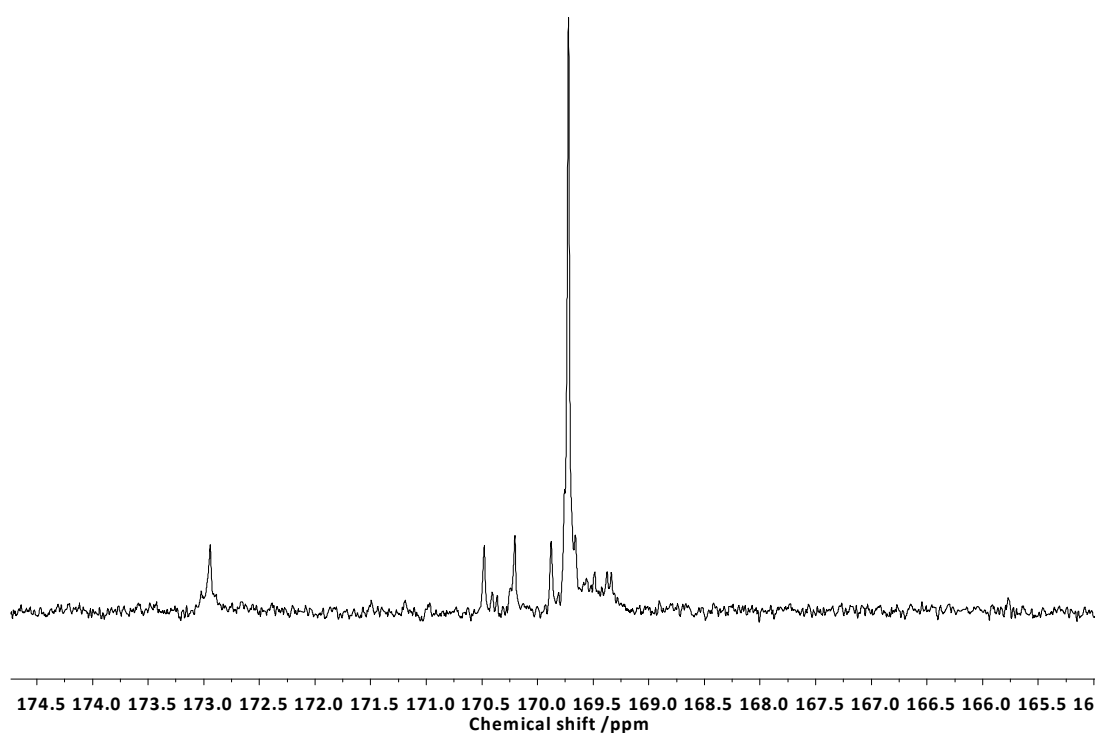


Figure S23. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, CDCl_3) of the isolated polymer (Table 2, run 2).

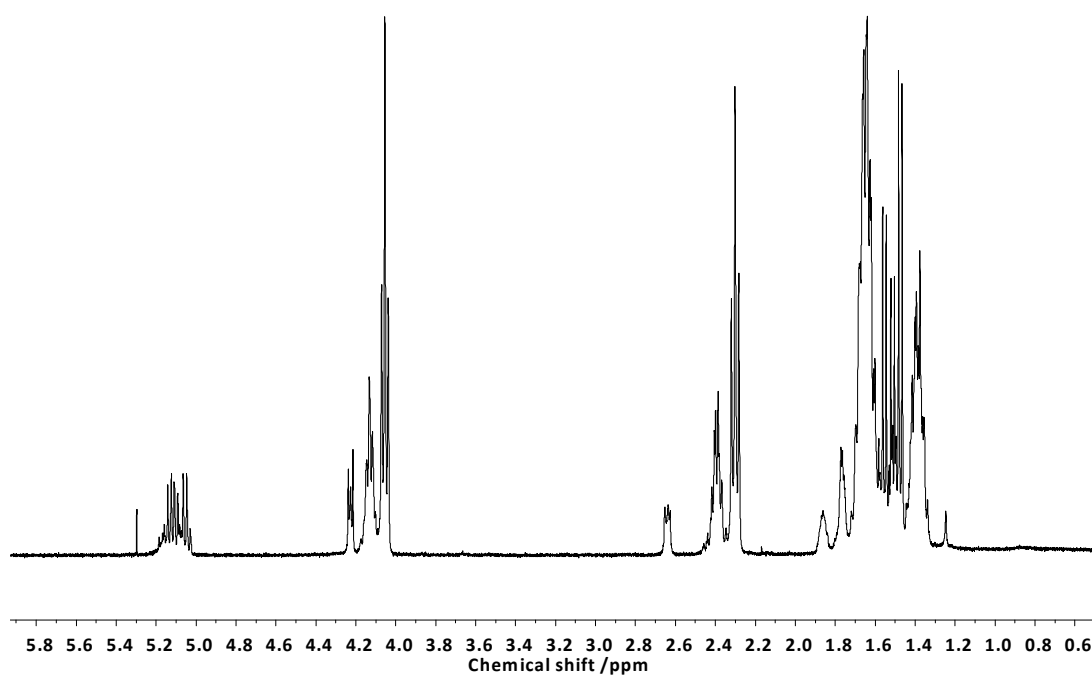


Figure S24. ^1H NMR spectrum (400 MHz, CDCl_3) of the crude polymerization mixture (Table 2, run 3).

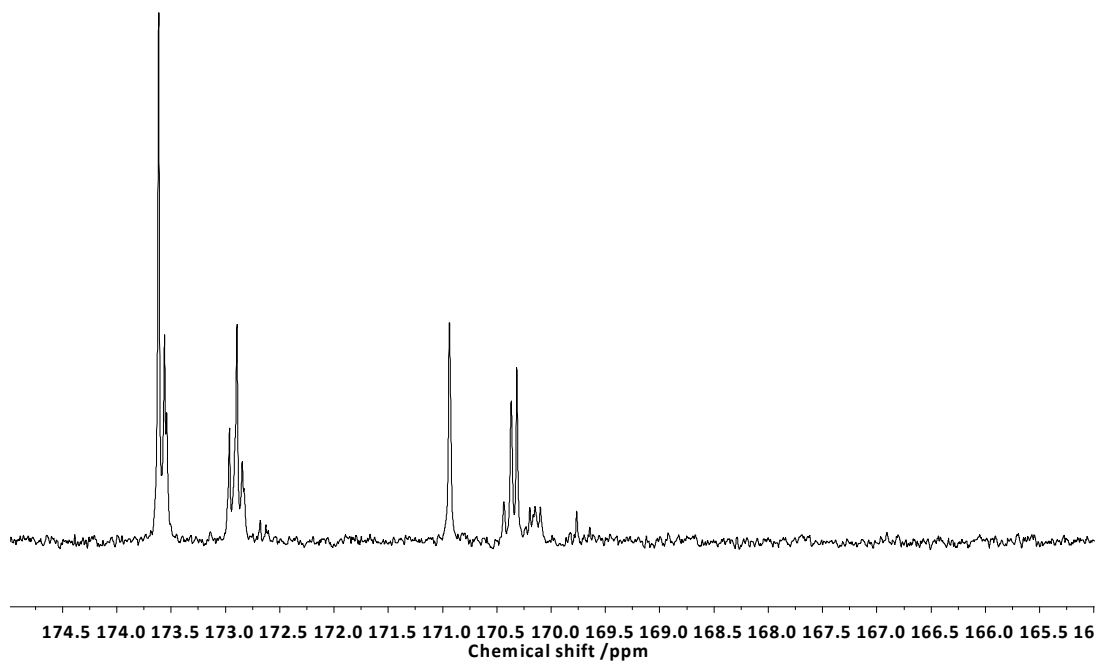


Figure S25. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, CDCl_3) of the isolated polymer (Table 2, run 3).

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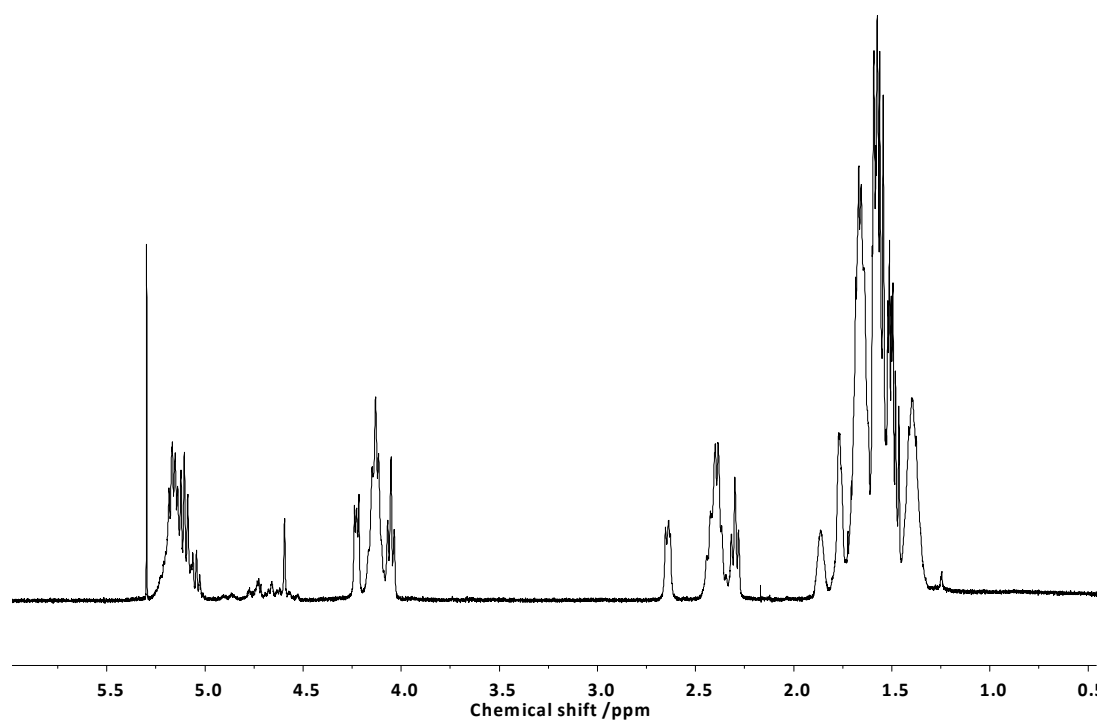


Figure S26. ^1H NMR spectrum (400 MHz, CDCl_3) of the crude polymerization mixture (Table 2, run 4). $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the isolated polymer see Figure 4.

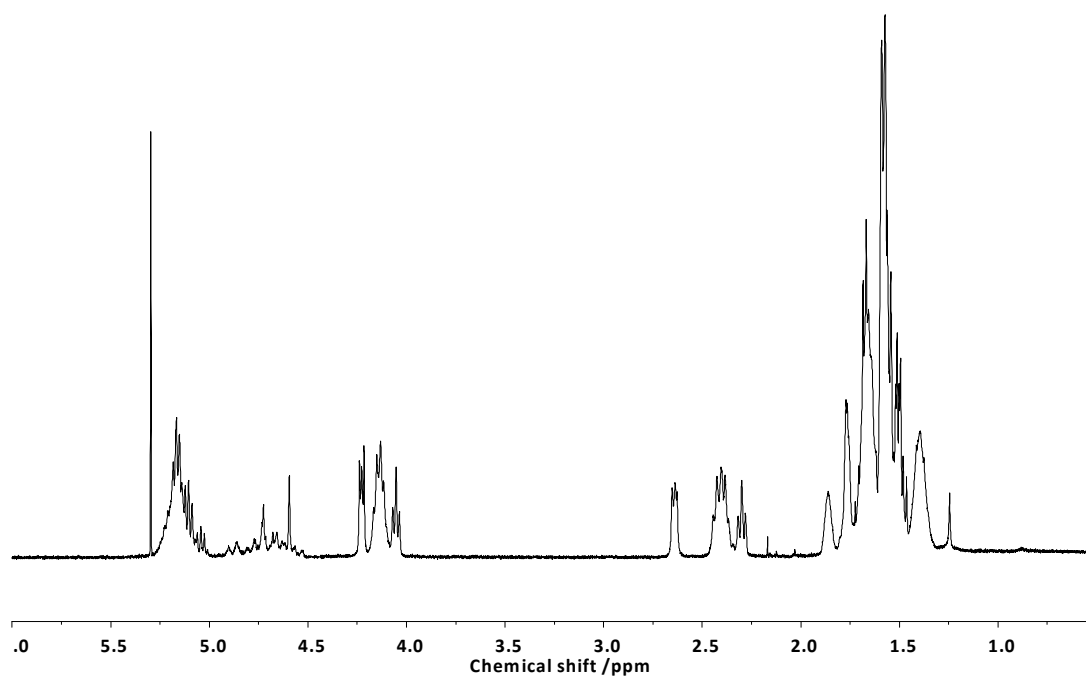


Figure S27. ^1H NMR spectrum (400 MHz, CDCl_3) of the crude polymerization mixture (Table 2, run 5). $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the isolated polymer see Figure 4.

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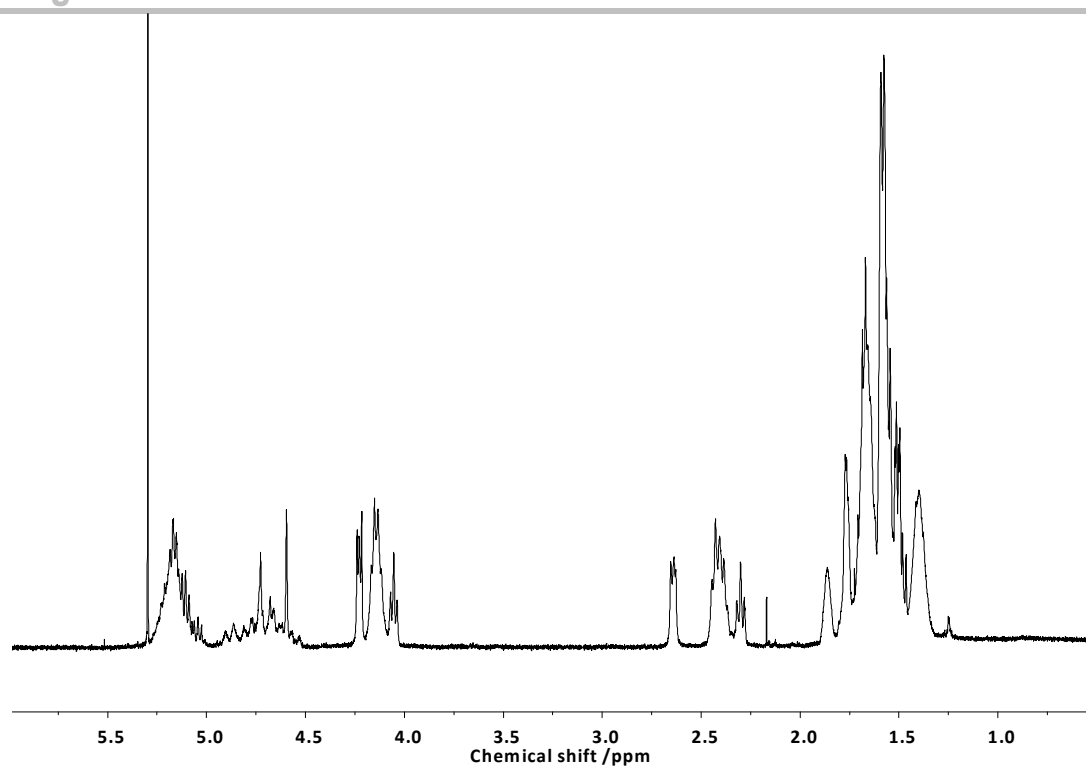


Figure S28. ^1H NMR spectrum (400 MHz, CDCl_3) of the crude polymerization mixture (Table 2, run 6). $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the isolated polymer see Figure 4.

Supporting Information

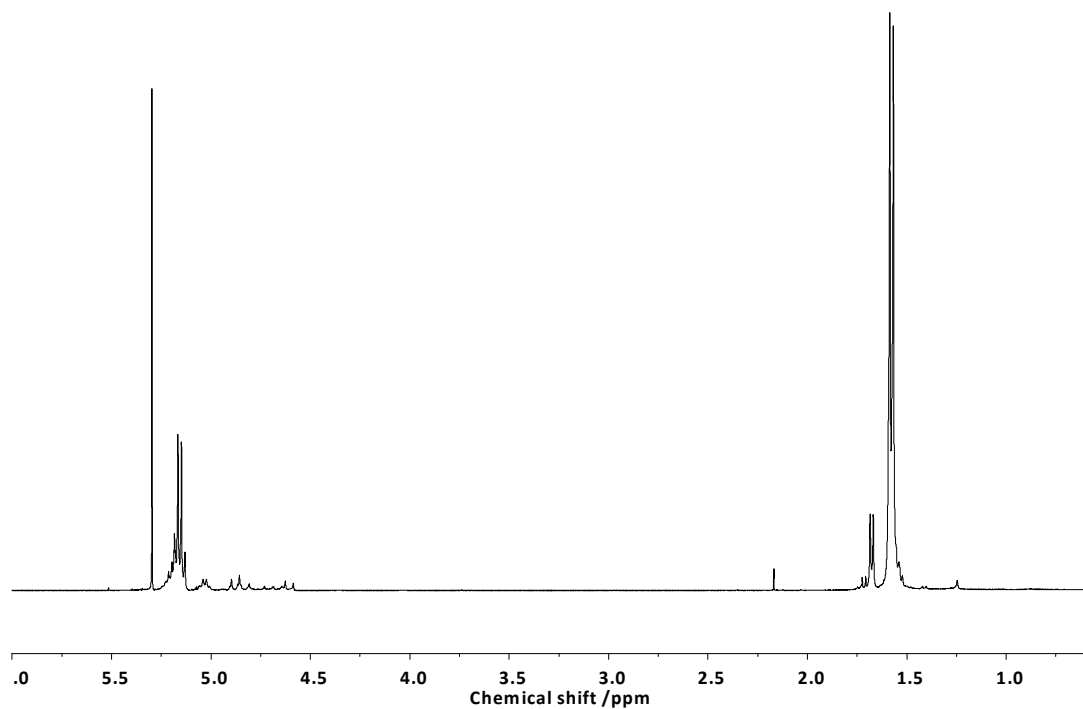


Figure S29. ^1H NMR spectrum (400 MHz, CDCl_3) of the crude polymerization mixture (Table 2, run 7).

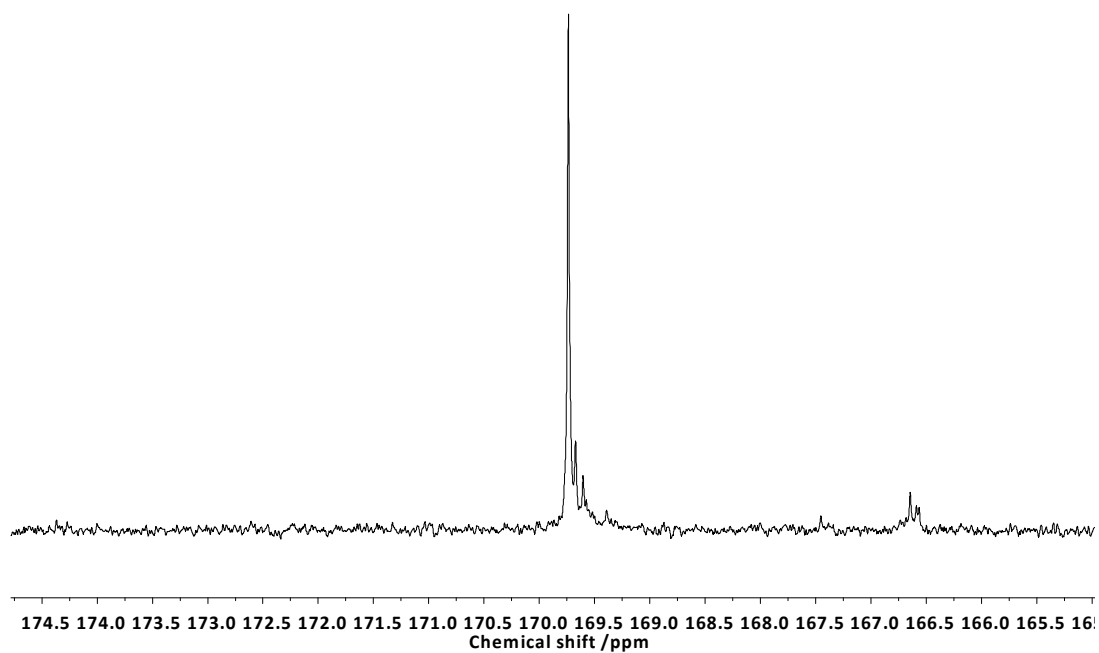


Figure S30. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, CDCl_3) of the isolated polymer (Table 2, run 7).

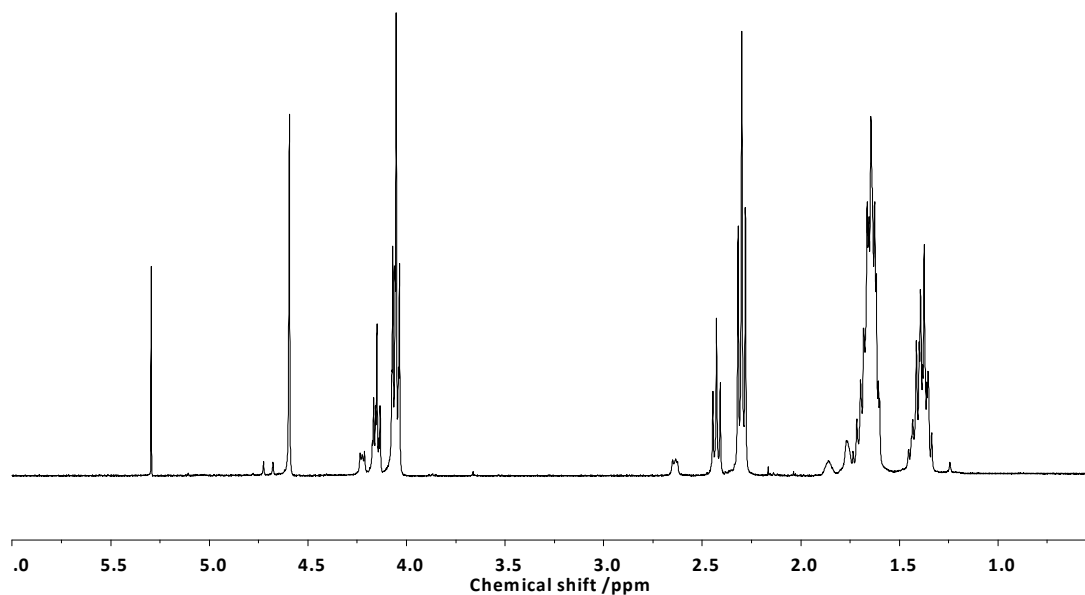


Figure S31. ^1H NMR spectrum (400 MHz, CDCl_3) of the crude polymerization mixture (Table 2, run 8).

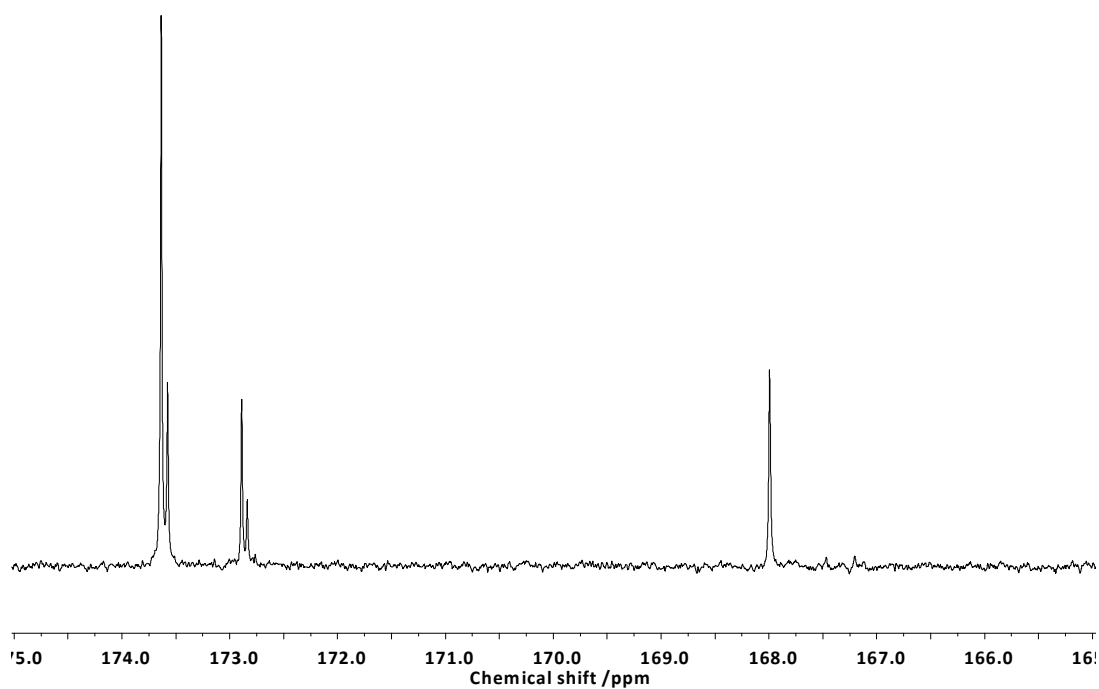


Figure S32. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, CDCl_3) of the isolated polymer (Table 2, run 8).

Supporting Information

3.3. MALDI-ToF-MS

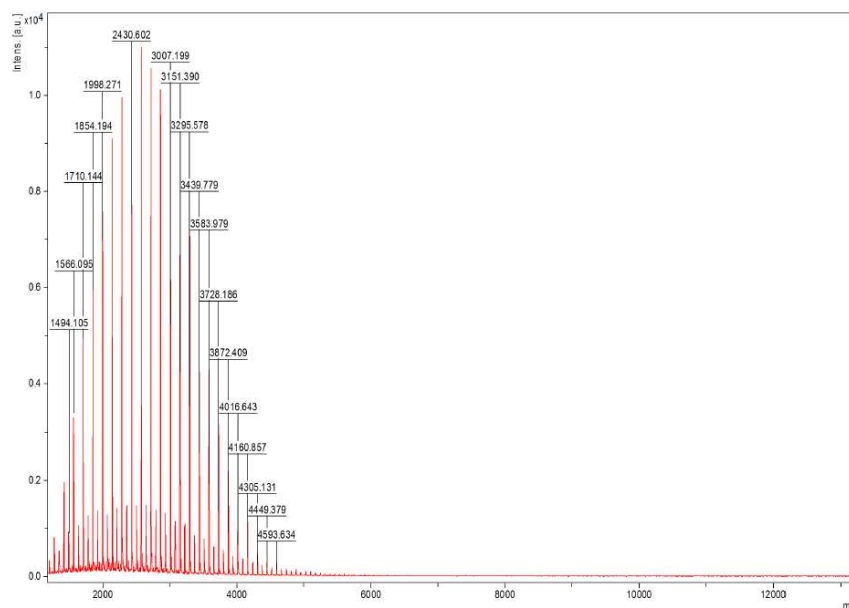


Figure S33. MALDI-ToF MS results of the polymerization of LL with **1**, M/CoI/Cat ratio 10.000:500:1 (Table S2, run 4). Analyzed with Polymerix (Sierra Analytics): 58.24% of the spectrum refer to the series with OH as alpha and C₇H₇O (Benzyl alcohol) as omega end group. No further series with possible end groups could be assigned.

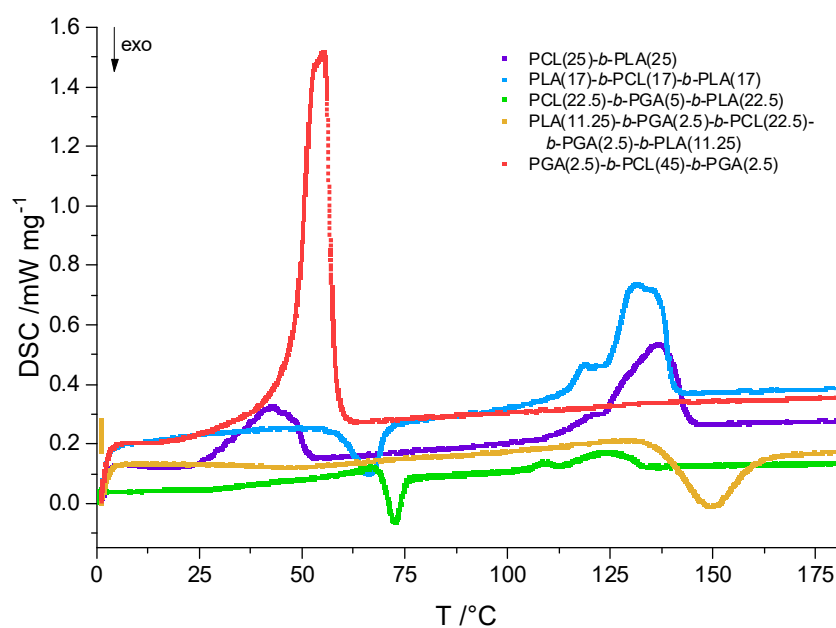
Supporting Information

3.4. DSC

Table S4. Summary of DSC data.

Sample	T_g / °C ^[a]	T_m / °C ^[a]	ΔH_m / Jg ⁻¹ ^[a]	X_c (PCL / PLA) / % ^[b]
PCL(25)- <i>b</i> -PLA(25) (Table 1, run 1)	n.m.	43 / 137	17 / 27	12 / 29
PLA(17)- <i>b</i> -PCL(17)- <i>b</i> -PLA(17) (Table 1, run 2)	n.m.	132	35	n.d. / 38
PCL(22.5)- <i>b</i> -PGA(5)- <i>b</i> -PLA(22.5) (Table 1, run 3)	n.m.	123	26	n.d. / 18
PLA(11.25)- <i>b</i> -PGA(2.5)- <i>b</i> -PCL(22.5)- <i>b</i> -PGA(2.5)- <i>b</i> -PLA(11.25) (Table 1, run 4)	n.m.	121	20	n.d. / 22
PGA(2.5)- <i>b</i> -PCL(45)- <i>b</i> -PGA(2.5) (Table 1, run 5)	n.m.	55	65	47 / -
PCL(500)- <i>ran</i> -PLA(500) (Table 2, run 1)	n.m.	n.m.	n.m.	n.d.
PCL(250)- <i>ran</i> -PLA(750) (Table 2, run 2)	30	n.m.	n.m.	n.d.
PCL(750)- <i>ran</i> -PLA(250) (Table 2, run 3)	n.m.	n.m.	n.m.	n.d.
PCL(475)- <i>ran</i> -PGA(50)- <i>ran</i> -PLA(475) (Table 2, run 4)	n.m.	n.m.	n.m.	n.d.
PCL(450)- <i>ran</i> -PGA(100)- <i>ran</i> -PLA(450) (Table 2, run 5)	n.m.	n.m.	n.m.	n.d.
PCL(425)- <i>ran</i> -PGA(150)- <i>ran</i> -PLA(425) (Table 2, run 6)	n.m.	n.m.	n.m.	n.d.
PGA(100)- <i>ran</i> -PLA(900) (Table 2, run 7)	55	n.m.	n.m.	n.d.
PCL(900)- <i>ran</i> -PGA(100) (Table 2, run 8)	n.m.	35	40	29 / -

[a] Values of second heating, n.m.: not measured, n.d.: not determined. [b] $X_c = \Delta H_m / \Delta H_m^0 \cdot 100$ with $\Delta H_m^0(\text{PLA}) = 93 \text{ Jg}^{-1[5]}$ and $\Delta H_m^0(\text{PCL}) = 139 \text{ Jg}^{-1[6]}$.

**Figure S34.** DSC thermograms of second heating of block copolymers.

Supporting Information

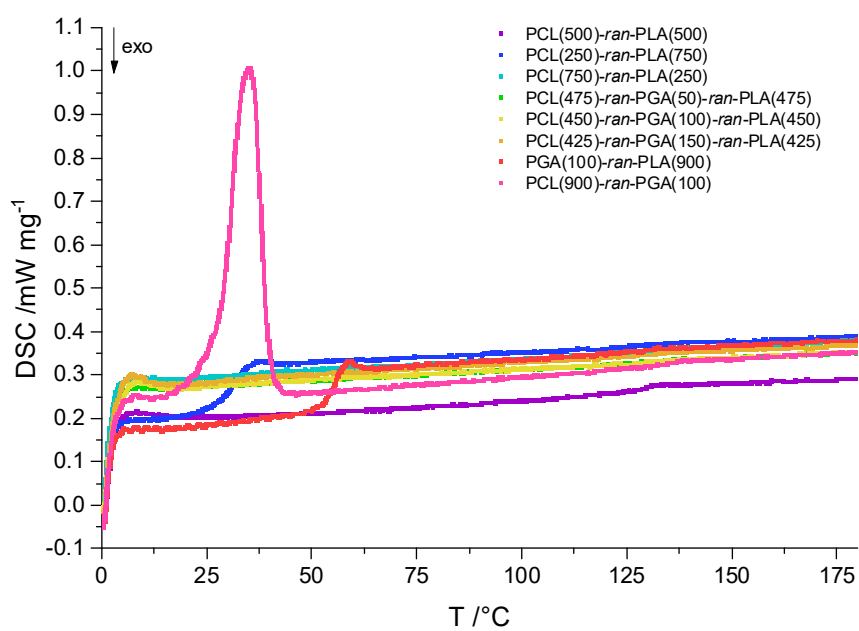


Figure S35. DSC thermograms of second heating of random copolymers.

Supporting Information

References

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