Electronic Supporting Information for:

Synthesis and depolymerization studies of biohybrid polycarbonates derived from terpenes

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Table of Contents:

1. General information

Chemicals

Solvents were dried using an Innovative Technology PURE SOLV solvent purification system. Reactions were monitored by ^{1}H NMR ($CDCl_3$). (+)-Limonene oxide (**LO**: mixture of *cis* and *trans*, ≥ 97%, Aldrich) was stirred over calcium hydride and filtered prior to use. *L*-Menthol (≥99%, Aldrich), citronellol (≥95%, Aldrich), oxetane, 3chloroperoxybenzoic acid (≤77%, Aldrich), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) (98%, Aldrich), potassium *tert*-butoxide (≤ 98%, Aldrich), *N*-methyl pyrrolidine (NMP), methanesulfonyl chloride (≥ 99.7%, Aldrich) and pyridine (≥ 99%, Aldrich) were all purchased commercially and used as received unless otherwise noted. The known **OX** monomer was prepared as reported in: T. M. McGuire, J. Bowles, E. Deane, E. H. E. Farrar, M. N. Grayson, and A. Buchard, Control of Crystallinity and Stereocomplexation of Synthetic Carbohydrate Polymers from d- and l-xylose, *Angew. Chem. Int. Ed.*, **2021**, 60, 4524 – 4528).

NMR Spectroscopy

NMR spectra were obtained on a Bruker 400 MHz, 500 MHz or a 500 MHz with cryoprobe spectrometers equipped with probe-heads capable of producing gradients in the *z* direction with a maximum strength of 53.5 G/cm. ^{1}H, ^{13}C and ^{19}F NMR chemical shifts are reported in parts per million (ppm), relative to tetramethylsilane (TMS) for ^{1}H and ^{13}C NMR experiments with the residual solvent peak used as an internal reference. Multiplicities are reported as follows: singlet (s), d (doublet), dd (doublet of doublets), triplet (t) and multiplet (m).

Thermal Analysis

Differential scanning calorimetry (DSC) analyses to determine glass transition temperatures (T_g) were measured under an N_2 atmosphere using a Mettler Toledo model DSC822e. Samples were weighed into 40 μL aluminum crucibles and subjected to three heating cycles typically at a heating rate of 10 °C/min. Thermogravimetric analyses (TGA) were recorded under an N_2 atmosphere using Mettler Toledo model TGA/SDTA851. Samples were weighed into 40 μL aluminum crucibles and heated to 600 ºC typically at a heating rate of 10 °C/min. All thermal data were collected by the Research Support Unit at ICIQ. For the DSC analyses, typically the data referring to the second heating/cooling were selected to determine the T_g, T_m and T_c values.

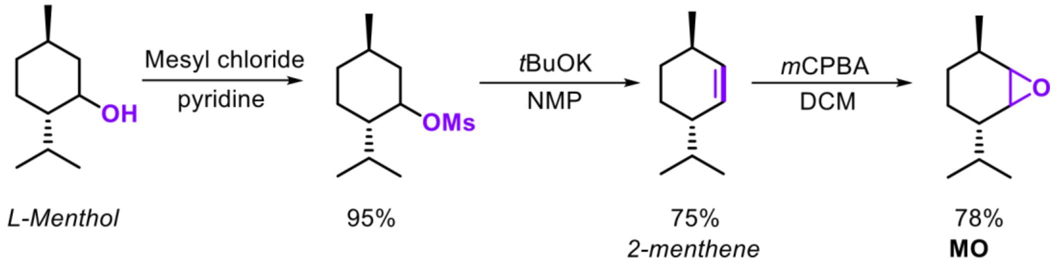
Gel permeation chromatography

Measurements were performed using an Agilent 1200 series HPLC system, equipped with PSS SDV analytical linear M GPC column (8 □ 300 mm; 5 μm particle size) in tetrahydrofuran at 30 °C at a flow rate of 1 $mL \cdot min^{-1}$. Samples were analyzed at a concentration of around 1 $mg \cdot mL^{-1}$ after filtration through a 0.45 μm pore-size membrane. M_n, M_w, and $Đ$ data were derived from the RI signal by a calibration curve based on polystyrene standards (PSs obtained from Polymer Standards Service) for the analysis of the polymers. The GPC samples were prepared by dissolving the polymer (3−5 mg) in THF (2 mL) and filtering the solution through a 0.45 μm pore-size membrane.

2. Monomer synthesis

Menthene oxide (**MO**):

For a literature preparation of **MO**, consult: A. Wambach, S. Agarwal, A. Greiner, Synthesis of Biobased Polycarbonate by Copolymerization of Menth-2-ene Oxide and CO_2 with Exceptional Thermal Stability. *ACS Sustainable Chem. Engin*. **2020**, *8*, 14690−14693. The intermediates were analyzed by ^{1}H NMR, and the data was consistent with that of the literature.



Synthesis of menthyl mesylate:

L-Menthol (260 mmol, 1 equiv) was dissolved in DCM and pyridine (522 mmol, 2 equiv) was added at 0 °C. Then, methanesulfonyl chloride (280 mmol, 1.1 equiv) was added over a period of 30 min. After stirring for 24 h at room temperature, the mixture was dissolved in DCM and washed twice with 4 M hydrochloric acid solution, saturated Na_2CO_3, and brine. The DCM layer was separated, filtered and dried over $MgSO_4$. The solvent was removed under reduced pressure to obtain a crystalline solid (95%), which was directly used in the next step (see below).

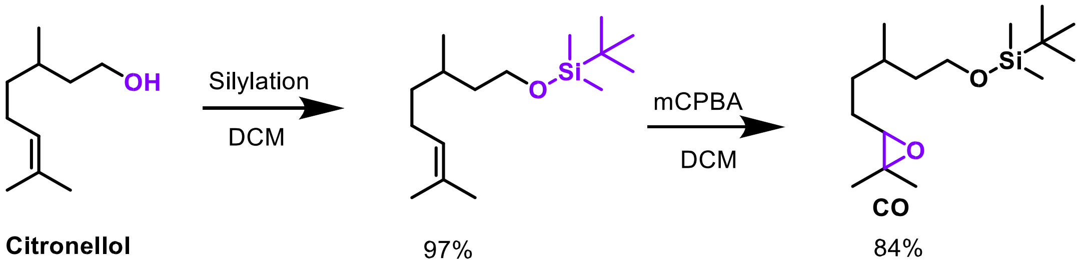
Formation of 2-menthene

L-Menthyl tosylate (242 mmol, 1 equiv) was suspended in NMP (200 mL) under vigorous stirring and cooled to 0 °C. Potassium *tert*-butoxide (466 mmol, 1.9 equiv) was added in portions over 30 min to the reaction mixture. While heating at 80 °C for 3 h, all reactants dissolved and a deep green solution was formed. Afterwards, water was slowly added, which resulted in a phase separation of the product and aqueous NMP. Pentane was added to extract the crude product. A clear layer was obtained, which after removal of the solvent under reduced pressure and distillation under dynamic vacuum resulted into the isolated of the desired 2-menthene (75%) as a colorless oil. The compound was directly used in the next step (see below). Appearance = colorless liquid.

Epoxidation of 2-menthene

2-Menthene (210 mmol, 1 equiv) and dichloromethane were mixed and cooled with an ice bath. *m*CPBA (270 mmol, 1.3 equiv) was added slowly over 30 min and stirring was continued for an additional 8 h. Afterwards, the reaction mixture was allowed to warm to room temperature and stirred for a further 16 h. The formed precipitate was removed via filtration and the filtrate washed once with aqueous 1 M NaOH, a saturated aqueous $NaHCO_3$ solution and brine. The organic phase was dried over $MgSO_4$, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography as reported in the literature to give the desired **MO** in 78% yield. Column eluent = 3−5% ethyl acetate in petroleum ether as eluent. Appearance = colorless liquid.

Citronellol oxide (CO) synthesis



Procedure for the silylation of citronellol

In a round-bottom, two-necked flask with a stirring bar charged with the starting alcohol (10 g, 64 mmol, 1 equiv) in DCM (100 mL), 2,6-lutidine (14.9 mL, 128 mmol, 2 equiv) and *tert*-butyldimethylsilyl trifluoromethanesulfonate (25.3 g, 96 mmol, 1.5 equiv) were added under argon atmosphere at 0 °C over a period of 30 min. Subsequently, the reaction mixture was stirred at 0 °C for half an hour and then slowly allowing the mixture to reach room temperature, after which it was stirred for 16 h. TLC, confirmed the completion of the reaction and the crude product was washed with brine. The crude product was without further purification taken in to next step. Appearance = colorless liquid.

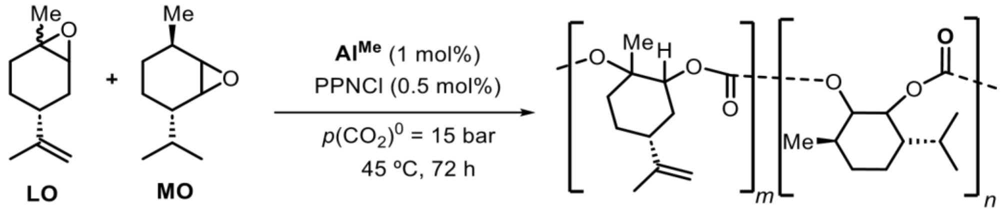
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.15 – 5.10 (m, 1H), 3.81 – 3.55 (m, 2H), 2.06 – 1.94 (m, 2H), 1.70 (s, 3H), 1.62 (s, 3H), 1.61 – 1.52 (m, 2H), 1.40 – 1.31(m, 2H), 1.22 – 1.13 (m, 1H), 0.92 (s, 9H), 0.90 – 0.88 (m, 3H), 0.07 (s, 6H).

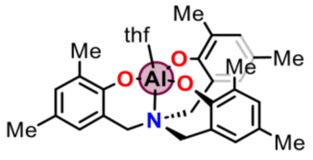
Epoxidation of silylated citronellol

Silylated citronellol (7.5 g, 27 mmol, 1 equiv) was dissolved in dichloromethane (100 mL) and cooled with an ice bath (0 ºC). After 10 min, *m*CPBA (5.7 g, 33 mmol, 1.2 equiv) was added slowly over 30 min and stirring was continued for an additional 1 h. Afterwards, the reaction mixture was allowed to room temperature and stirred for further 16 h. The formed precipitate was removed via filtration and the filtrate washed once with aqueous 1 M NaOH, saturated aqueous $NaHCO_3$ solution, and brine. The organic phase was dried over $MgSO_4$, and the solvent was removed under reduced pressure. The crude product was purified through column chromatography yielding the target product in 84%. Column eluent = 3−5% ethyl acetate in petroleum ether as eluent. Appearance = colorless liquid.

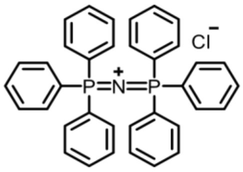
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.78 – 3.57 (m, 2H), 2.70 (t, *J* = 6.3, 1H), 1.77 – 1.43 (m, 5H), 1.42 – 1.32 (m, 2H), 1.31 (s, 3H), 1.27 (s, 3H), 0.93 – 0.92 (m, 3H), 0.91 (s, 9H), 0.05 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 64.62, 64.59, 61.27, 61.24, 58.25, 58.15, 39.86, 39.75, 33.66, 33.62, 29.39, 26.43, 26.38, 25.95, 24.91, 19.57, 19.52, 18.69, 18.65, 18.30, -5.29. **HRMS** (ESI/TOF) *m*/*z*: $[M + Na]^+$ Calcd for. $C_{16}H_{34}O_2SiNa$: 286.2331; found 286.2397.

3. General procedure for hybrid biopolymer (PLMC) synthesis





Al^{Me}



PPNCl

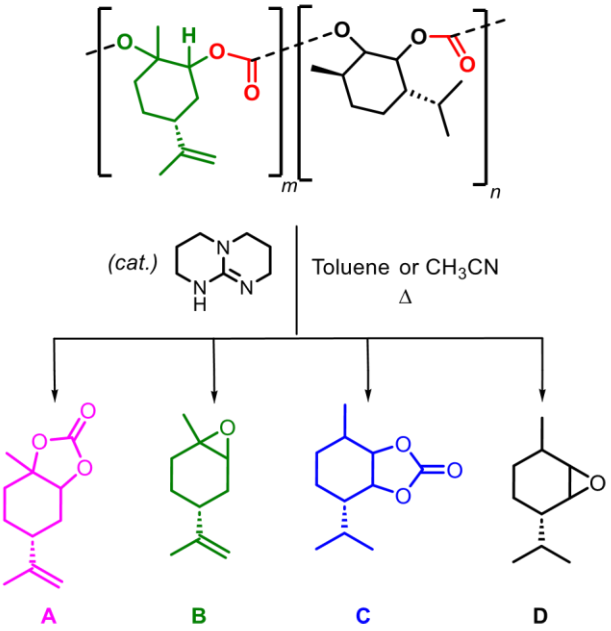
A 50 mL autoclave was charged inside a glove box with complex **Al^{Me}** (0.01 equiv) and PPNCl (0.005 equiv) dissolved in the respective epoxide/mixture (1 equiv). The closed reactor was flushed with CO_2 three times and pressurized finally to 15 bar CO_2. The mixture was stirred at 45 °C for 72 h. After the reactor was cooled with an ice bath, it was carefully depressurized. An aliquot of the reaction mixture was dissolved into a minimum amount of dichloromethane and used to determine the conversion by ^{1}H NMR ($CDCl_3$) analysis. The reaction mixture was poured into acidified methanol (1 M) under stirring causing typically precipitation of the polymeric product as a white solid. The latter was collected by filtration and washed twice with cold methanol. The isolated polymer was dried for 24 h under vacuum at 50 ºC. NB. *We have evaluated the reaction under inert atmosphere setups outside a glove box (e.g., using standard Schlenk techniques or inertgas purging systems), and observed comparable yields and selectivity, suggesting that scale-up under these more practical conditions is feasible.*

Below a specific example:

A 50 mL autoclave was charged inside a glove box with **Al^{Me}** (33.0 mg, 65.7 µmol, 0.01 equiv) and PPNCl (18.3 mg, 32.8 µmol, 0.005 equiv) dissolved in limonene oxide (**LO**, 3.28 mmol, 1 equiv) and menthene oxide (**MO**, 3.28 mmol, 1 equiv). The closed reactor was flushed with CO_2 three times and then pressurized to 15 bar of CO_2. The mixture was allowed to stir at 45 °C for 72 h. After the reactor was depressurized and cooled to room temperature. After the reactor was cooled with an ice bath, it was carefully depressurized. An aliquot of the reaction mixture was dissolved into a minimum amount of dichloromethane and used to determine the conversion by ^{1}H NMR ($CDCl_3$) analysis. The reaction mixture was poured into acidified methanol (1 M) under stirring causing typically precipitation of the polymeric product as a white solid. The latter was collected by filtration and washed twice with cold methanol. The isolated polymer was dried for 24 h under vacuum at 50 ºC.

Yields after precipitation, filtration and drying: **P1** = 57% (white solid), **P2** = 34% (white solid), **P3** = 50% (white solid), **P5** = 33% (pale yellow solid), and **P7** = 31% (off-white solid).

4. Depolymerization of selected PLMC samples



Typical conditions: in a glovebox, a Schlenk tube equipped with a stirring bar was charged with a hybrid polymer sample **PLMC** (0.10 g, 0.654 mmol carbonate repeat units) and TBD (16.5 mg, 0.118 mmol, 0.18 equiv). The mixture was dissolved in 0.5 mL CH_3CN and refluxed at 90 °C for 15 h. The reaction was monitored by ^{1}H NMR spectroscopy ($CDCl_3$), taking an aliquot from the reactive mixture. ^{1}H NMR spectroscopy an was carried out on the crude reaction mixture to determine the percentage of depolymerization and the relative amount of **MO** and **LO** (see next pages for a visual).

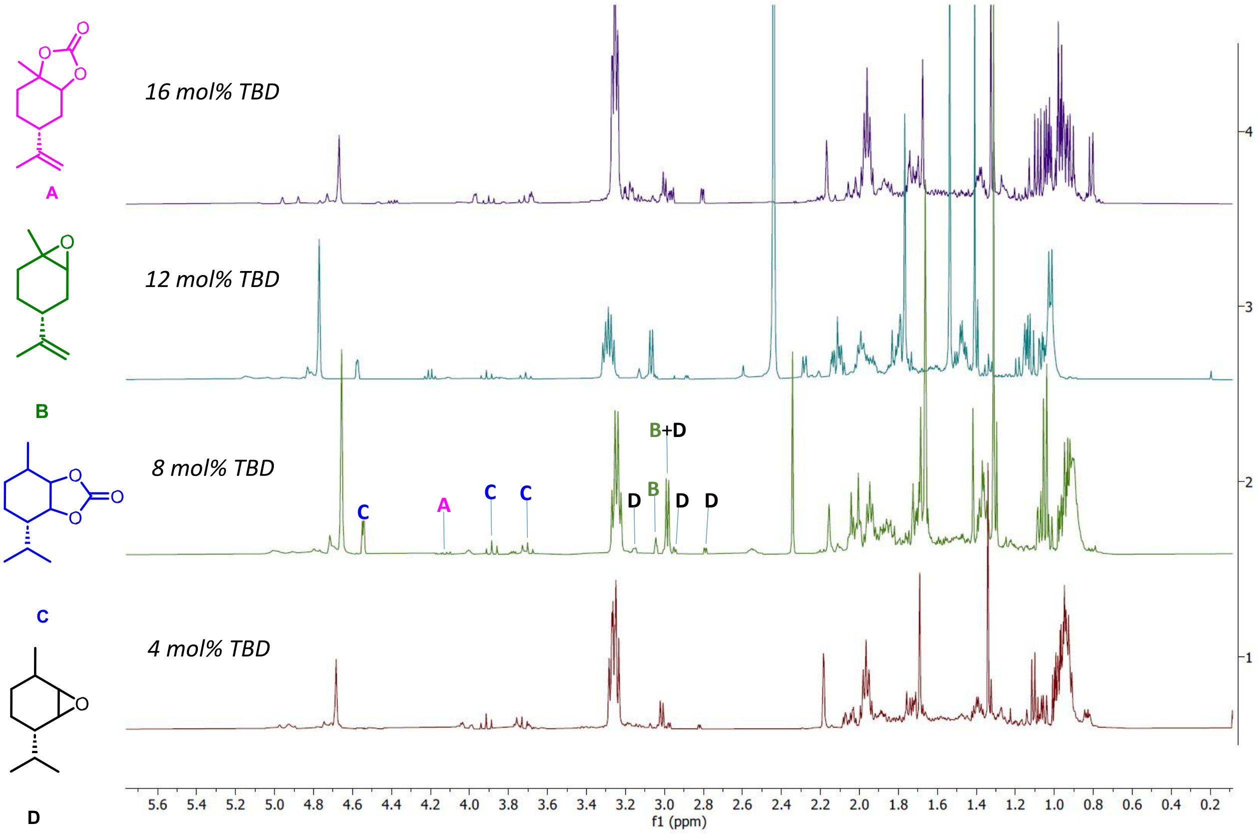


Figure S1: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) comparison related to different amounts of catalytic TBD used for the depolymerization of **PLMC** (**P1**). For the different conditions, also refer to Table 2 in the main text. Blue trace: @16mol% TBD, dark green trace: @12 mol% TBD, lightgreen trace: @8 mol% TBD, red-brown trace: @4 mol% TBD.

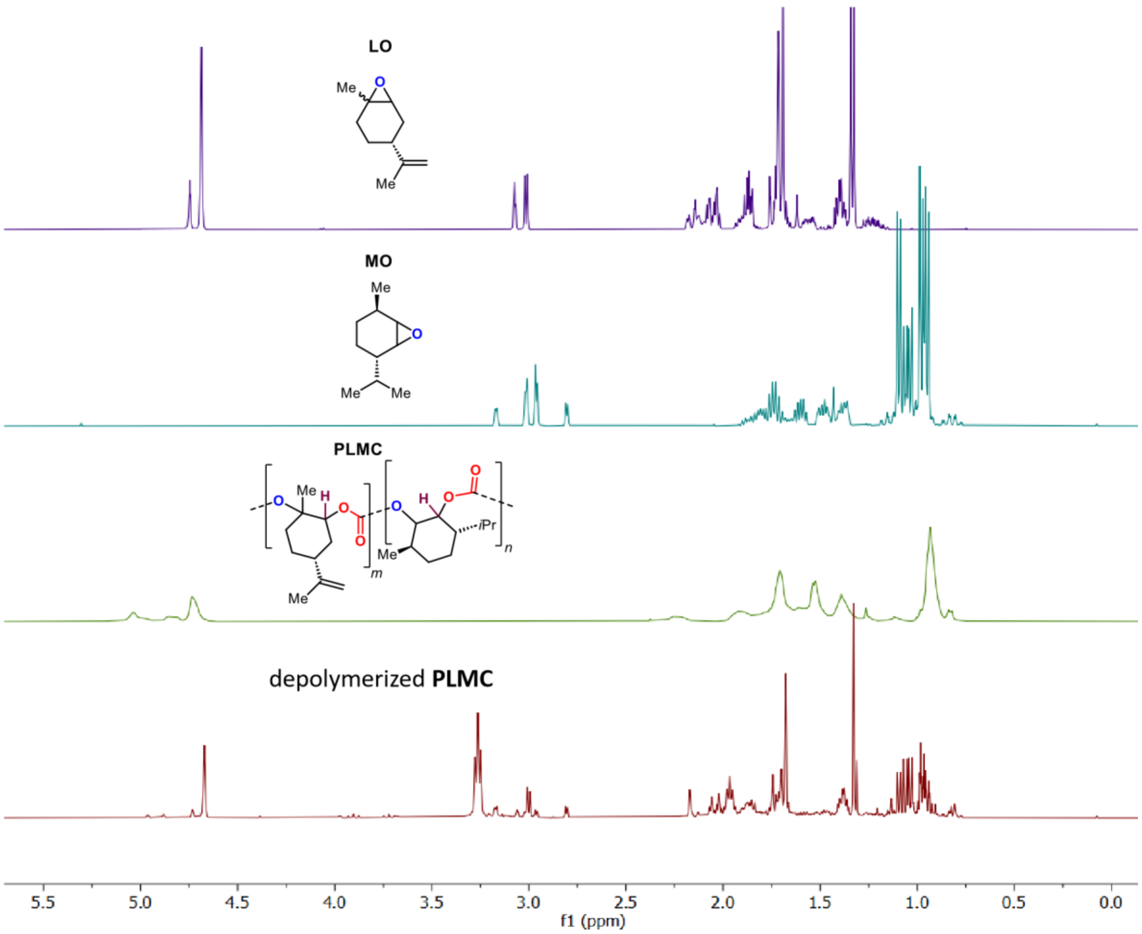


Figure S2: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) comparison (region 0-5.5 ppm) from top to bottom) between pristine **LO** (dark blue), **MO** (dark green), **PLMC** (light-green, entry 13, Table 1) and the depolymerized **PLMC** (red-brown) and the depolymerized sample.

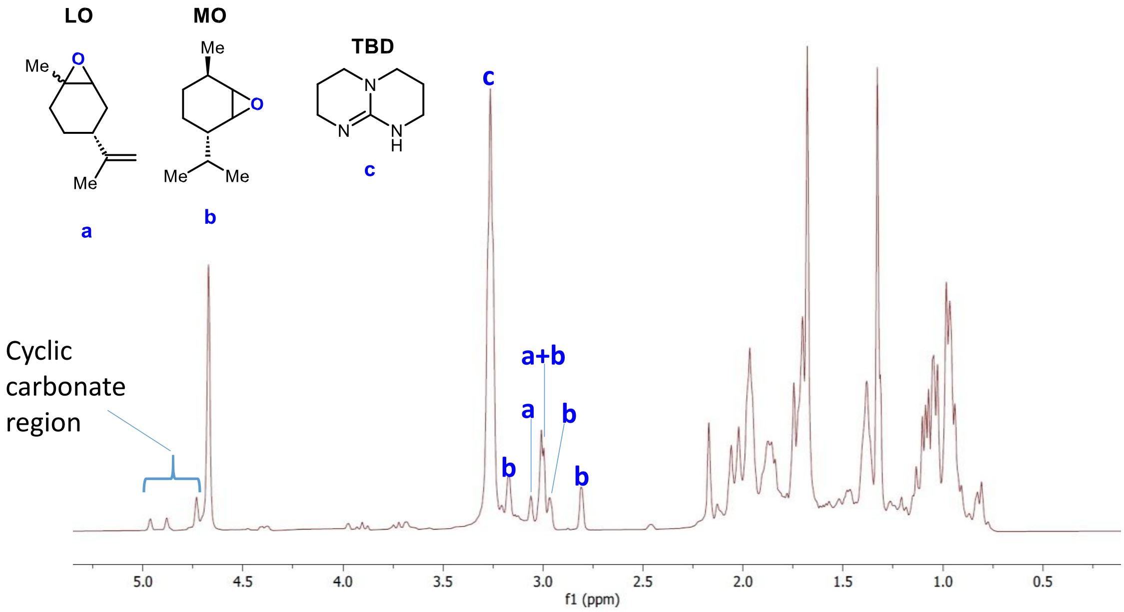


Figure S3A. ^{1}H NMR spectrum (CDCl$_3$, 400 MHz) explaining which resonances were used to calculate the amounts of **LO**, **MO**, LC (limonene carbonate) and MC (2-methene carbonate) using mesitylene as an internal standard. Hydrogens **a** and **b** were used to calculate the amounts of **MO** and **LO**.

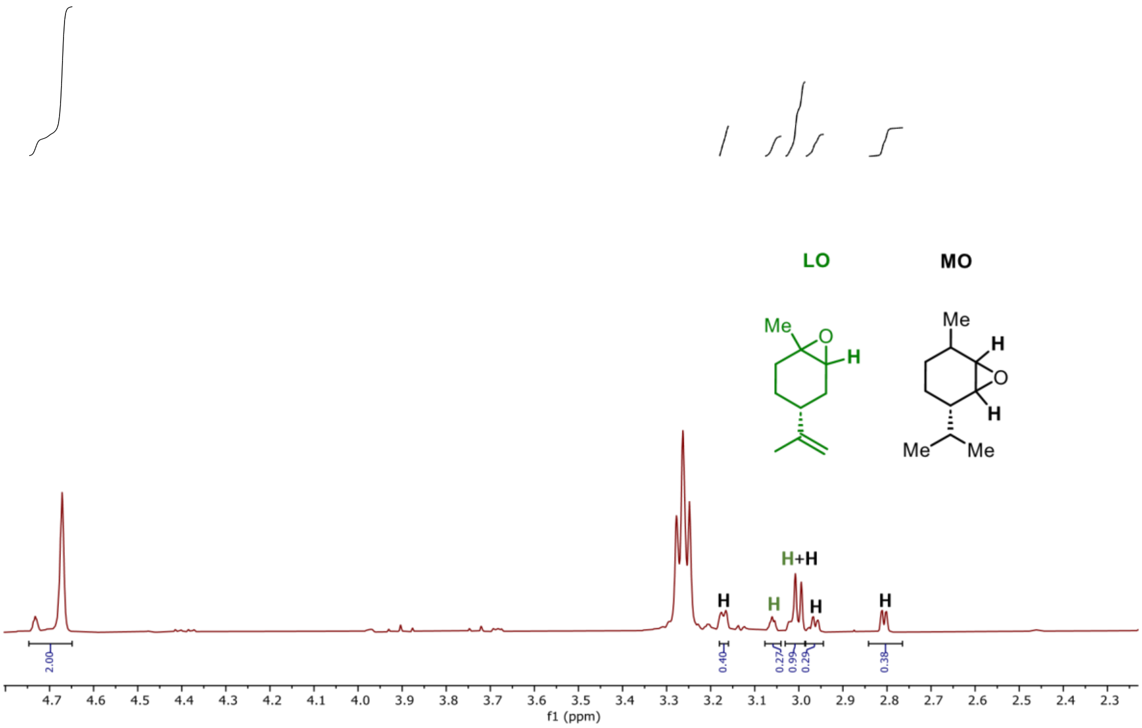


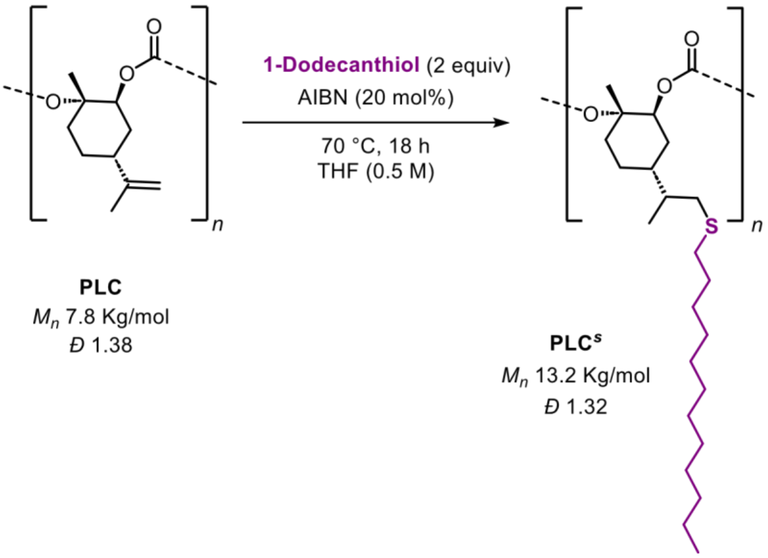
Figure S3B. Zoomed (*epoxide*) region of the ^{1}H NMR spectrum (CDCl$_3$, 400 MHz) of a depolymerized sample (relating to Table 2, entry 6 in the MS).

Calculation of the MO-to-LO ratio after depolymerization is as follows:

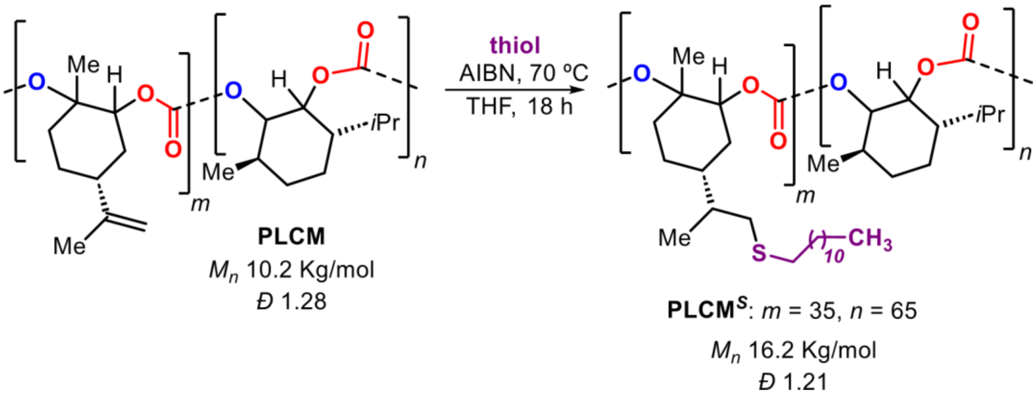
The amount of LO related to “**H**” and the amount of MO to “**H**” shown in Figure S3B. Note that different *diastereoisomers* are isolated upon epoxidation of the parent terpene compounds (Dlimonene and 2-menthene), therefore all peaks are “doubled” and in total 6 peaks are expected (two are overlapping as indicated). All peaks related to 1H whereas the overlapping one should relate to 2H in total. The peaks at = 3.18, 3.07, 2.97 and 2.81 can be used to calculate the relative contribution of LO and MO to the overlapping region at 2.99-3.07, and this allows to calculate the % of each of the epoxides in the crude mixture of depolymerization.

Amount of **MO**: major isomer (0.38 + 0.40) + minor isomer (0.29 + 0.29) = 1.36 (2H)
Amount of **LO**: major isomer (0.99-0.29) + minor isomer (0.27) = 0.70 + 0.27 = 0.99 (1H)
As the integrals of MO are represented by two H´s, it needs to be divided by 2: 1.36/2 = 0.68 (contribution per H). This then leads to a LO:MO ratio of 0.99:0.68, or expressed in %: 59 to 41 %.

5. Thiol-based functionalization of PLC and PLMC



Example procedure for PLC: To a solution of **PLC** (200 mg, 1.02 mmol, carbonate repeat units) in dry THF (2.0 mL, 0.5 M) under nitrogen was added 1-dodecanthiol (413 mg, 2.04 mmol, 2 equiv) followed by AIBN (33.5 mg, 0.20 mmol, 20 mol%). The resulting mixture was then stirred at 70 °C for 18 h. The volatiles were removed in vacuo, then the crude reaction product was dissolved in a minimum amount of DCM and precipitated from methanol two times. The resulting sticky polymer **PLC^s** was collected by decantation and dried under high vacuum. Glassy solid, 245 mg (60%) at 96% conversion of the C=C bonds in **PLC**.



To a solution of **PLMC** (entry 13, Table 1: 200 mg, 0.608 mmol of limonene repeat units) in dry THF (2 mL, 0.5 M) under nitrogen was added 1-dodecanthiol (246 mg, 1.22 mmol, 2 equiv) followed by AIBN (20.0 mg, 0.12 mmol, 20 mol%). The resulting mixture was then stirred at 70 °C for 18 h. The volatiles were removed in vacuo, and the crude reaction product was dissolved in a minimum amount of DCM and precipitated from methanol two times. The resulting sticky polymer **PLMC^s** was collected by decantation and dried in vacuo. Glassy solid, 210 mg (65%) at >96% conversion of the C=C bonds in **PLMC**.

6. Analytical data for relevant compounds and polymers

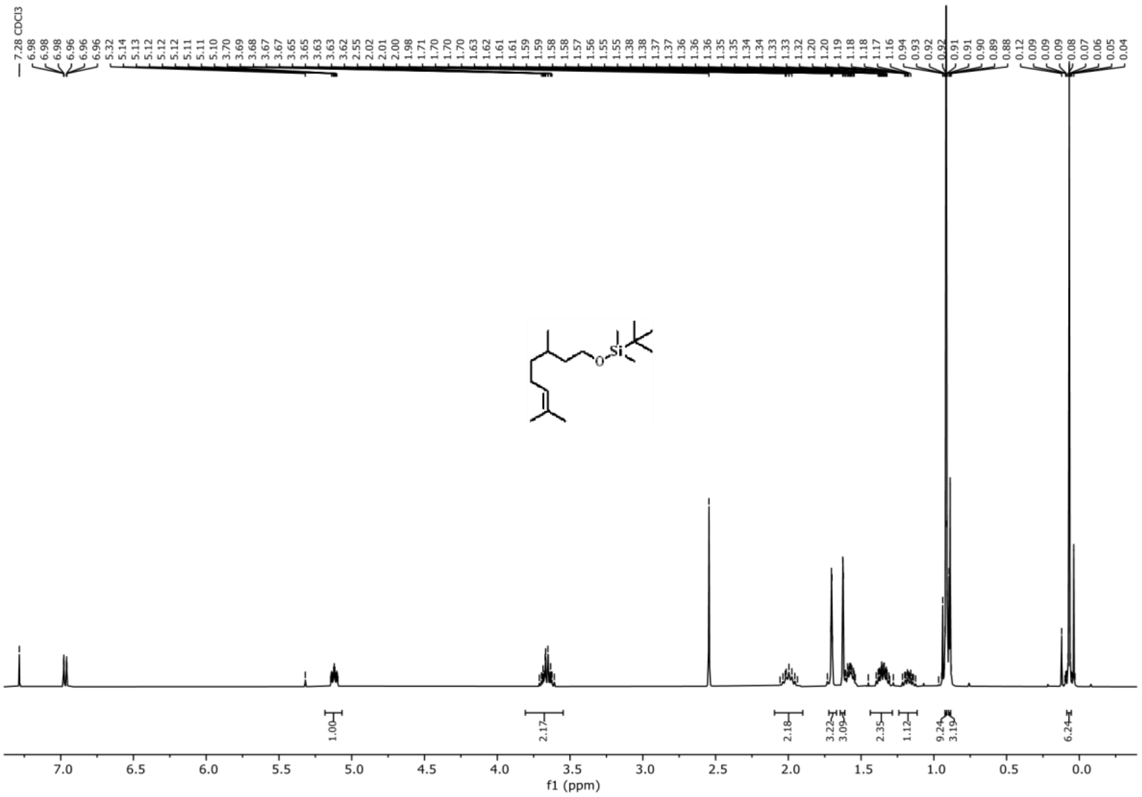


Figure S4: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) for silyl-protected citronellol. *Note that the spectrum refers to a crude, non-purified sample. It was directly used in the next step*.

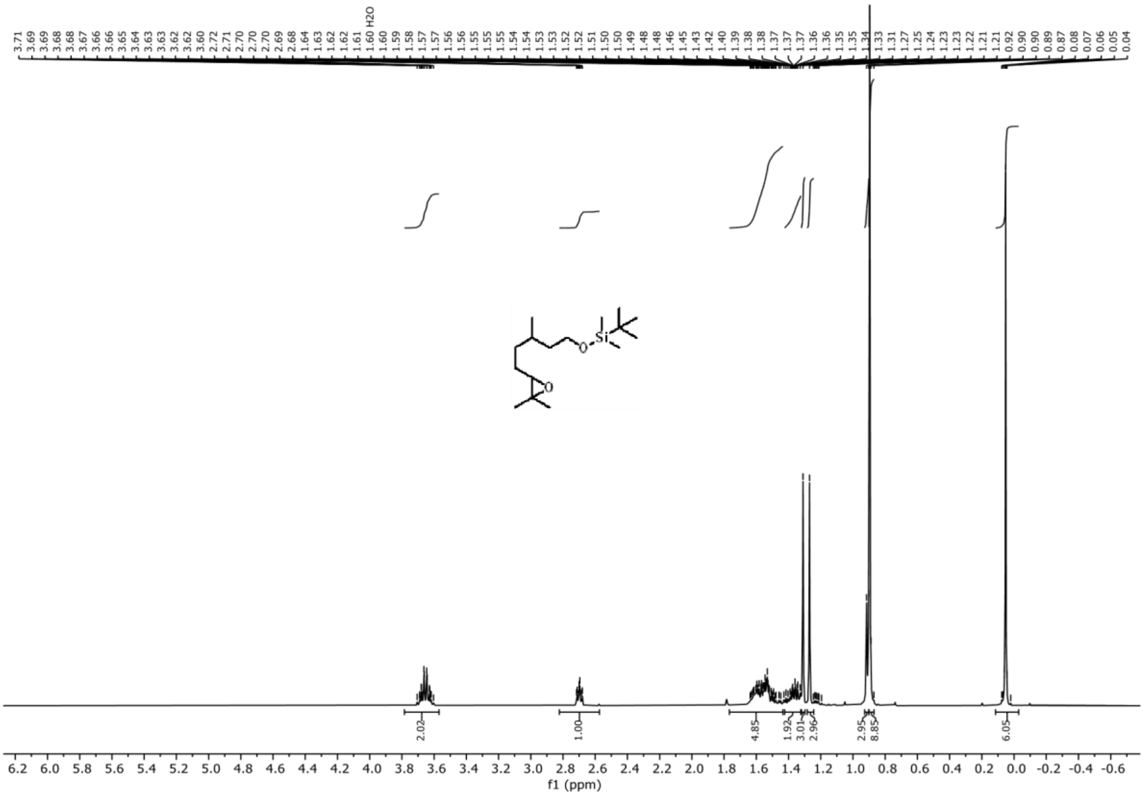


Figure S5: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) for silyl-protected citronellol oxide (**CO**).

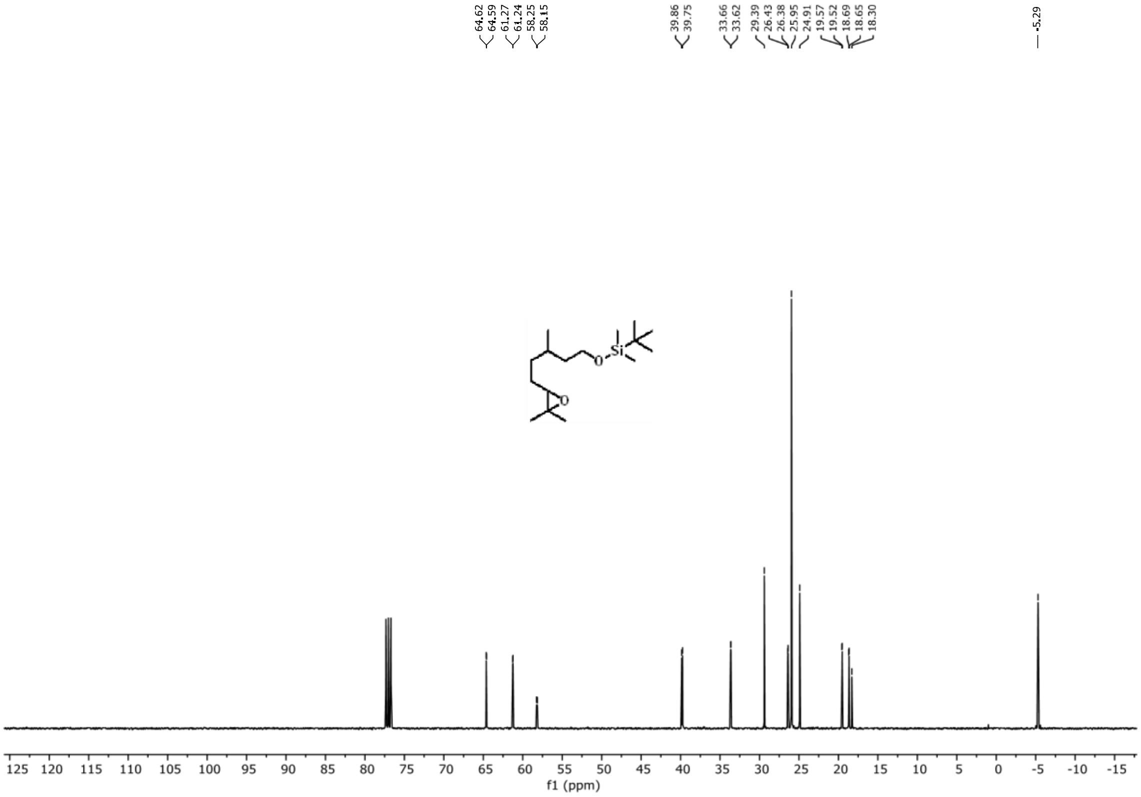


Figure S6: ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) for silyl-protected citronellol oxide (**CO**).

Thiol-functionalized polymer PLC^s

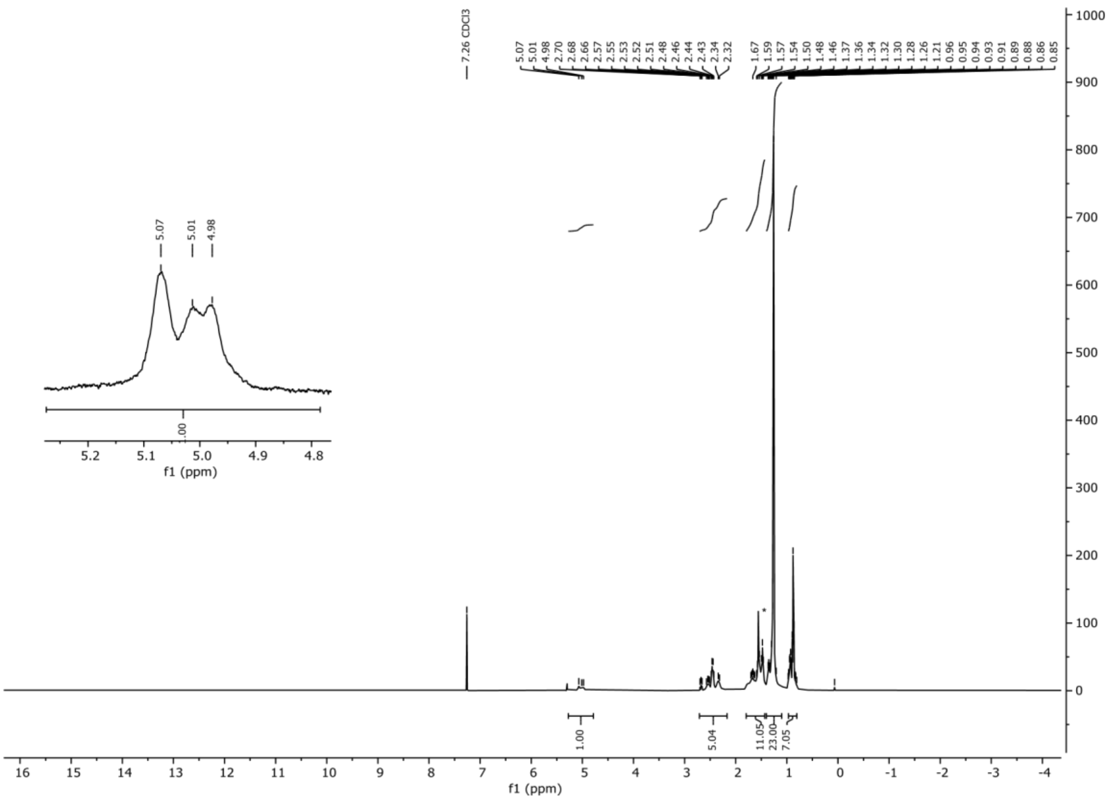


Figure S7: ^{1}H NMR spectrum (CDCl$_3$, 400 MHz) for **PLC*^{s}***.

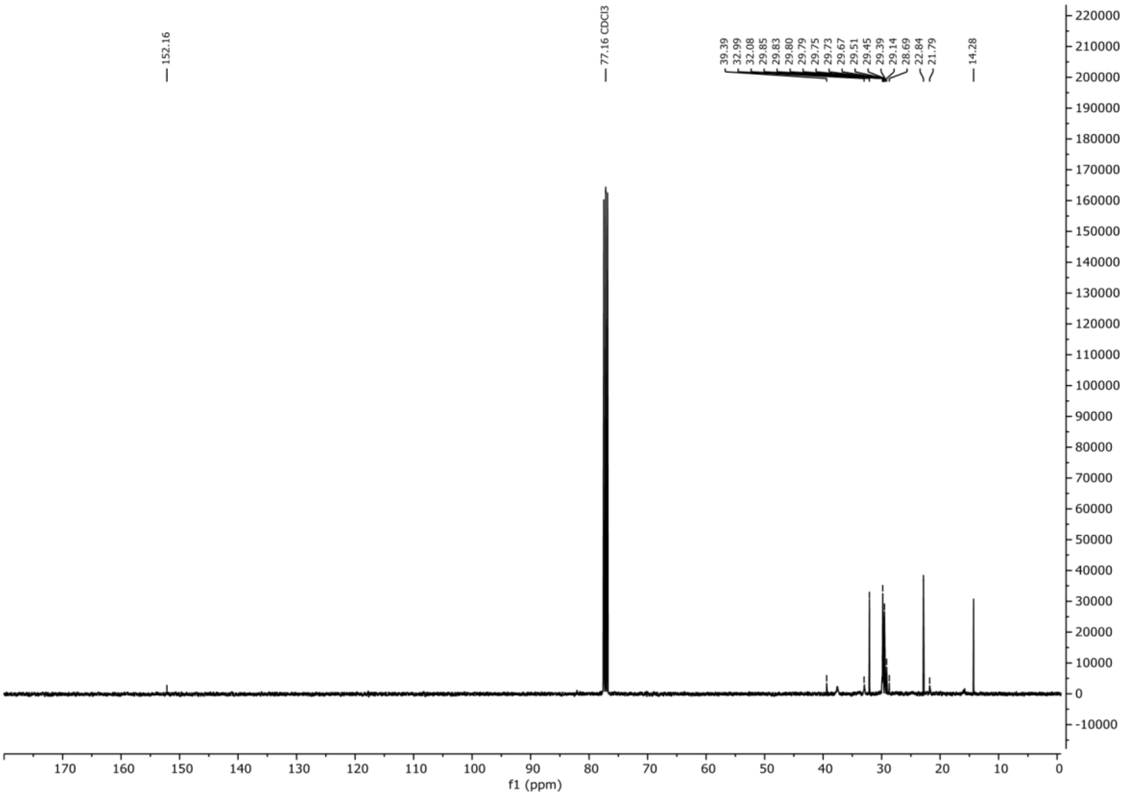


Figure S8: ^{13}C NMR spectrum (CDCl$_3$, 100 MHz) for **PLC*^{s}***.

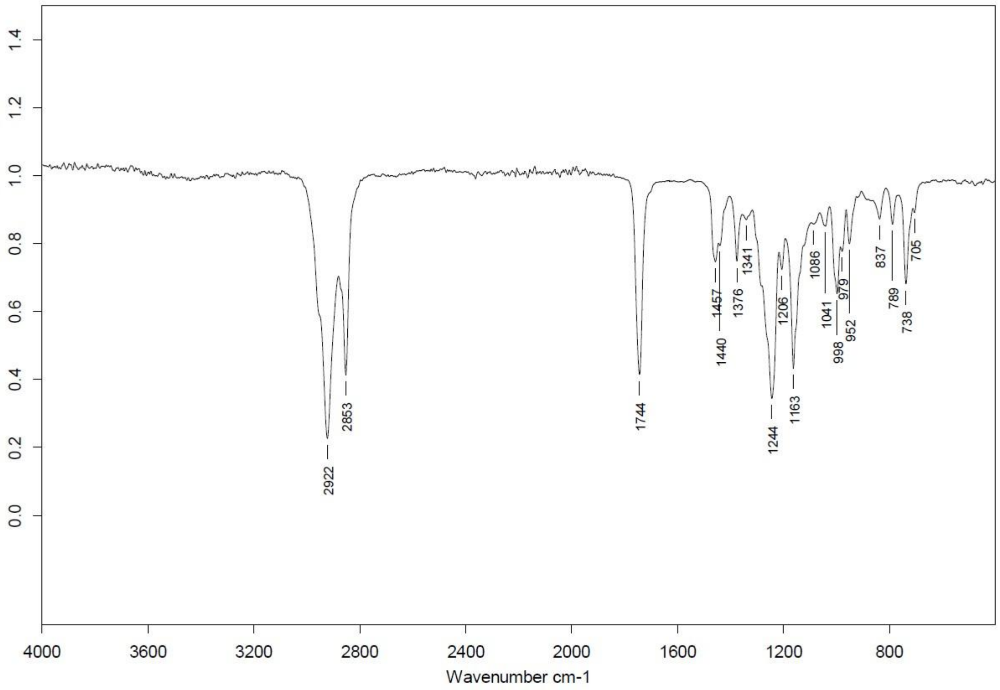
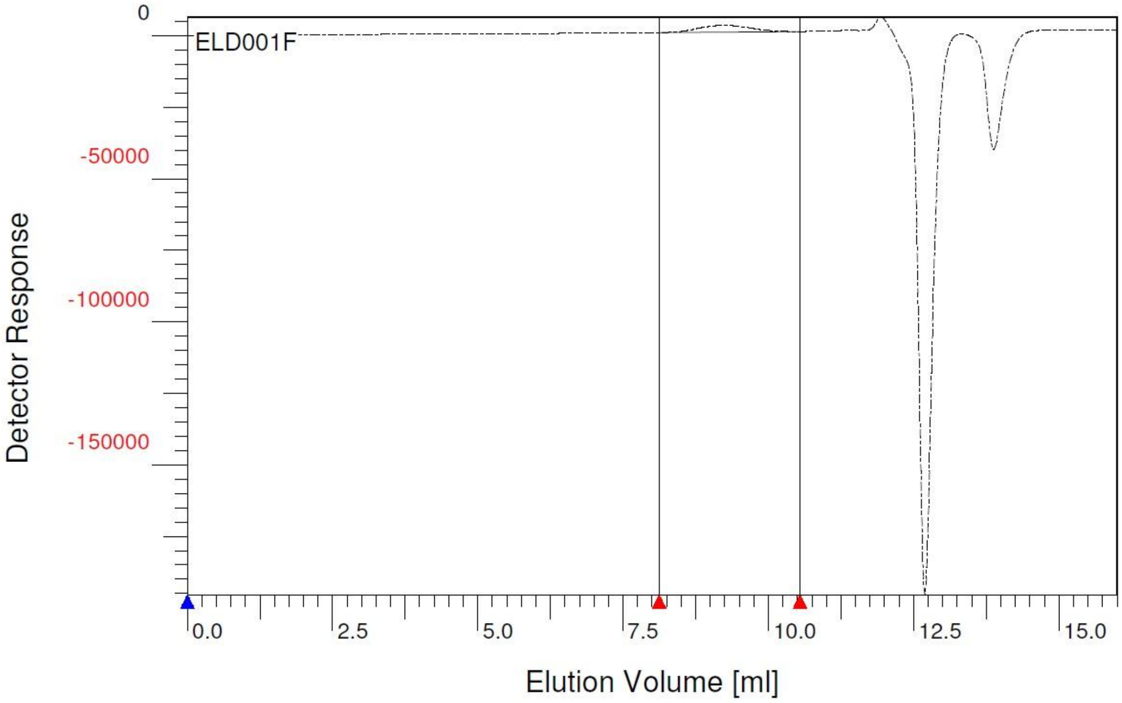


Figure S9: IR (neat) spectrum for **PLC**^{s}.



Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mp (g/mol)	Đ
1.3201e4	1.7425e4	2.2370e4	1.5711e4	1.3200

Figure S10: GPC analysis of **PLC^{s}**.

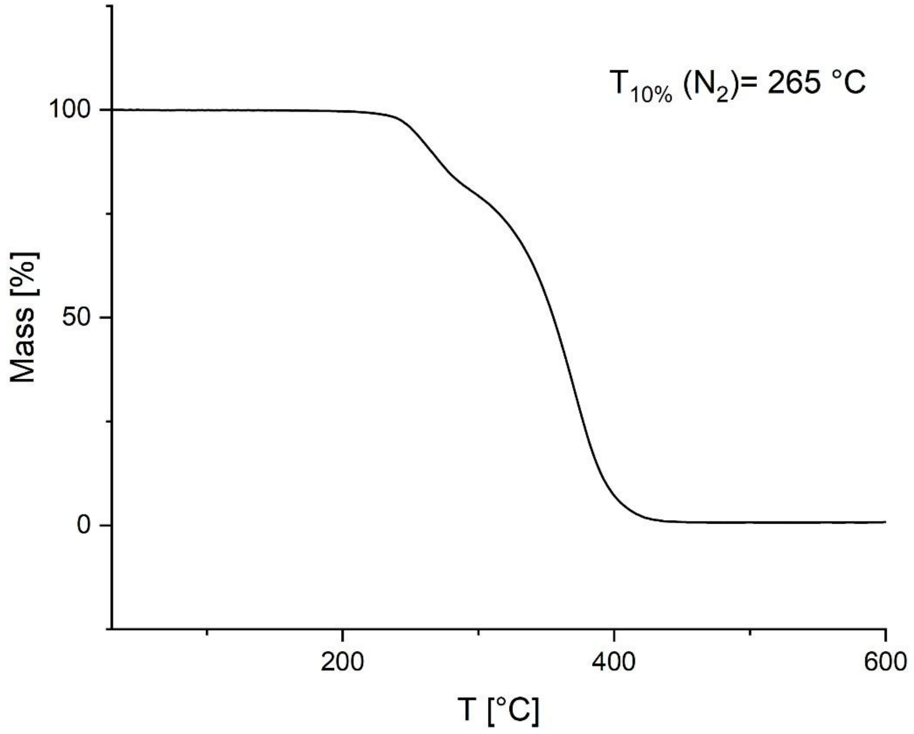
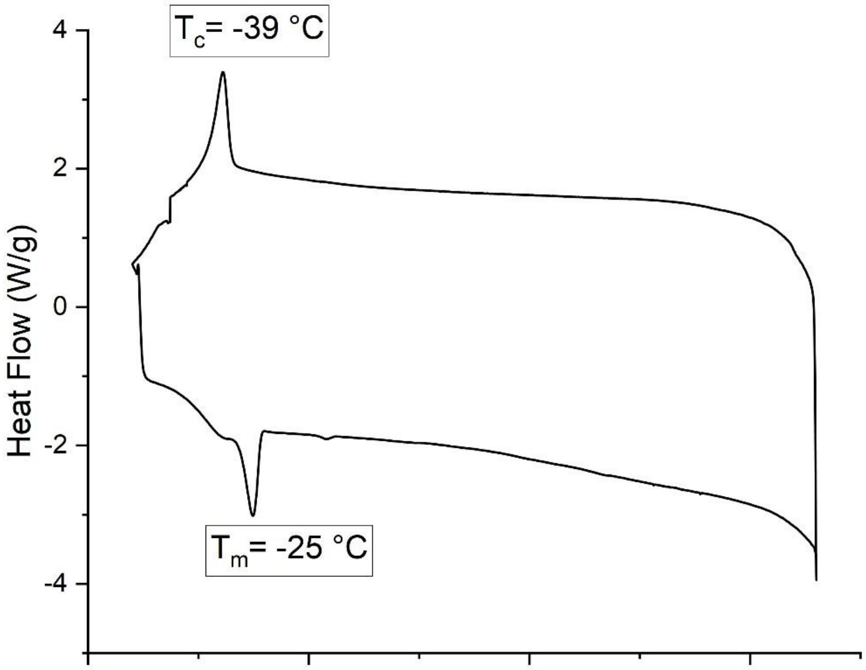


Figure S11: TGA analysis of **PLC*ˢ***.



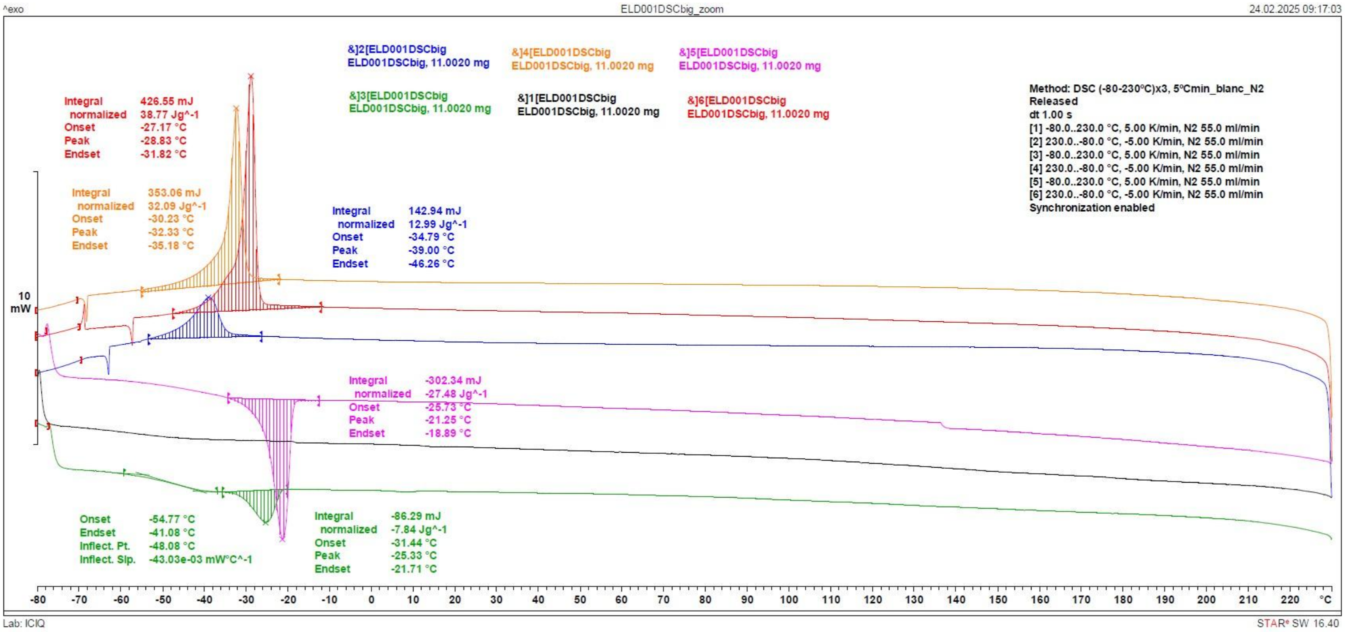
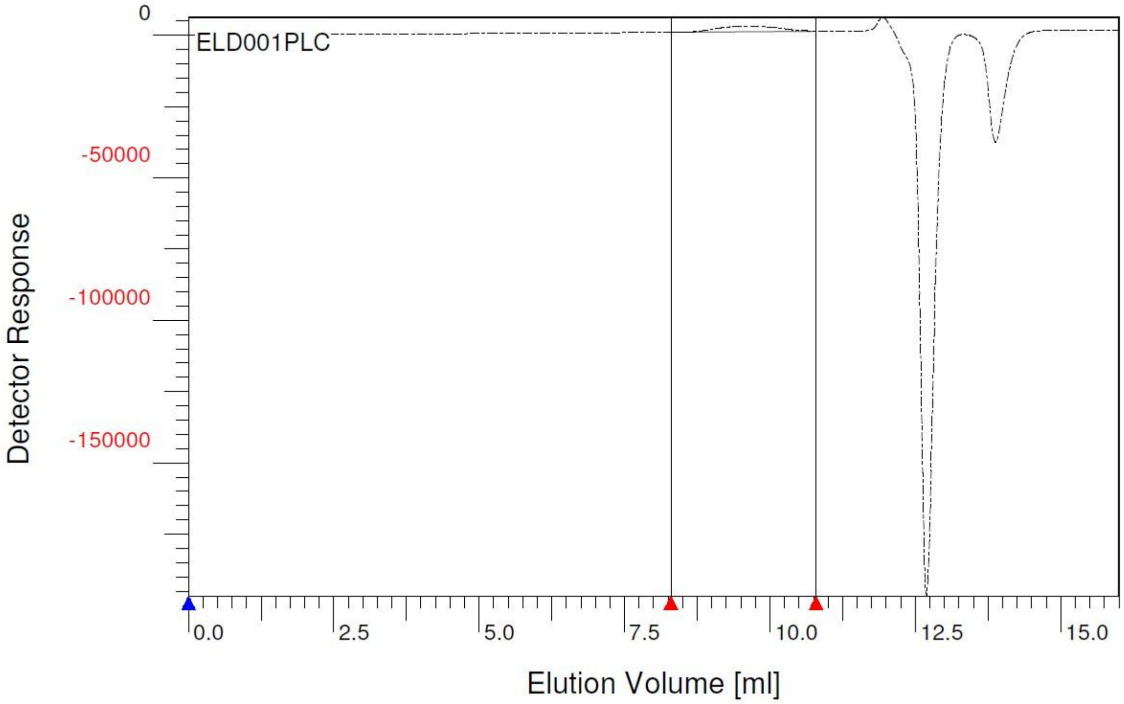


Figure S12: DSC analysis of **PLC**^{s}. Below the full data set.

Reference data for pristine PLC:



Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mp (g/mol)	Đ

7.7810e3	1.0712e4	1.4514e4	9.4807e3	1.3768

Figure S13: GPC data for **PLC**.

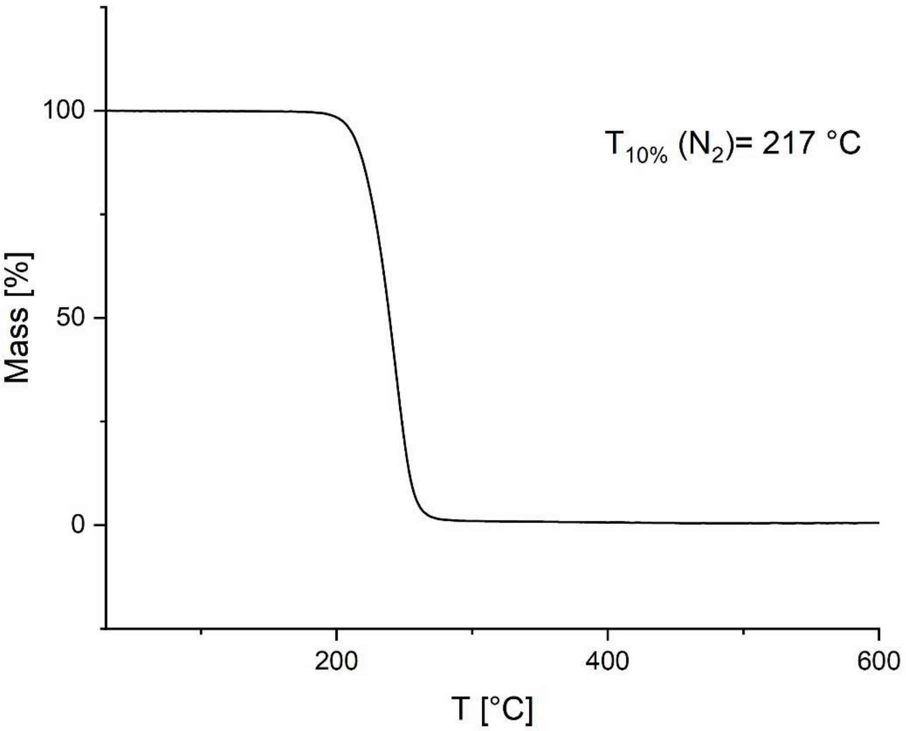


Figure S14: TGA analysis of **PLC**.

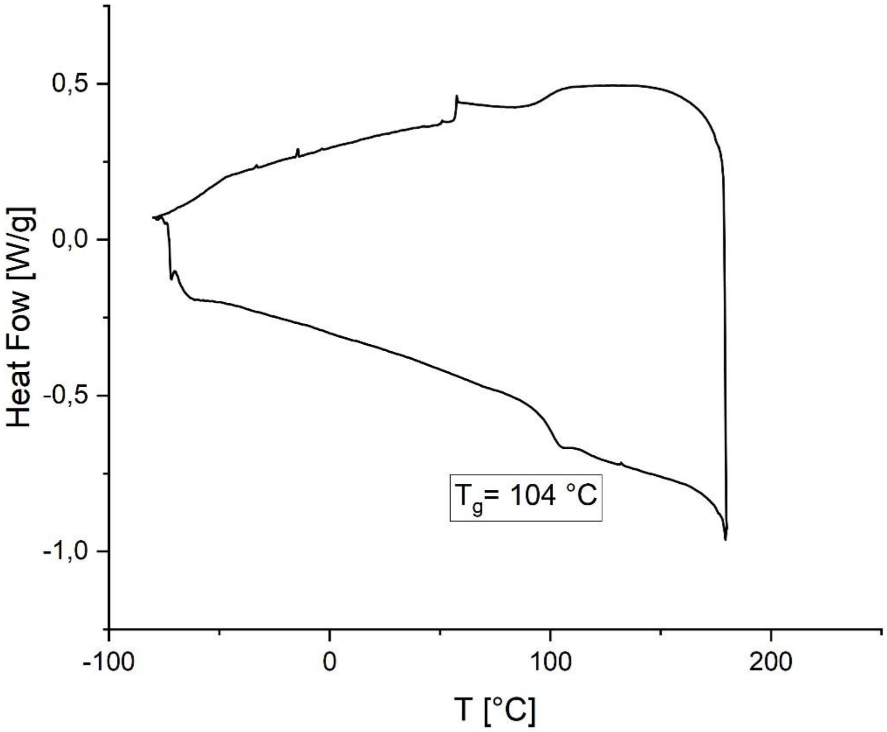


Figure S15: DSC analysis of **PLC**: The T_g mentioned here refers to the inflection point taken between the on- and end-set temperatures of the glass transition.

Thiol-functionalized polymer PLMC^s

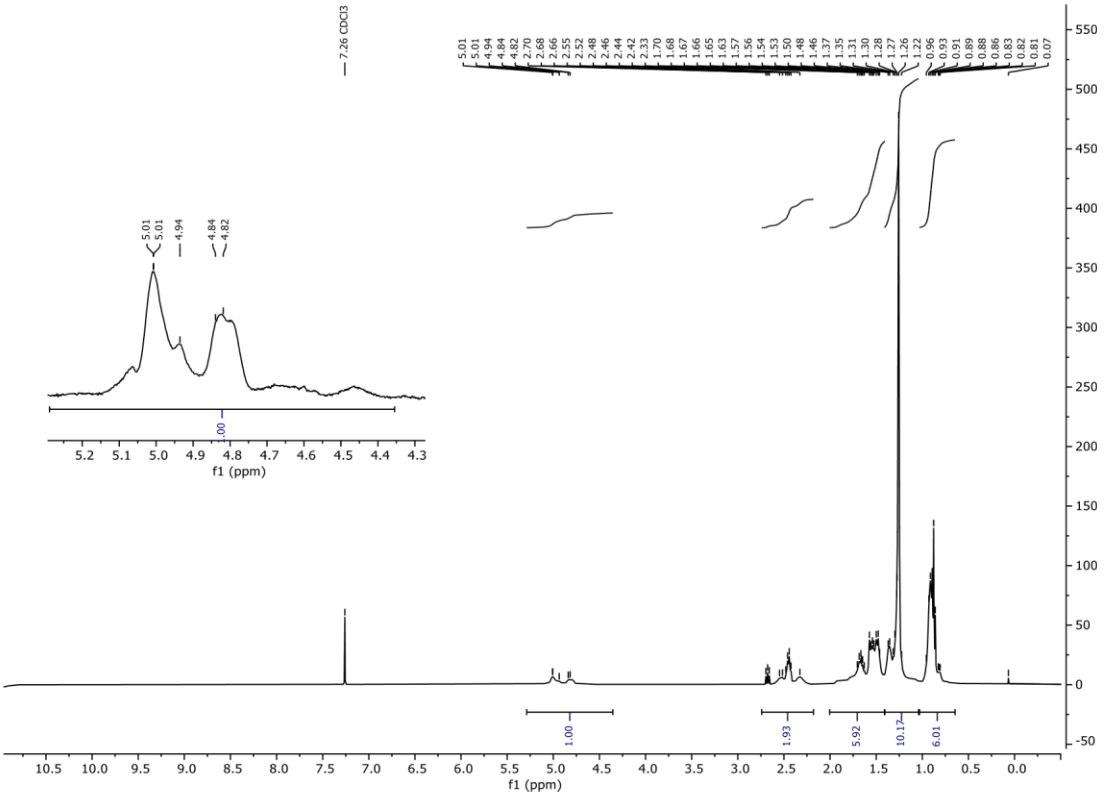


Figure S16: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) for **PLMC*s***.

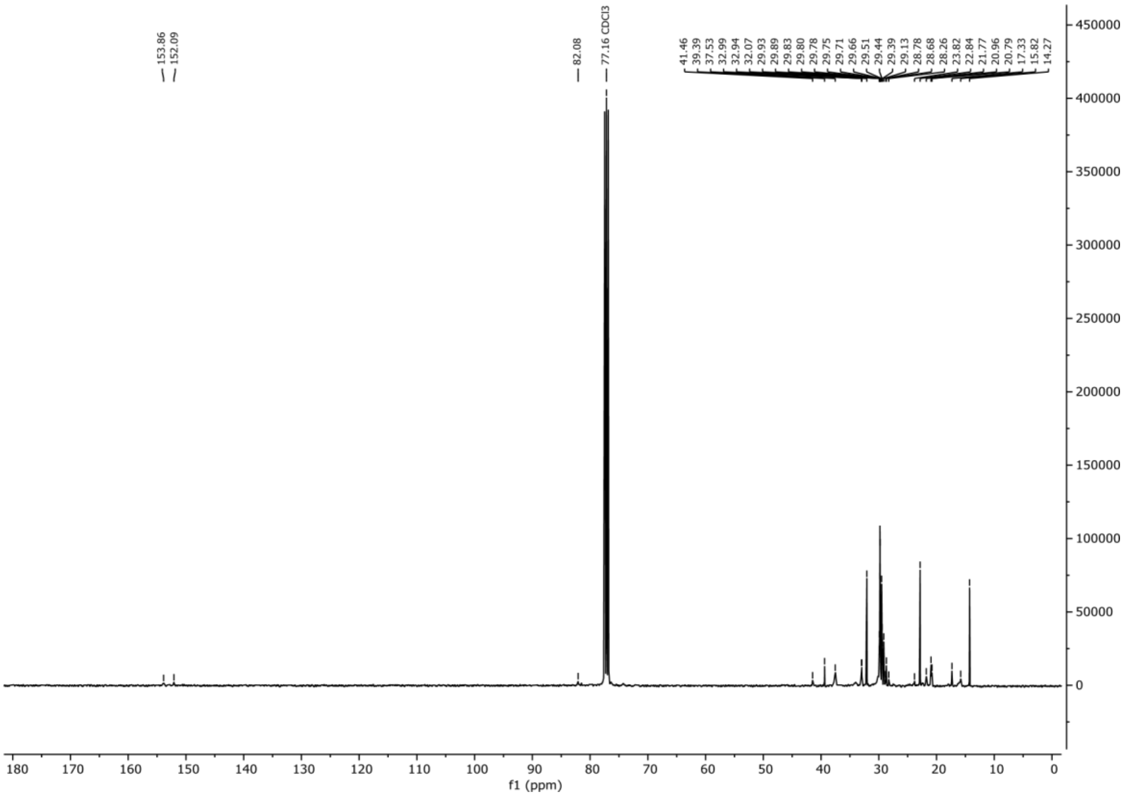


Figure S17: ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) for **PLMC*ˢ***.

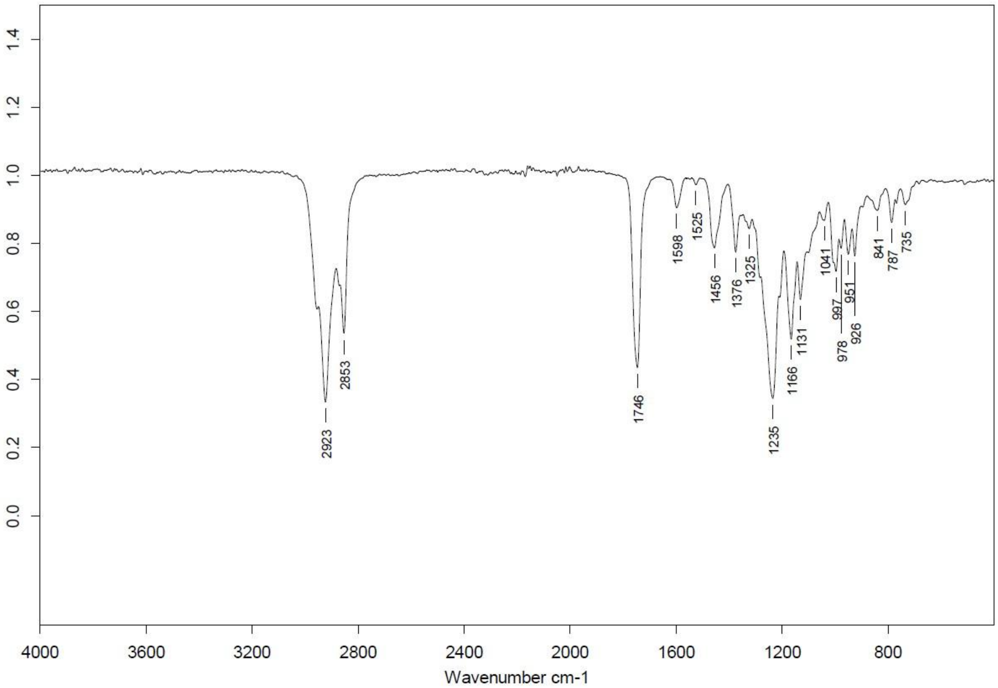
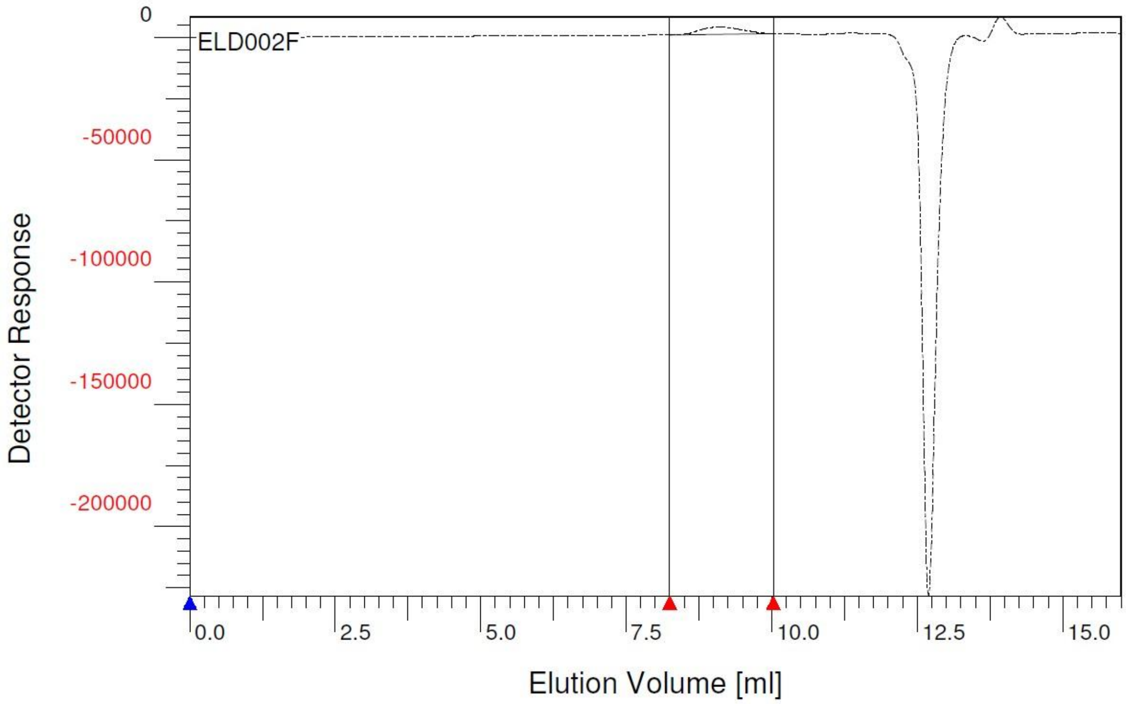


Figure S18: IR (neat) spectrum for **PLMC*ˢ***.



Mn Mw Mz Mp

Đ

(g/mol)	(g/mol)	(g/mol)	(g/mol)	
1.6230e4	1.9630e4	2.3237e4	1.9913e4	1.2095

Figure S19: GPC analysis for **PLMC^s**.

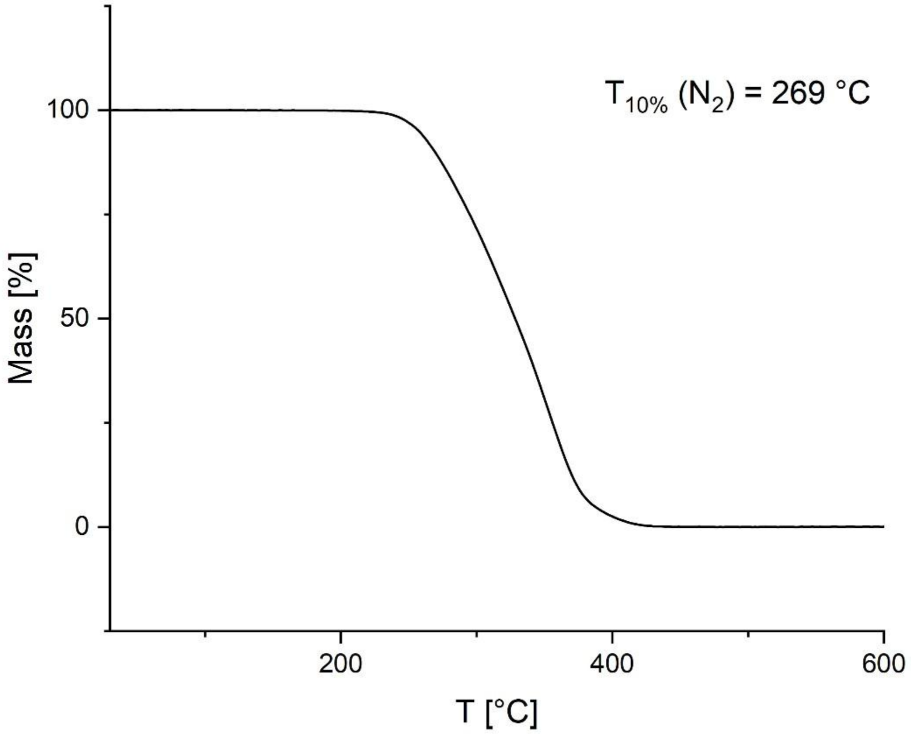
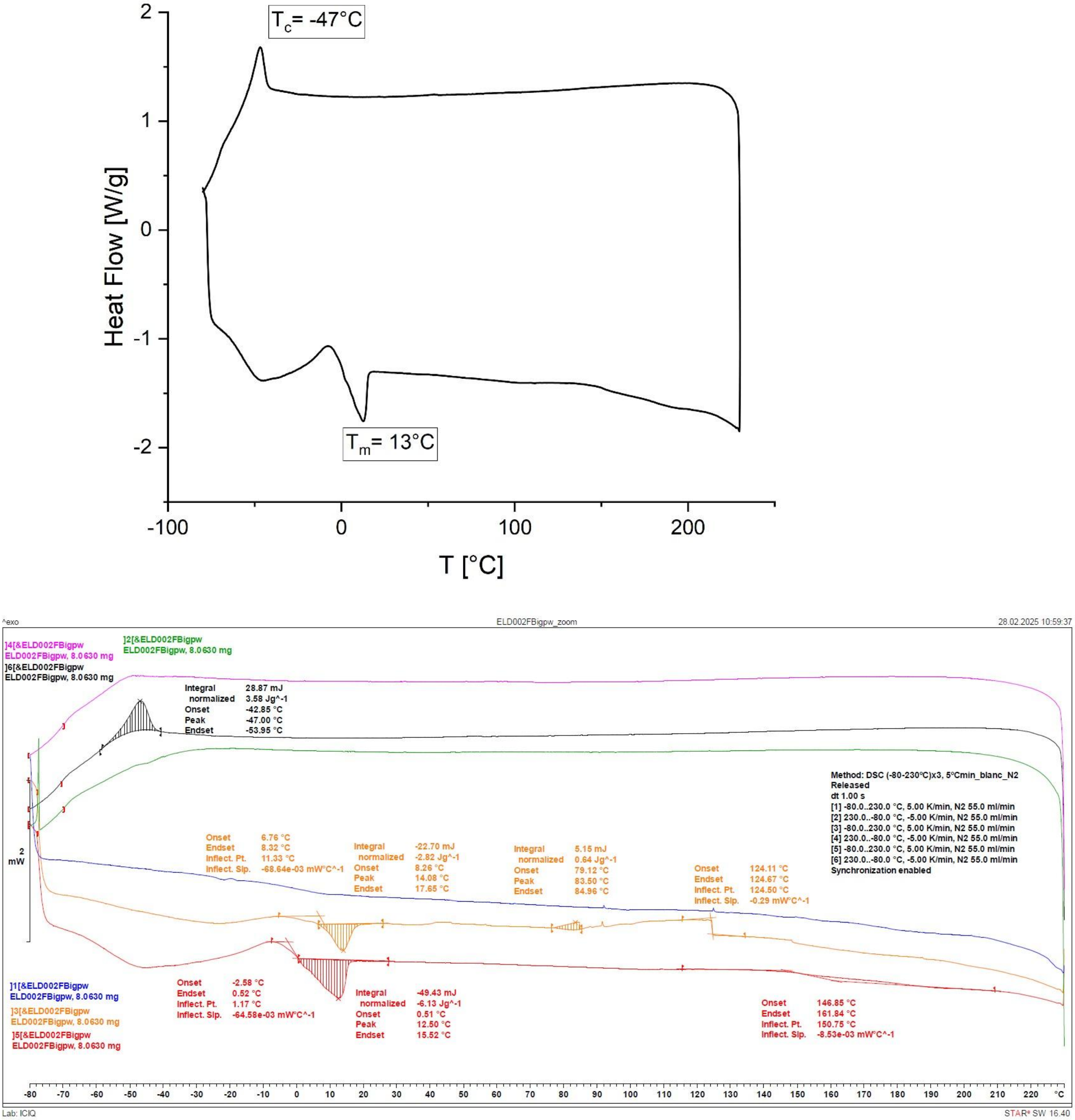


Figure S20: TGA analysis for **PLMC^s**.



Method: DSC (-80-230°C)x3, 5°Cmin_blanc_N2
Released
dt 1.00 s
[1] -80.0..230.0 °C, 5.00 K/min, N2 55.0 ml/min
[2] 230.0..-80.0 °C, -5.00 K/min, N2 55.0 ml/min
[3] -80.0..230.0 °C, 5.00 K/min, N2 55.0 ml/min
[4] 230.0..-80.0 °C, -5.00 K/min, N2 55.0 ml/min
[5] -80.0..230.0 °C, 5.00 K/min, N2 55.0 ml/min
[6] 230.0..-80.0 °C, -5.00 K/min, N2 55.0 ml/min
Synchronization enabled

Figure S21: DSC analysis for **PLMC**^{s} (note: data represent the 3rd heating/cooling). Below, the full DSC data.

PLMC polymer P1 – entry 13, Table 1

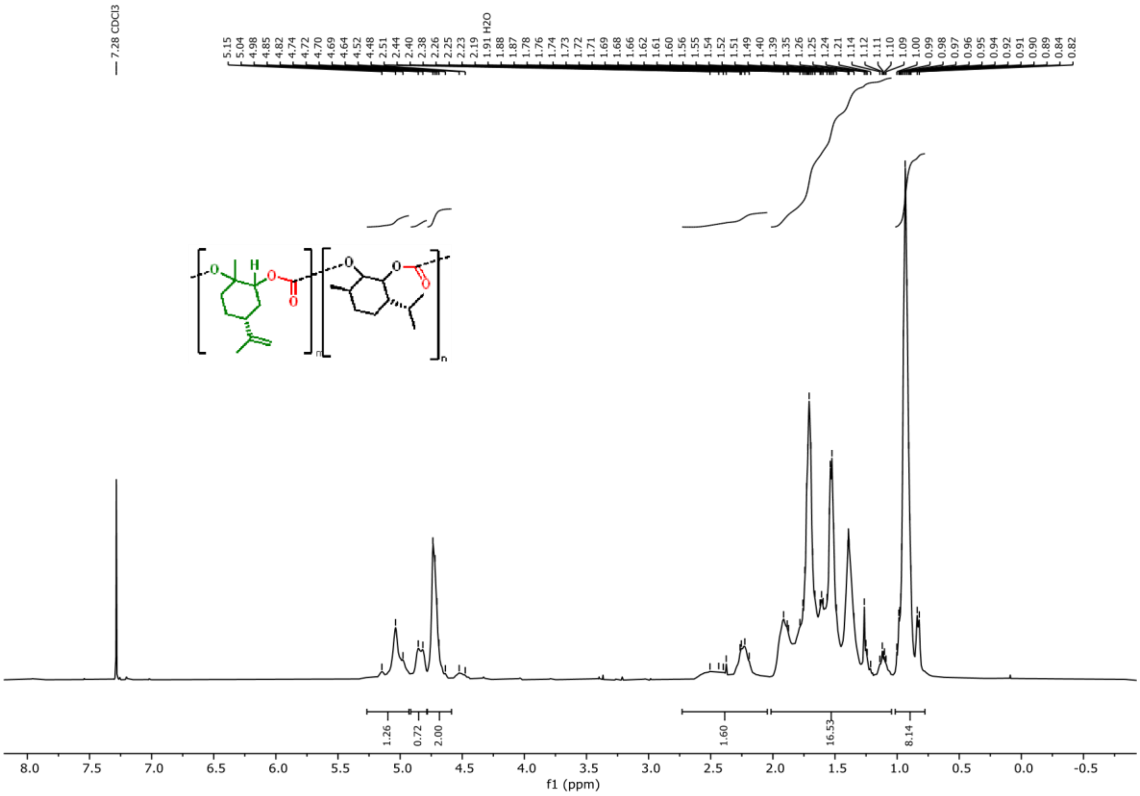


Figure S22A: ^{1}H NMR spectrum (CDCl$_3$, 400 MHz) for **PLMC** from entry 13, Table 1.

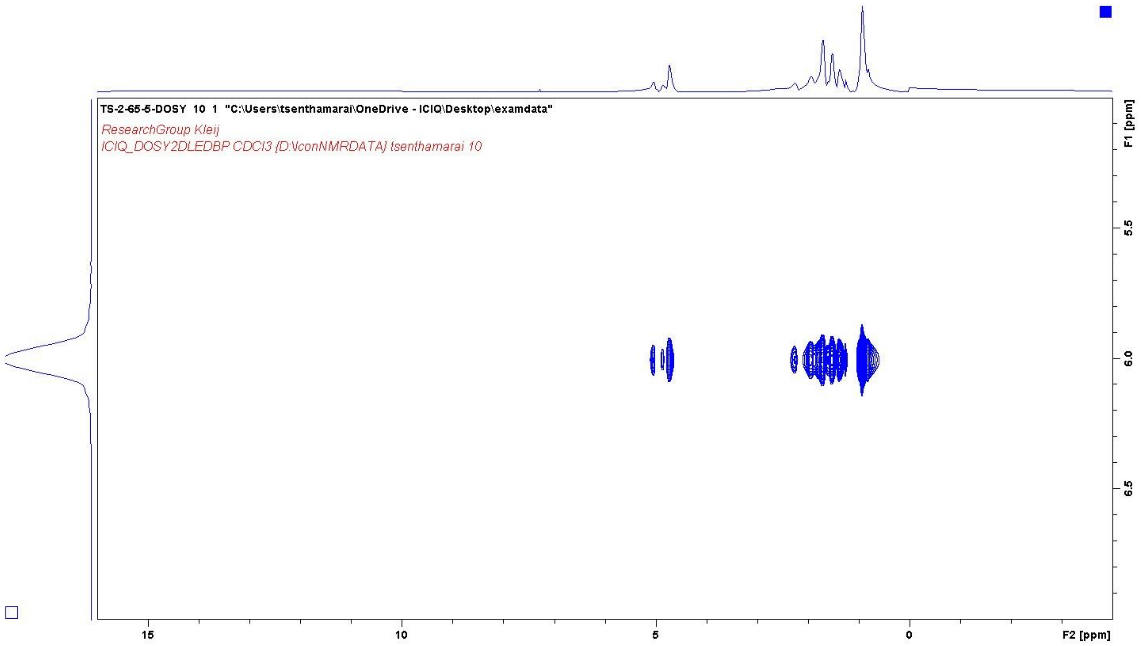

TS-2-65-5-DOSY 10 1 "C:\Users\tsenthamarai\OneDrive - ICIQ\Desktop\examdata"
ResearchGroup Kleij
ICIQ_DOSY2DLEDBP CDCl3 {D:\IconNMRDATA} tsenthamarai 10

Figure S22B: DOSY NMR spectrum (CDCl$_3$, 400 MHz) for **PLMC** from entry 13, Table 1.

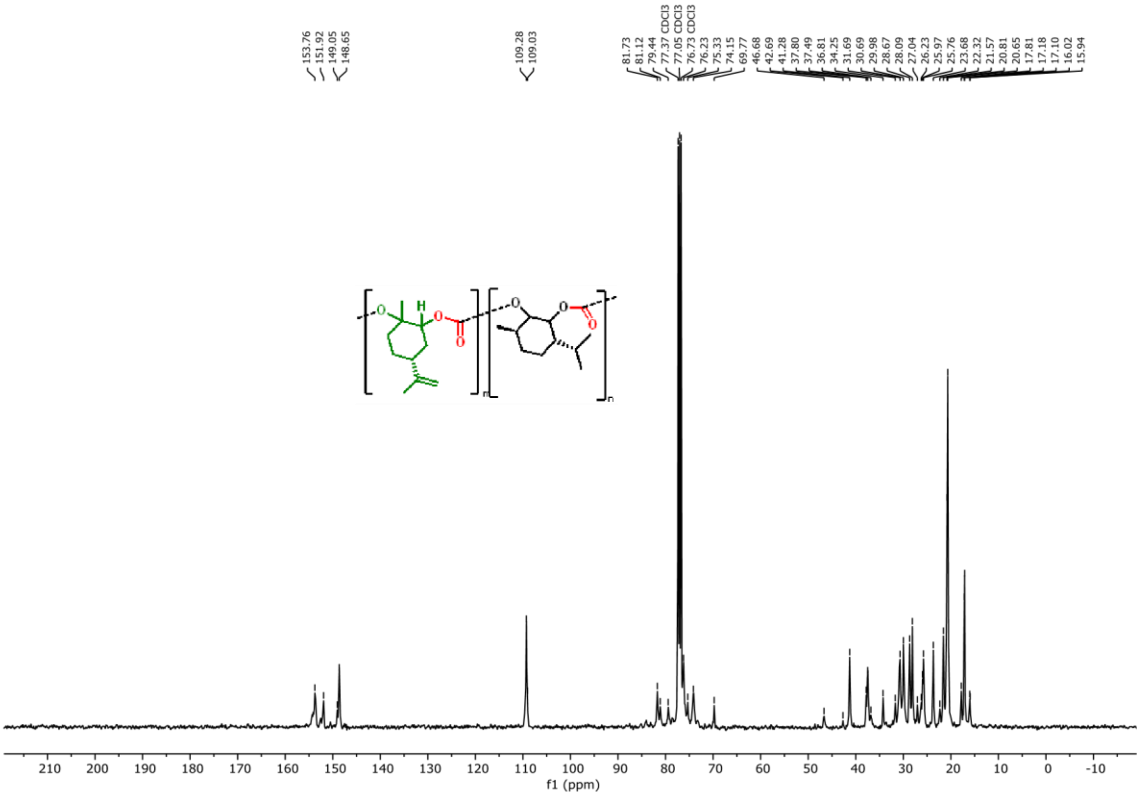


Figure S23: ^{13}C NMR spectrum (CDCl$_3$, 100 MHz) for **PLMC** from entry 13, Table 1.

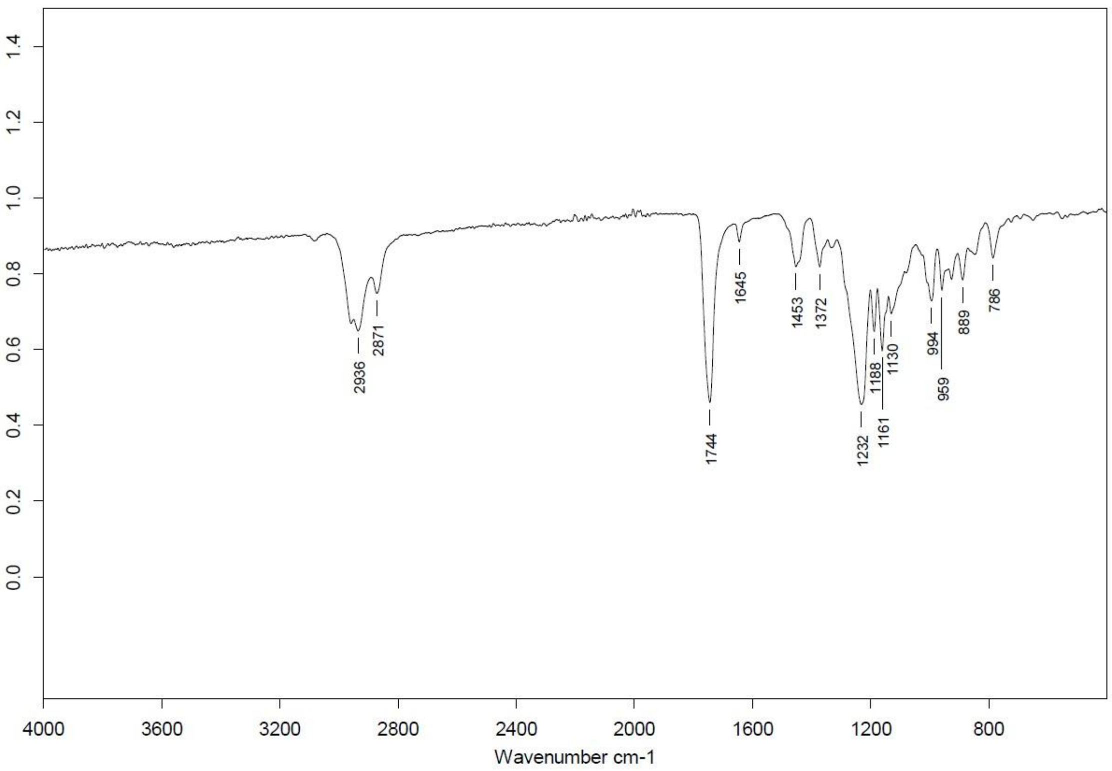
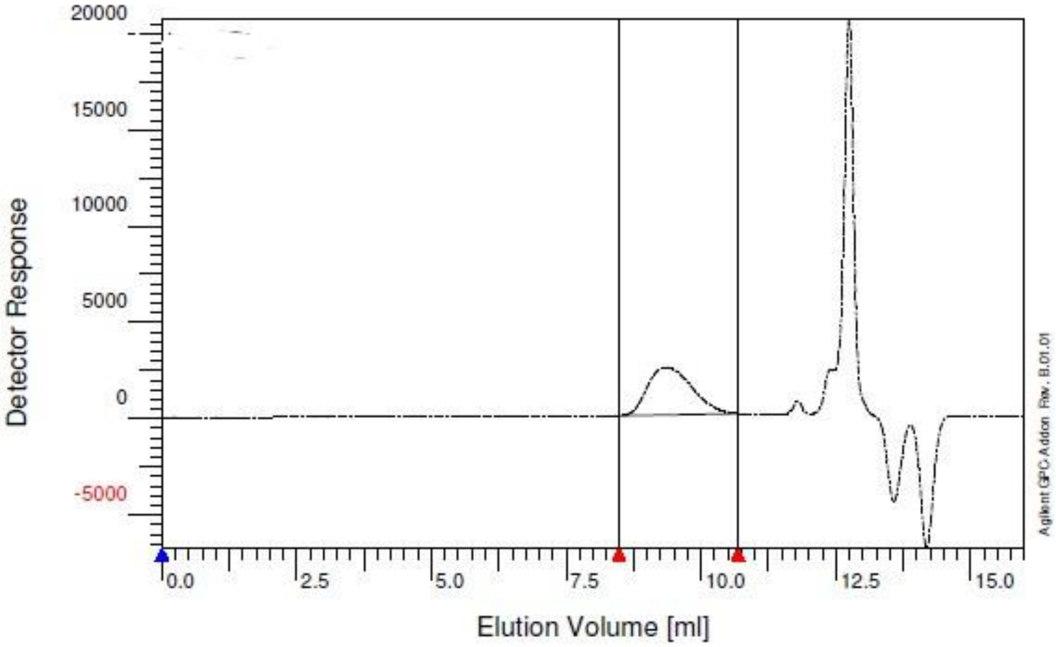


Figure S24: IR (neat) spectrum for **PLMC** from entry 13, Table 1.



Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mp (g/mol)	Đ
1.0931e4	1.2967e4	1.5973e4	1.3476e4	1.2970

Figure S25: GPC analysis for for **PLMC** from entry 13, Table 1

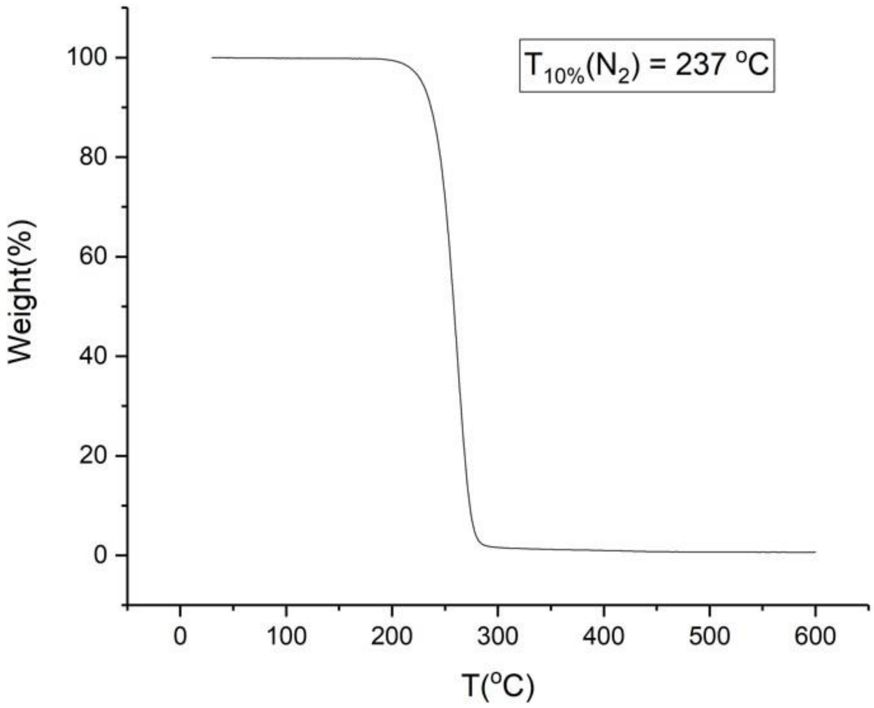
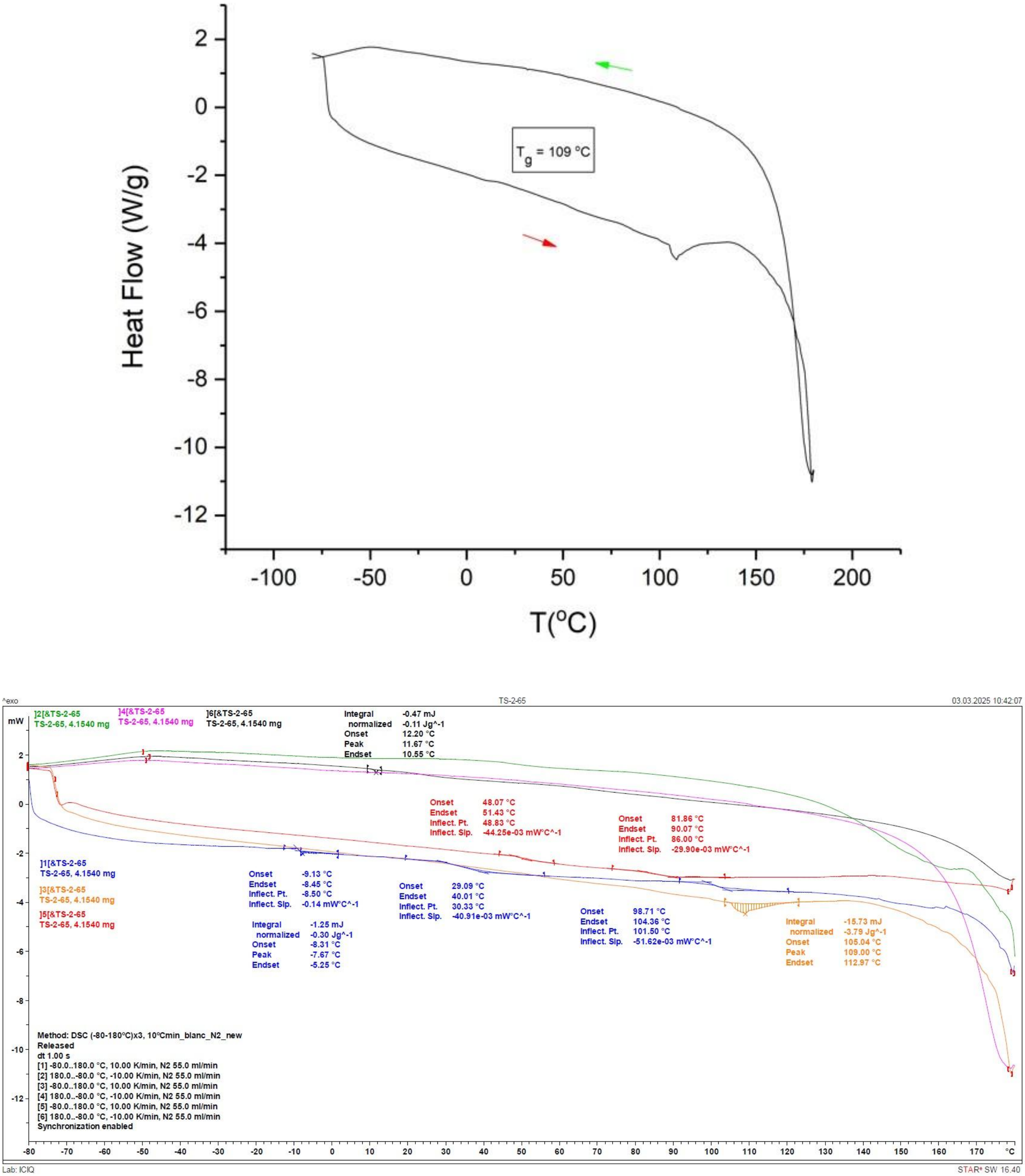


Figure S26: TGA analysis for **PLMC** from entry 13, Table 1.



Method: DSC (-80-180°C)x3, 10°Cmin_blanc_N2_new
Released
dt 1.00 s
[1] -80.0..180.0 °C, 10.00 K/min, N2 55.0 ml/min
[2] 180.0..-80.0 °C, -10.00 K/min, N2 55.0 ml/min
[3] -80.0..180.0 °C, 10.00 K/min, N2 55.0 ml/min
[4] 180.0..-80.0 °C, -10.00 K/min, N2 55.0 ml/min
[5] -80.0..180.0 °C, 10.00 K/min, N2 55.0 ml/min
[6] 180.0..-80.0 °C, -10.00 K/min, N2 55.0 ml/min
Synchronization enabled

Figure S27: DSC analysis (second heating/cooling) for **PLMC** from entry 13, Table 1. Below, the full data set is shown. Please note that the thermal transition appears more like a *T*$_m$ rather a *T*$_g$ thus pointing at a semi-crystalline material.

PLMC polymer P2 – entry 14, Table 1

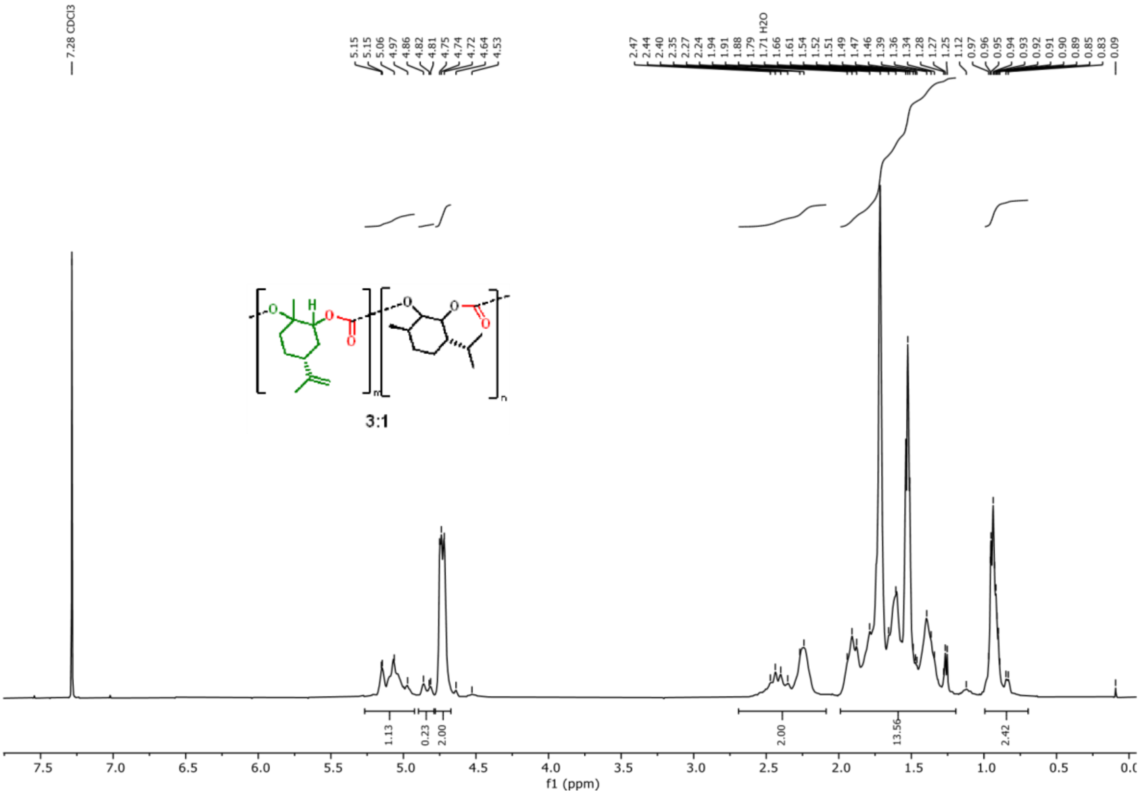


Figure S28: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) for **PLMC** from entry 14, Table 1.

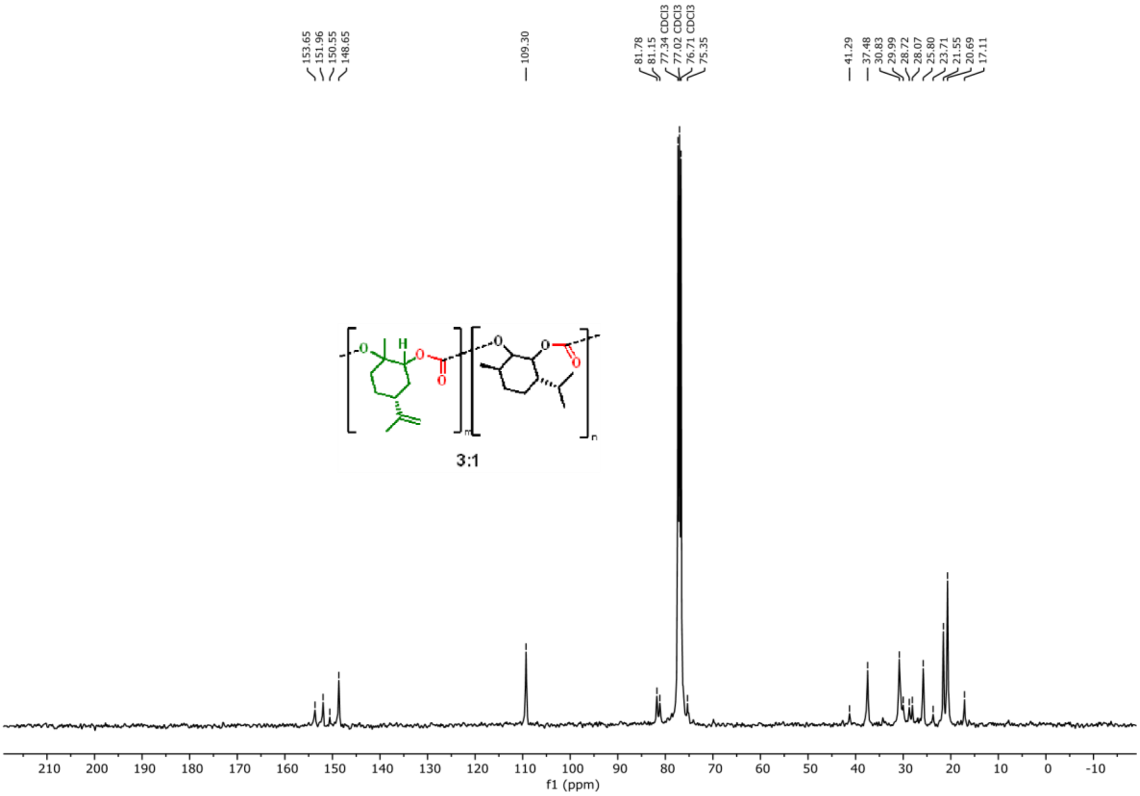


Figure S29: ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) for **PLMC** from entry 14, Table 1.

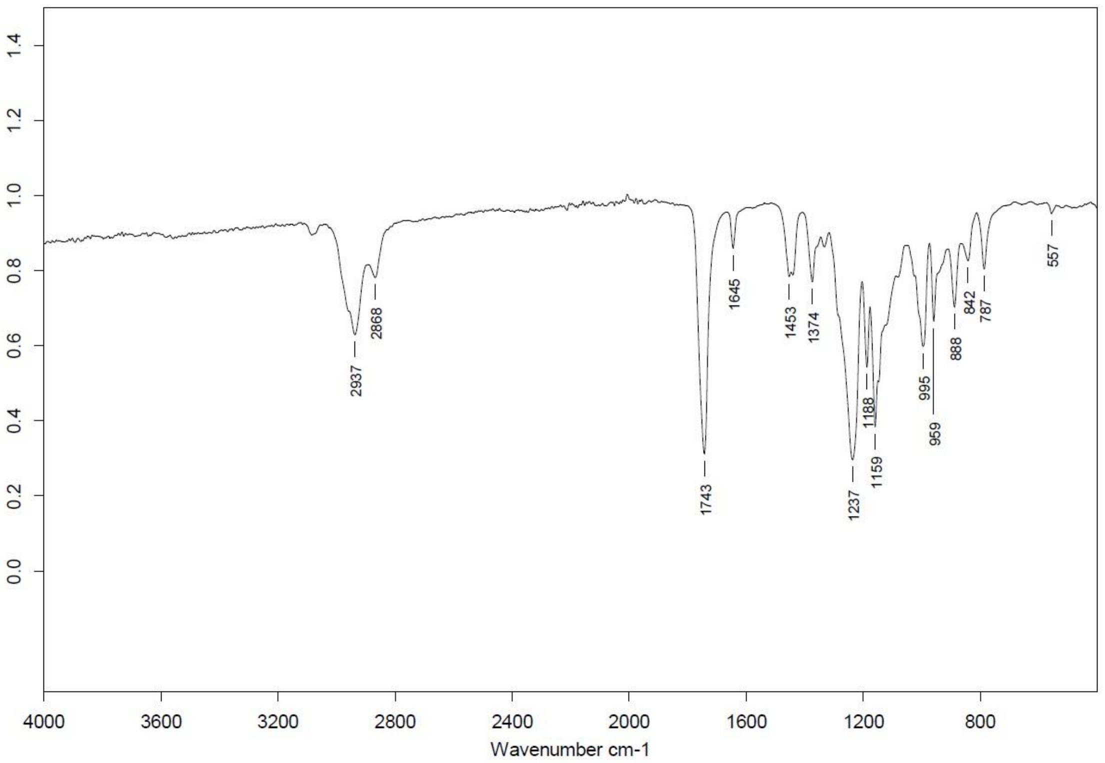
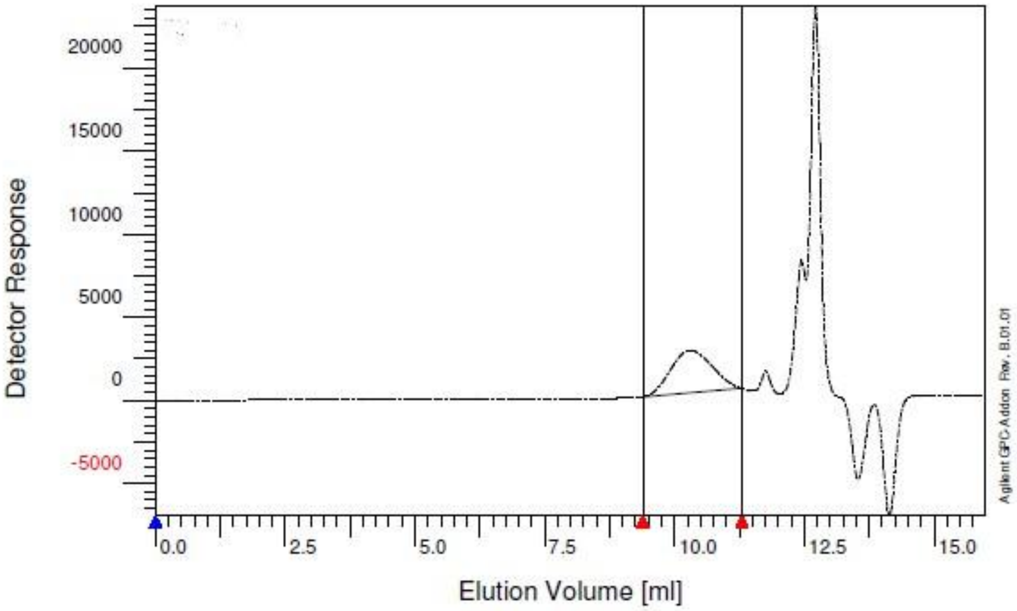


Figure S30: IR (neat) spectrum for **PLMC** from entry 14, Table 1.



Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mp (g/mol)	Đ
3.3642e3	4.0133e3	4.7496e3	3.8854e3	1.1965

Figure S31: GPC analysis for **PLMC** from entry 14, Table 1.

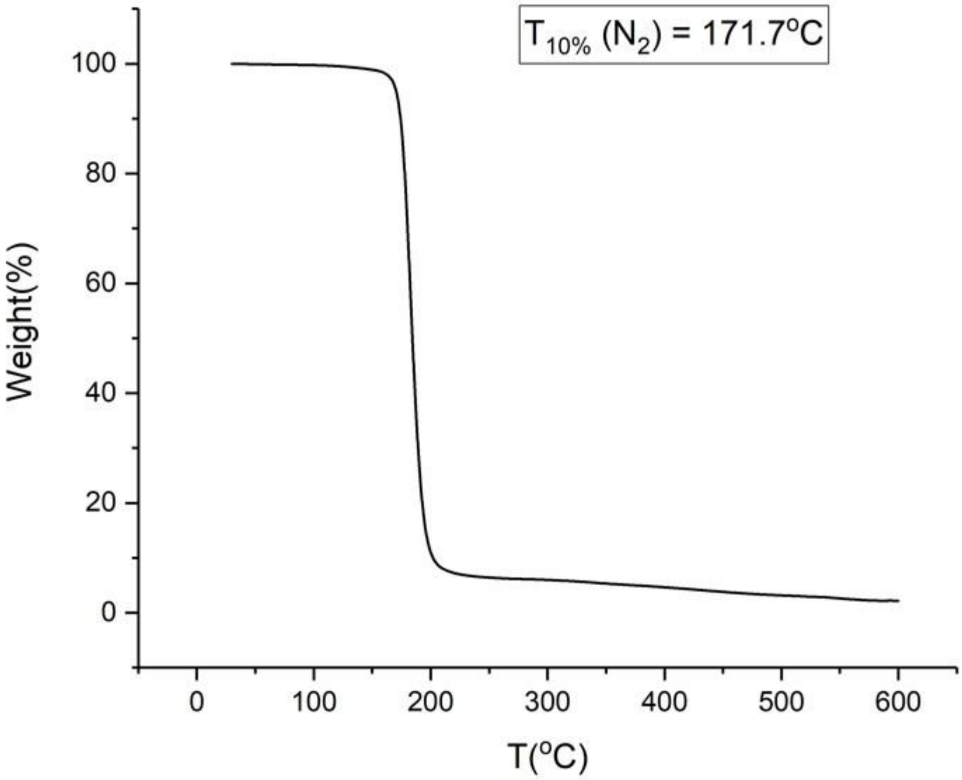
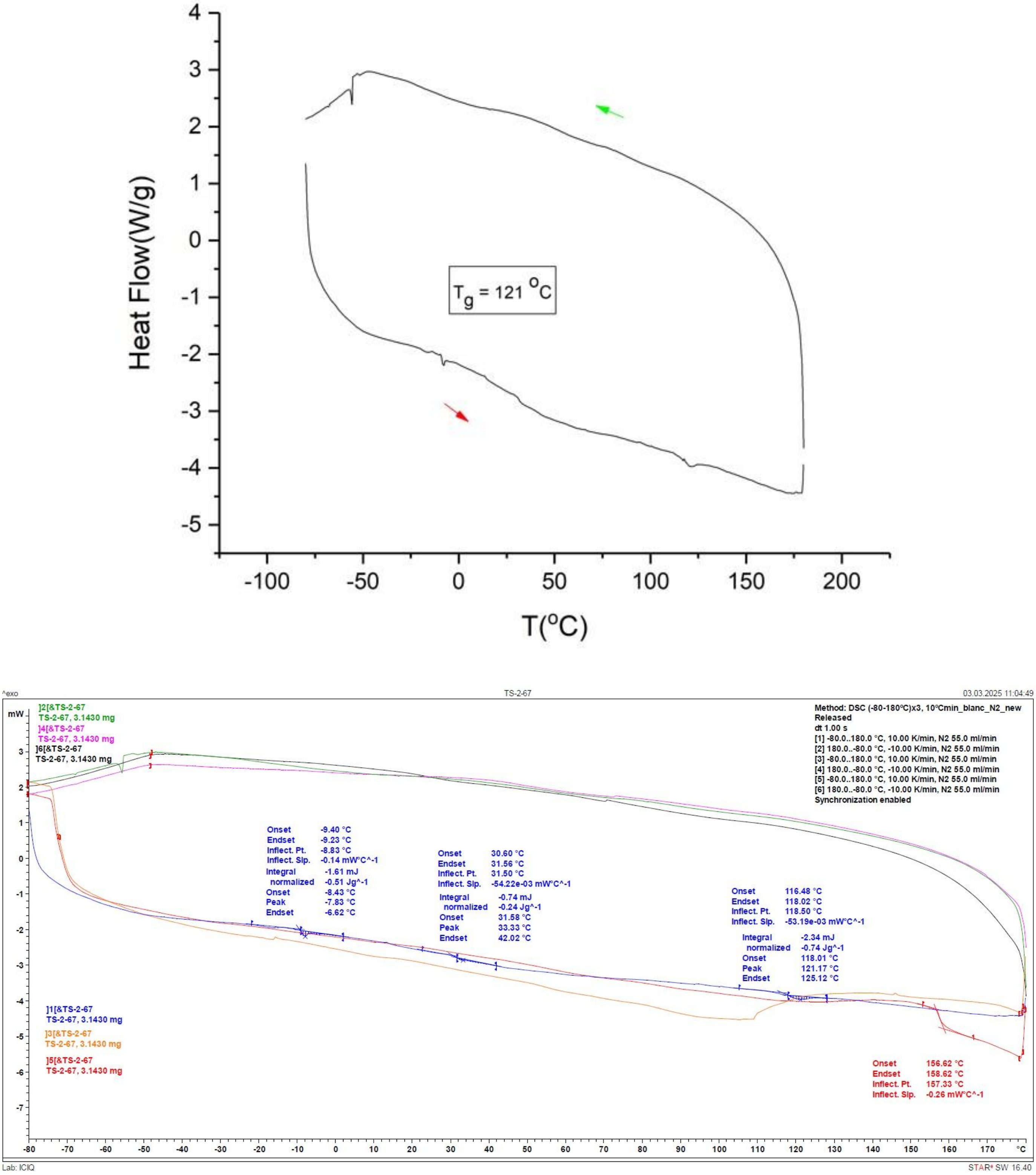


Figure S32: TGA analysis for **PLMC** from entry 14, Table 1.



Method: DSC (-80-180ºC)x3, 10ºCmin_blanc_N2_new
Released
dt 1.00 s
[1] -80.0..180.0 °C, 10.00 K/min, N2 55.0 ml/min
[2] 180.0..-80.0 °C, -10.00 K/min, N2 55.0 ml/min
[3] -80.0..180.0 °C, 10.00 K/min, N2 55.0 ml/min
[4] 180.0..-80.0 °C, -10.00 K/min, N2 55.0 ml/min
[5] -80.0..180.0 °C, 10.00 K/min, N2 55.0 ml/min
[6] 180.0..-80.0 °C, -10.00 K/min, N2 55.0 ml/min
Synchronization enabled

Figure S33: DSC analysis (second heating/cooling) for **PLMC** from entry 14, Table 1. Below, the full data set is shown. Please note that the thermal transition appears more like a T_m rather a T_g thus pointing at a semi-crystalline material.

PLMC polymer P3 – entry 15, Table 1

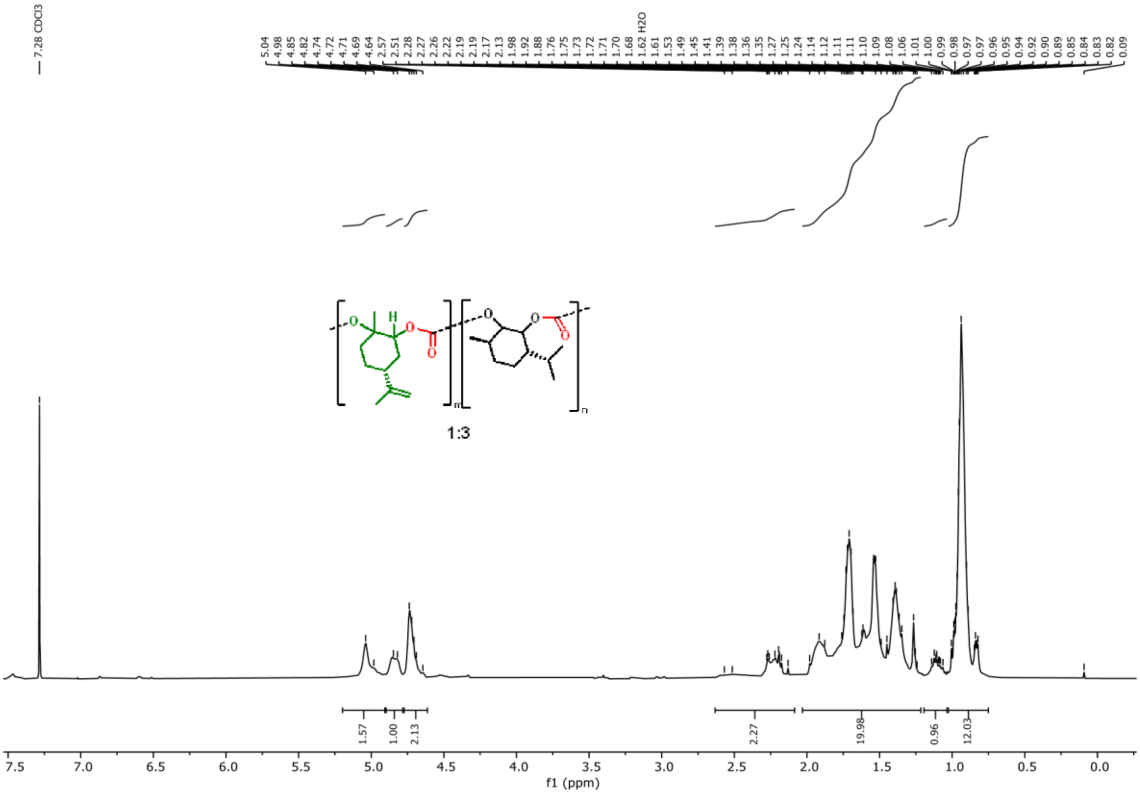


Figure S34: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) for **PLMC** from entry 15, Table 1.

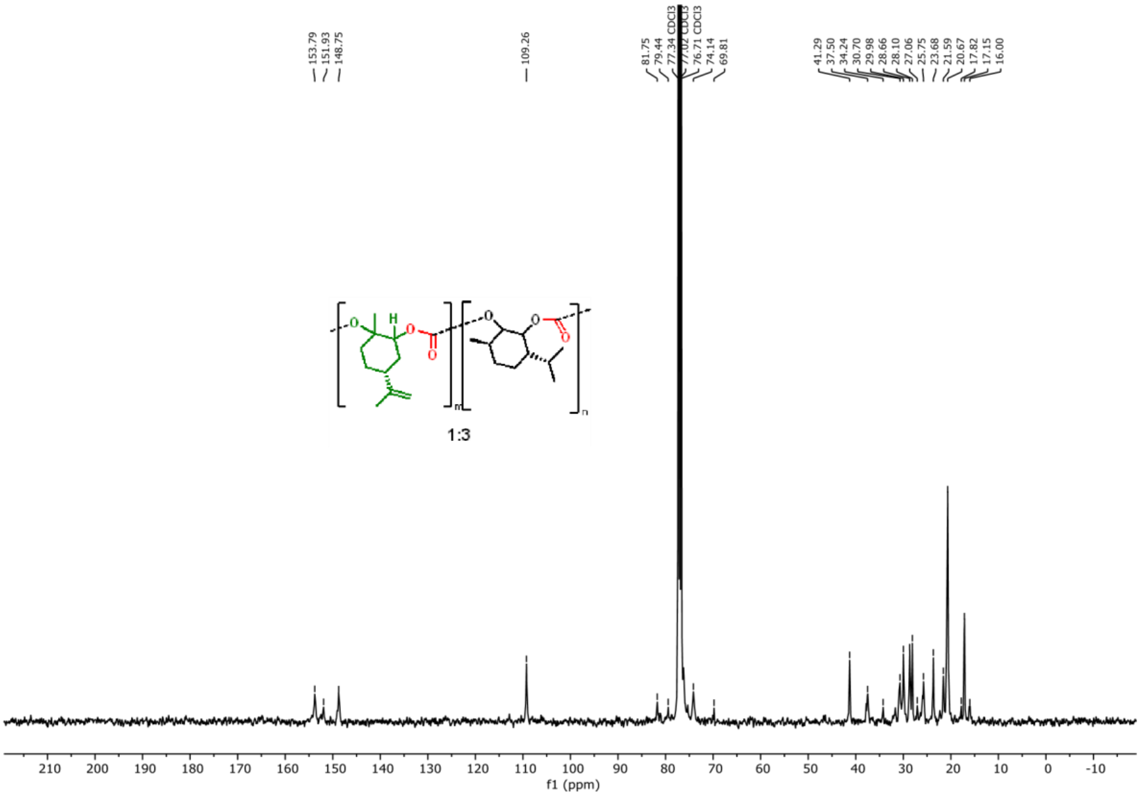


Figure S35: ^{13}C NMR spectrum (CDCl$_3$, 100 MHz) for **PLMC** from entry 15, Table 1.

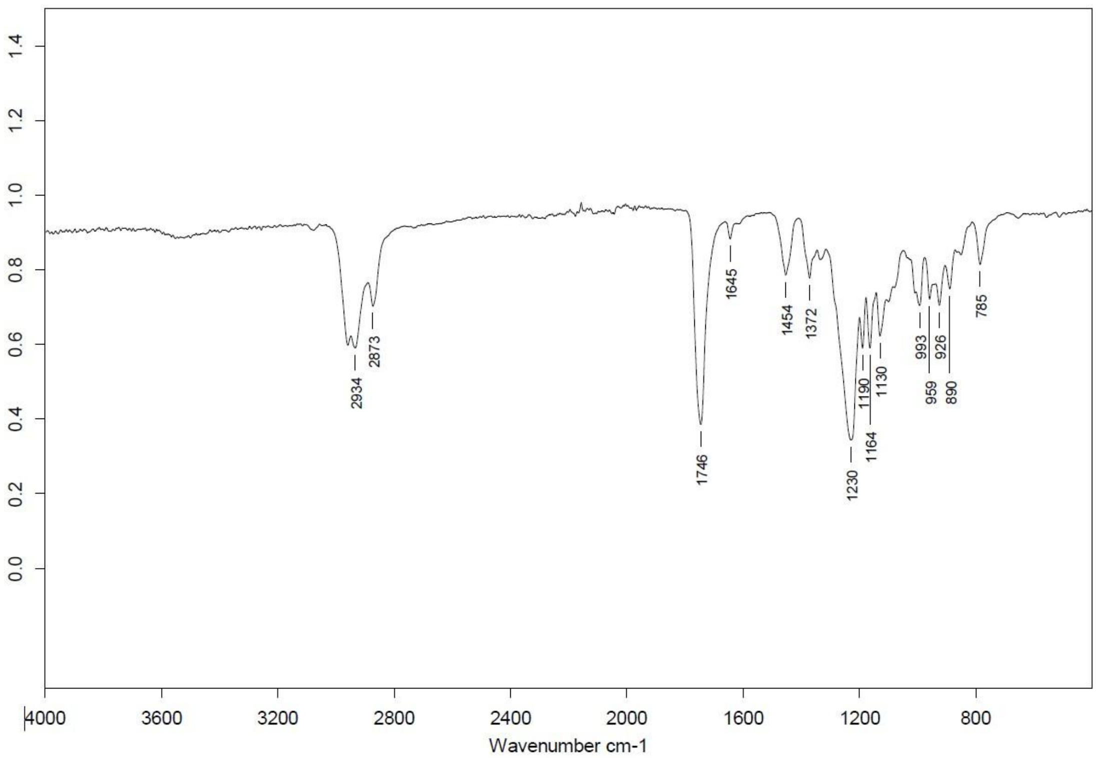
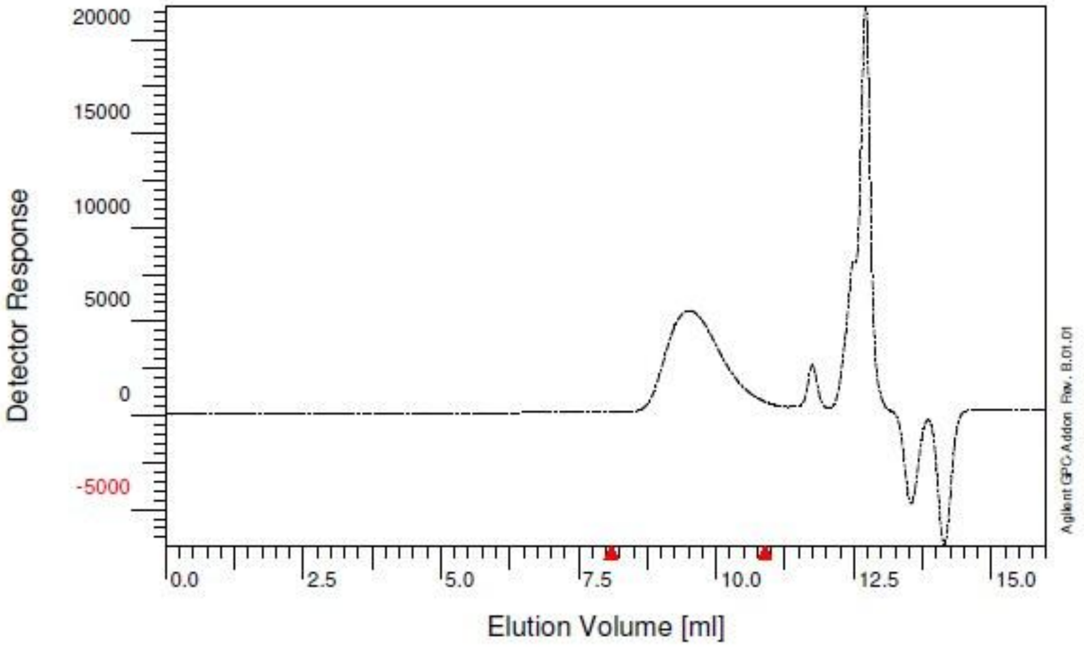


Figure S36: IR (neat) spectrum for **PLMC** from entry 15, Table 1.



Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mp (g/mol)	Đ
7.9278e3	1.0760e4	1.3915e4	1.0791e4	1.2172

Figure S37: GPC analysis for **PLMC** from entry 15, Table 1.

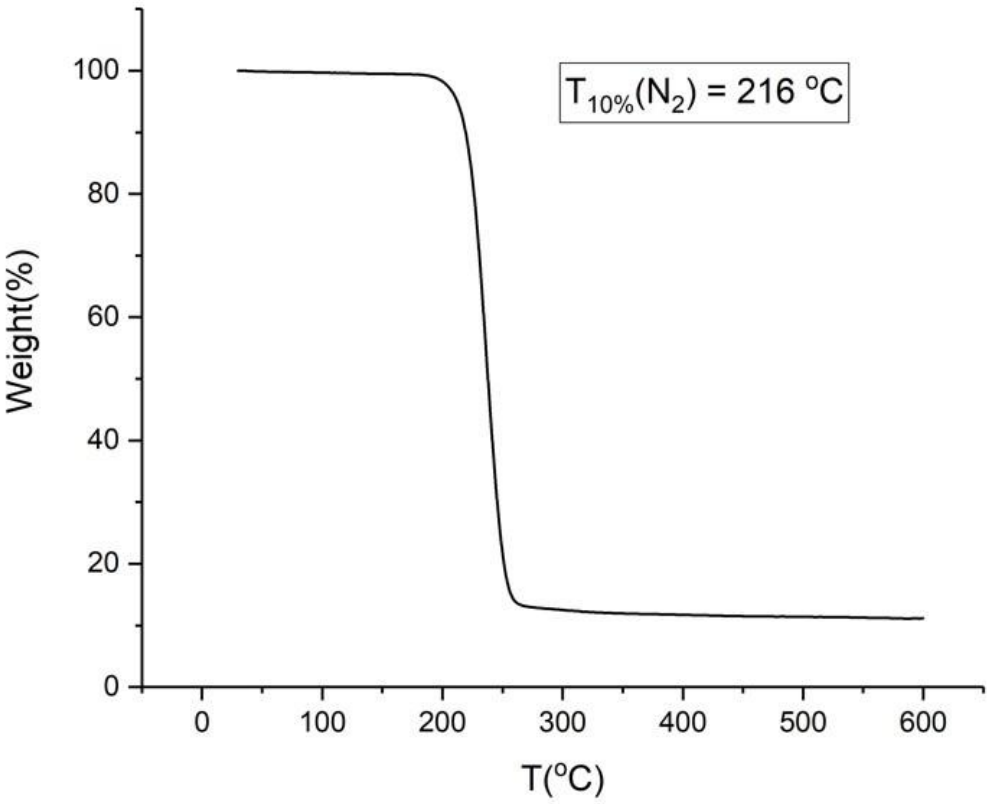


Figure S38: TGA analysis for **PLMC** from entry 15, Table 1.

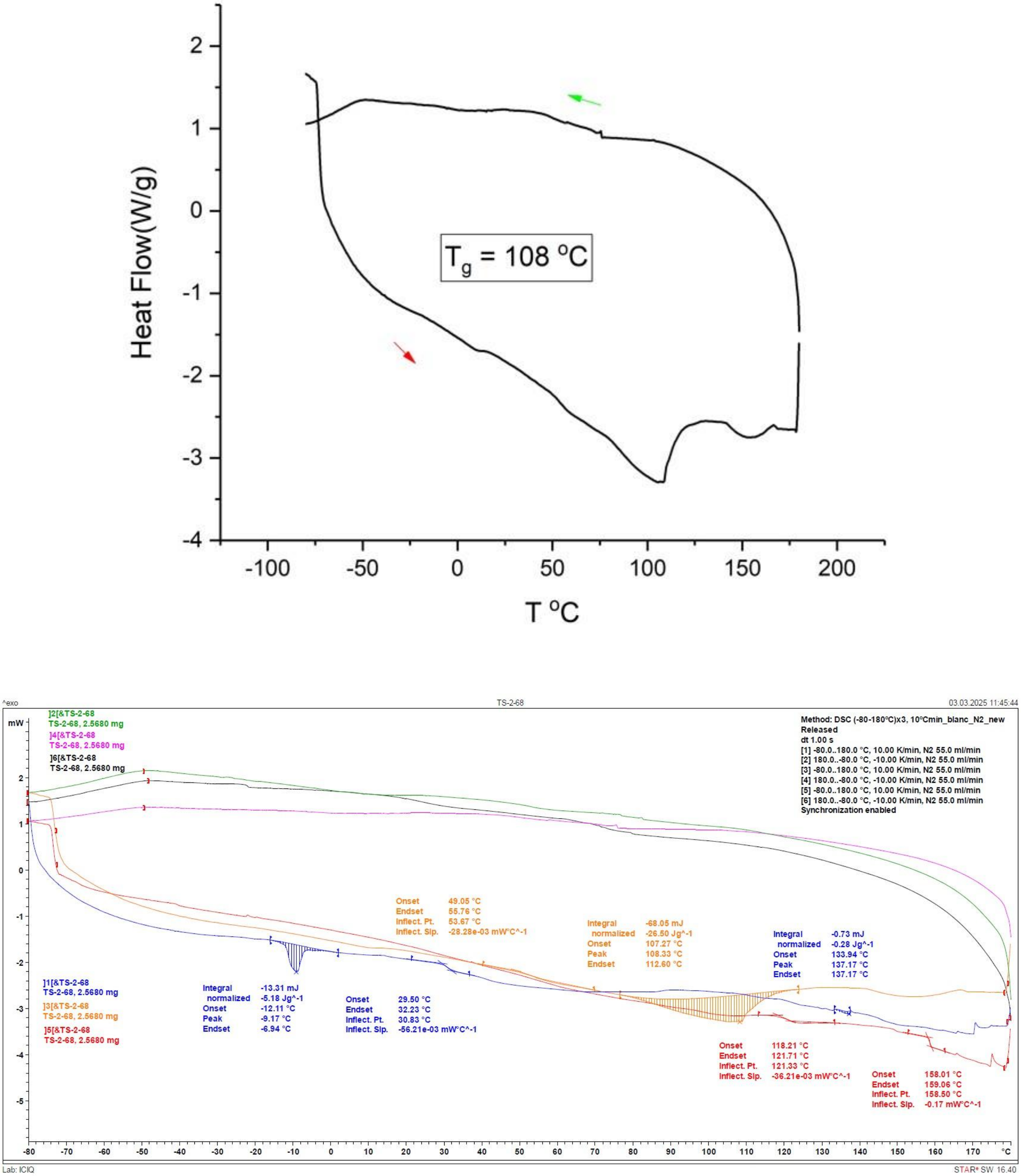


Figure S39: DSC analysis (second heating/cooling) for **PLMC** from entry 15, Table 1. Below, the full data set is shown. Please note that the thermal transition appears more like a T_m rather a T_g thus pointing at a semi-crystalline material.

Hybrid polycarbonate P5 – entry 2 from Table 4

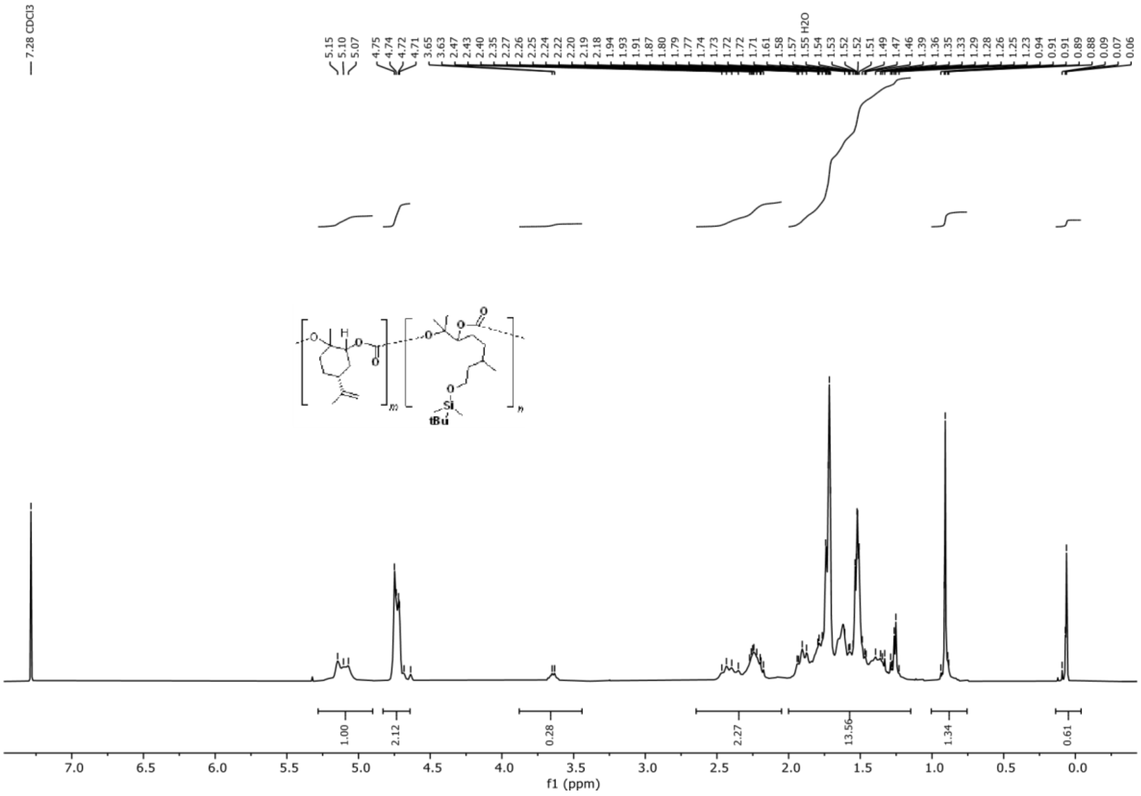


Figure S40: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) for **P5**.

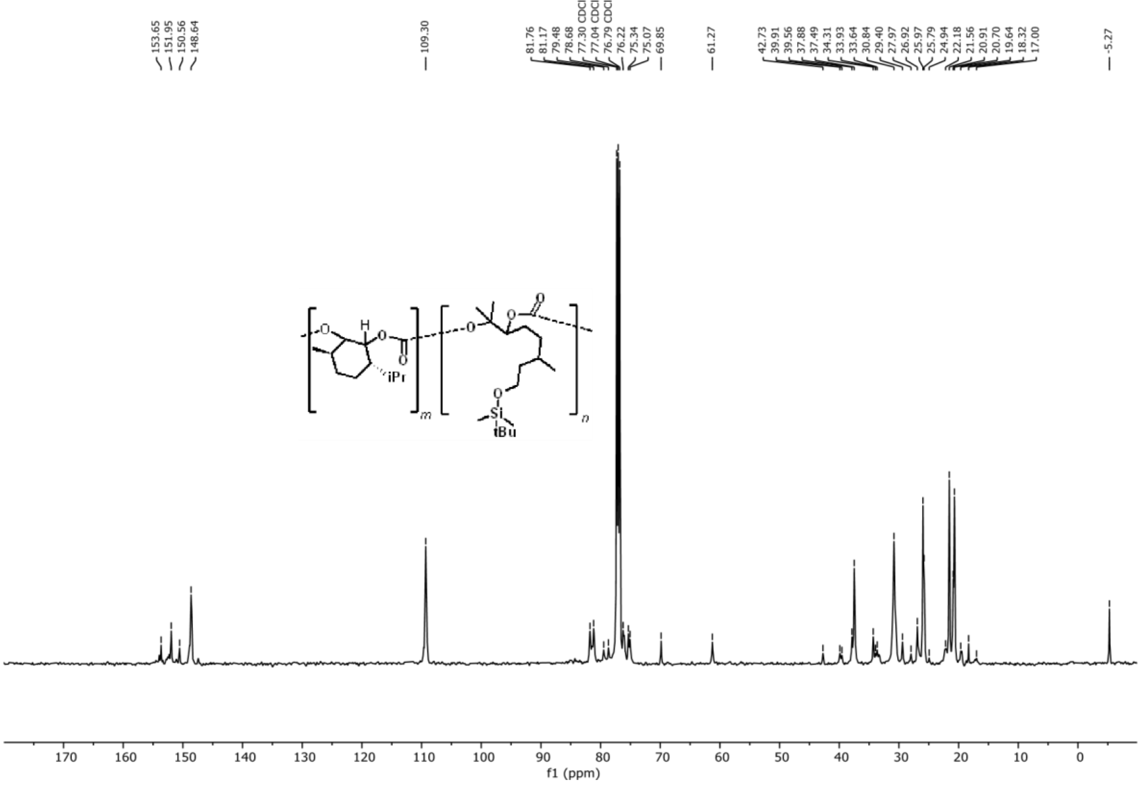


Figure S41: ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) for **P5**.

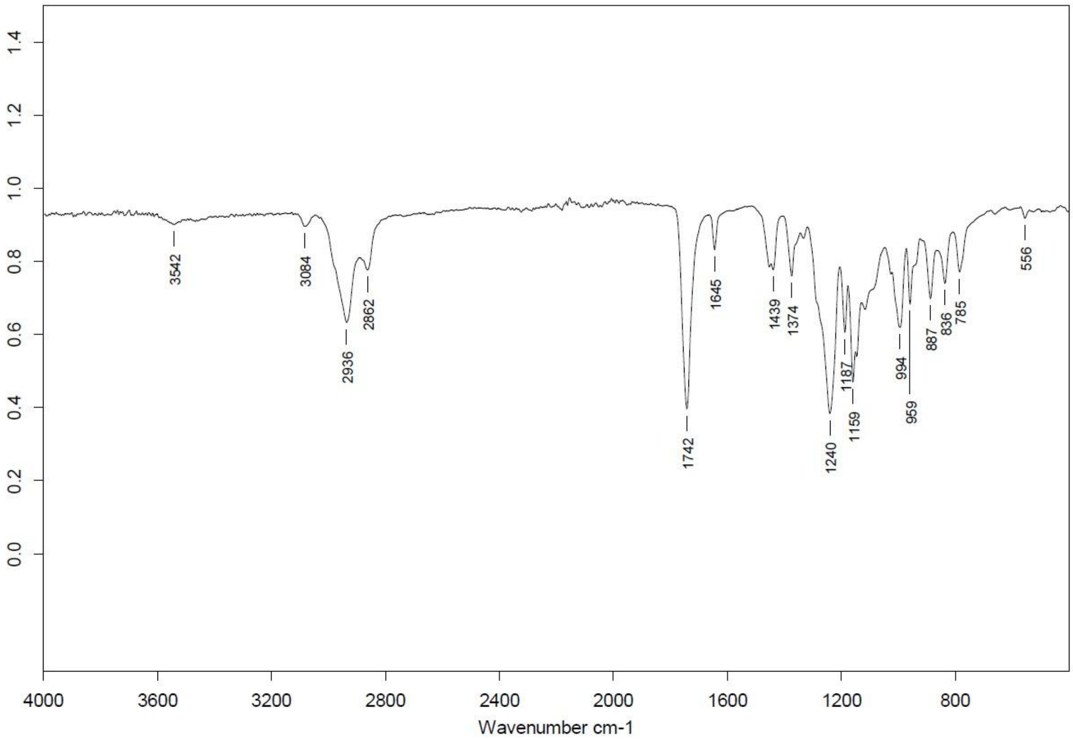
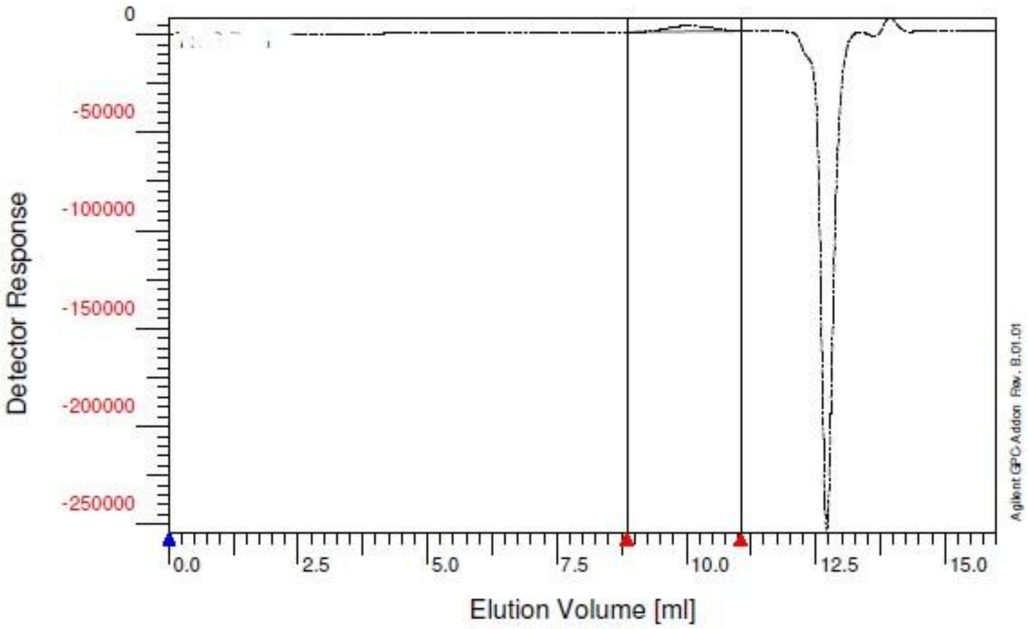


Figure S42: IR (neat) spectrum for **P5**.



Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mp (g/mol)	Đ
4.621e3	5.7467e3	6.9973e3	5.2568e3	1.2400

Figure S43: GPC analysis for **P5**.

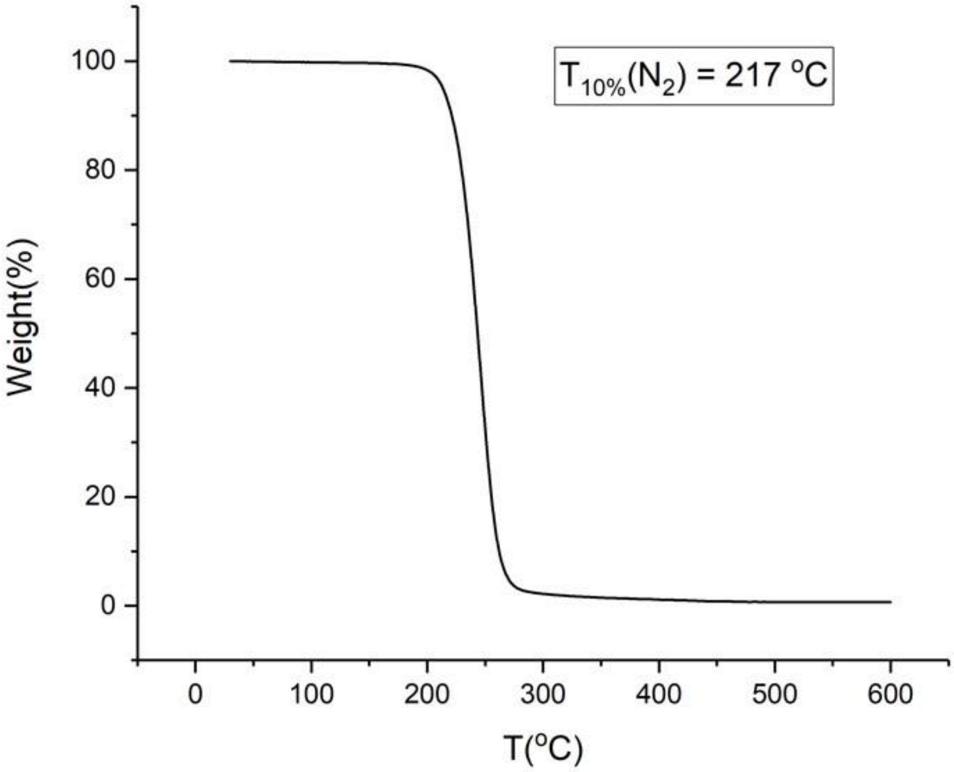


Figure S44: TGA analysis for **P5**.

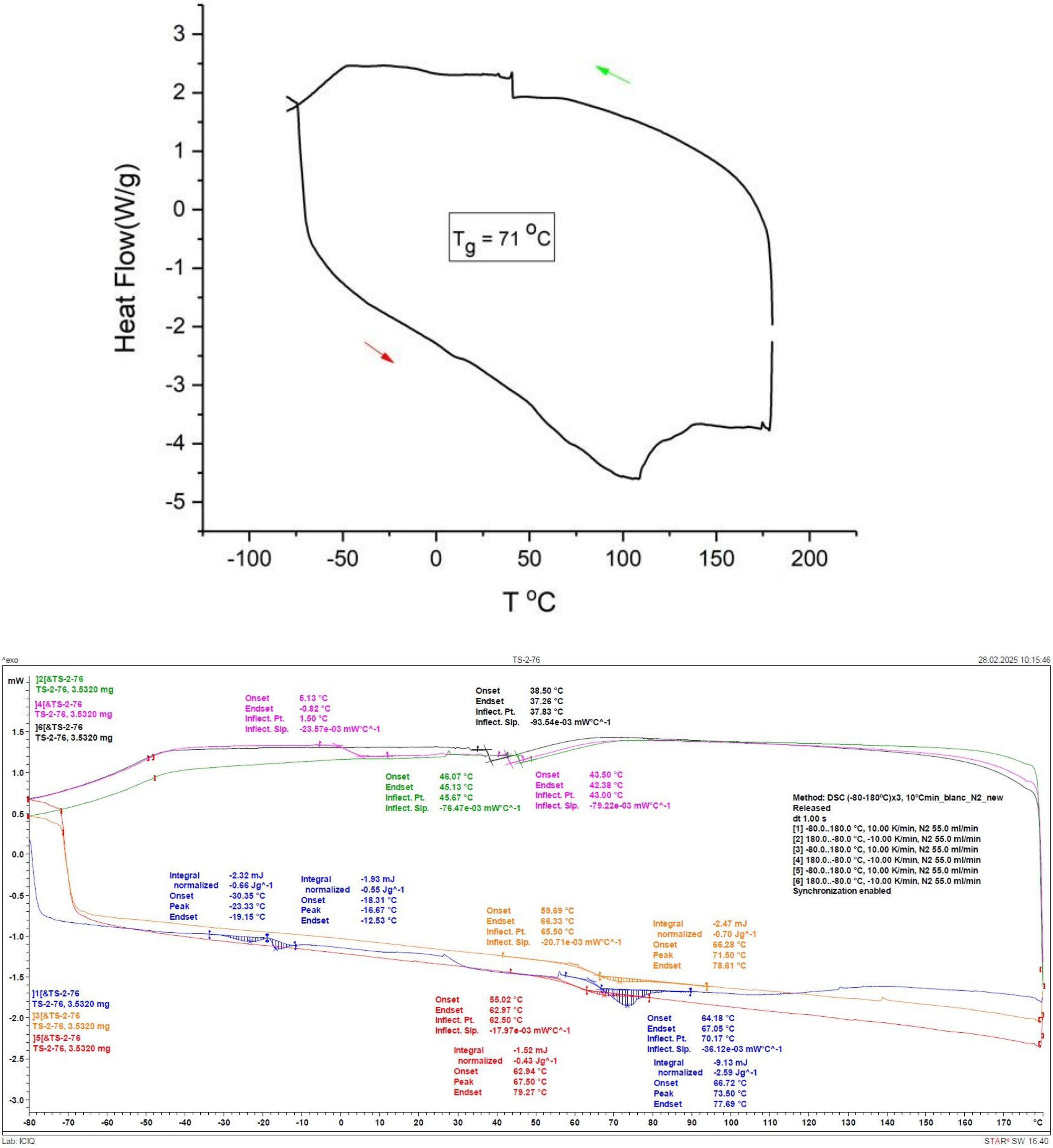


Figure S45: DSC analysis (second heating/cooling) for **P5**. Below the full data set is shown. Please note that the thermal transition appears more like a T_m rather a T_g thus pointing at a semicrystalline material.

Hybrid polycarbonate P7 – entry 5 from Table 4

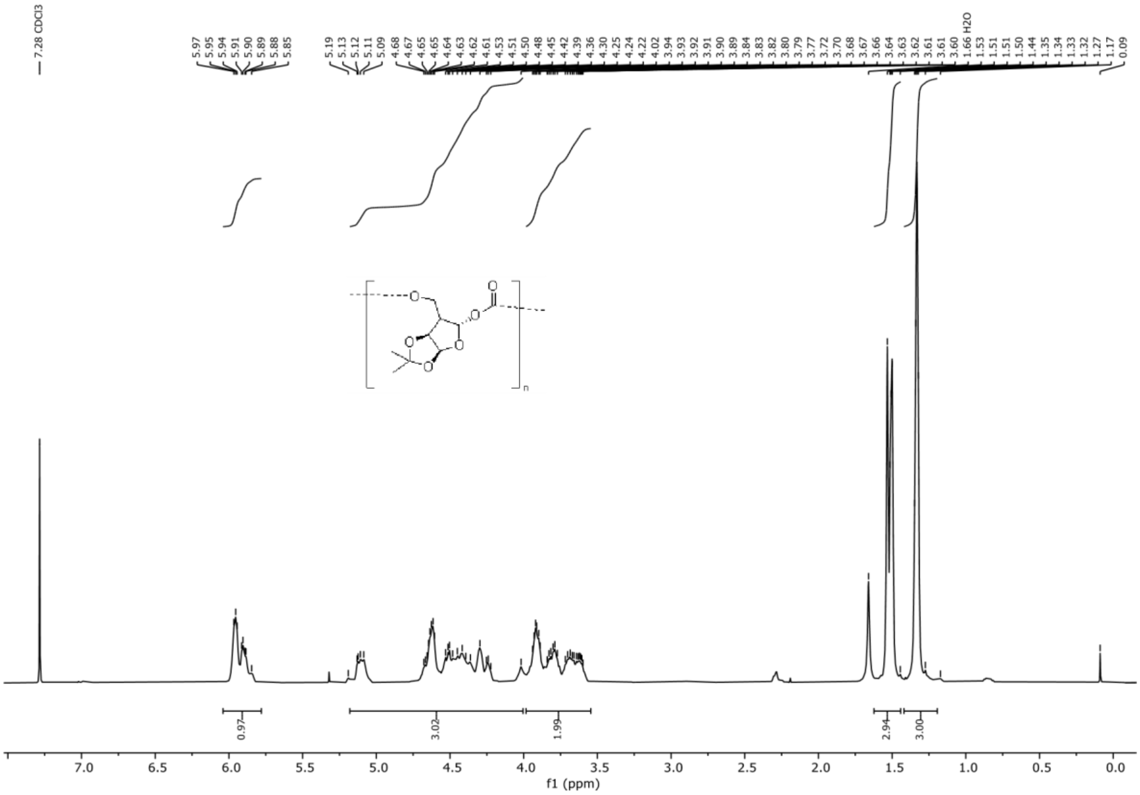


Figure S46: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) for **P7**.

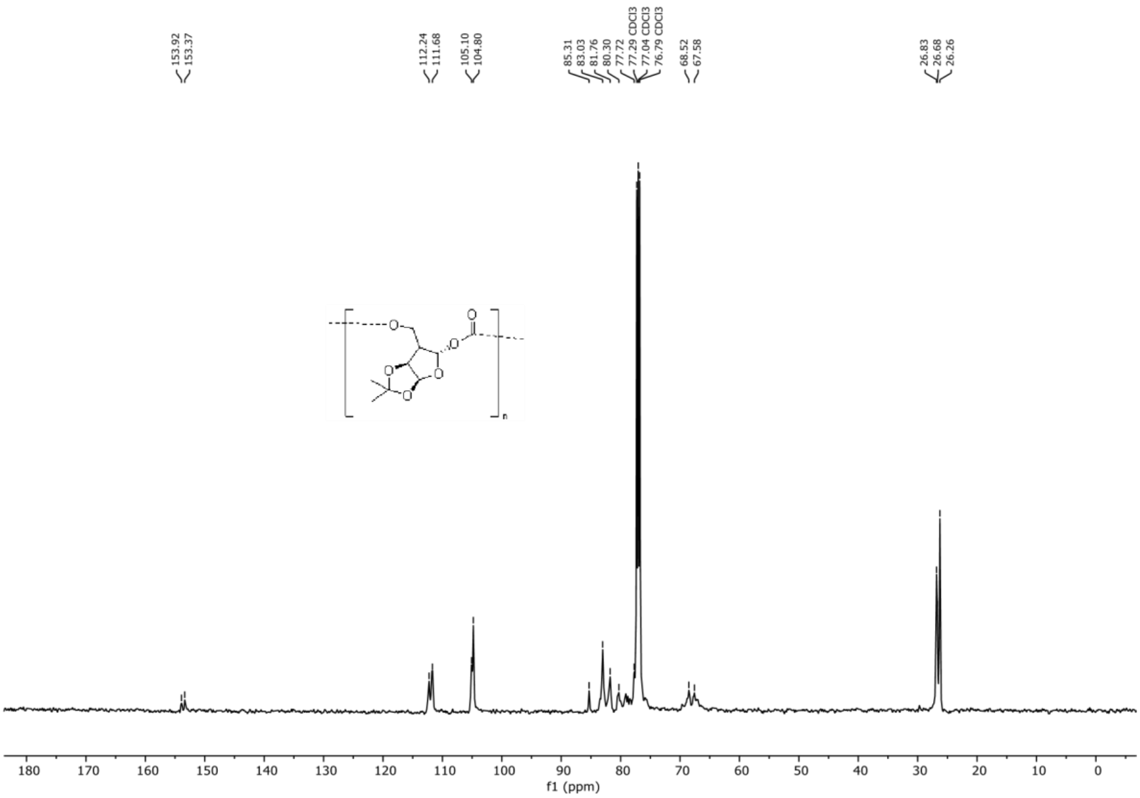


Figure S47: ^{13}C NMR spectrum (CDCl$_3$, 100 MHz) for **P7**.

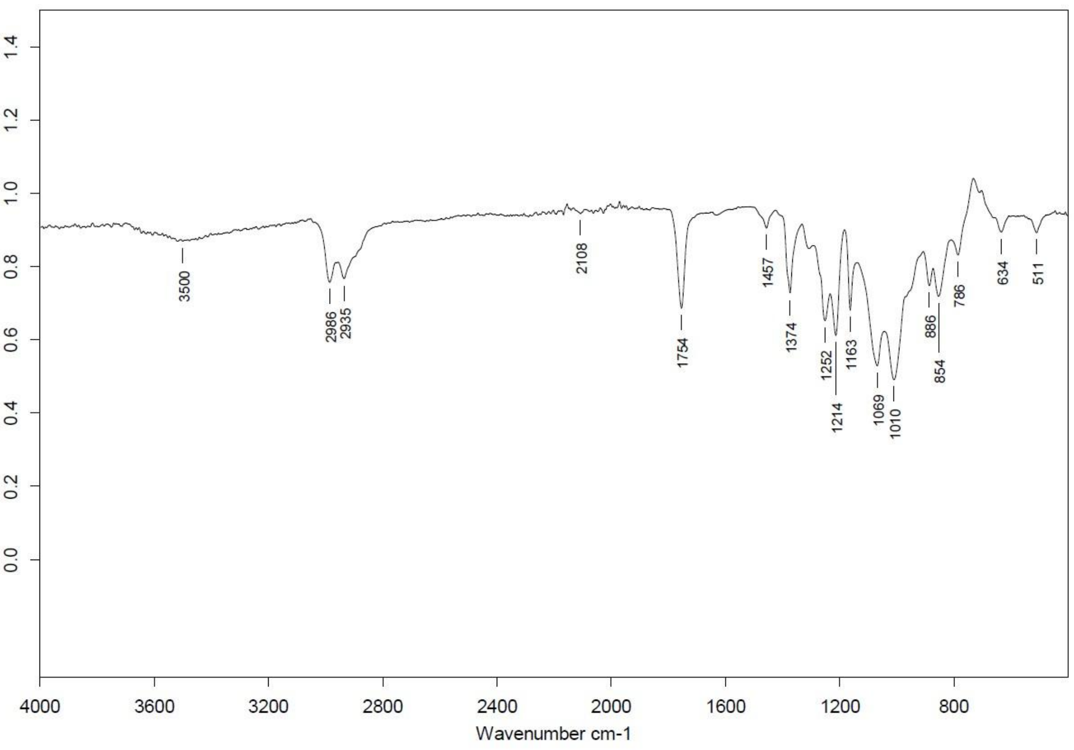
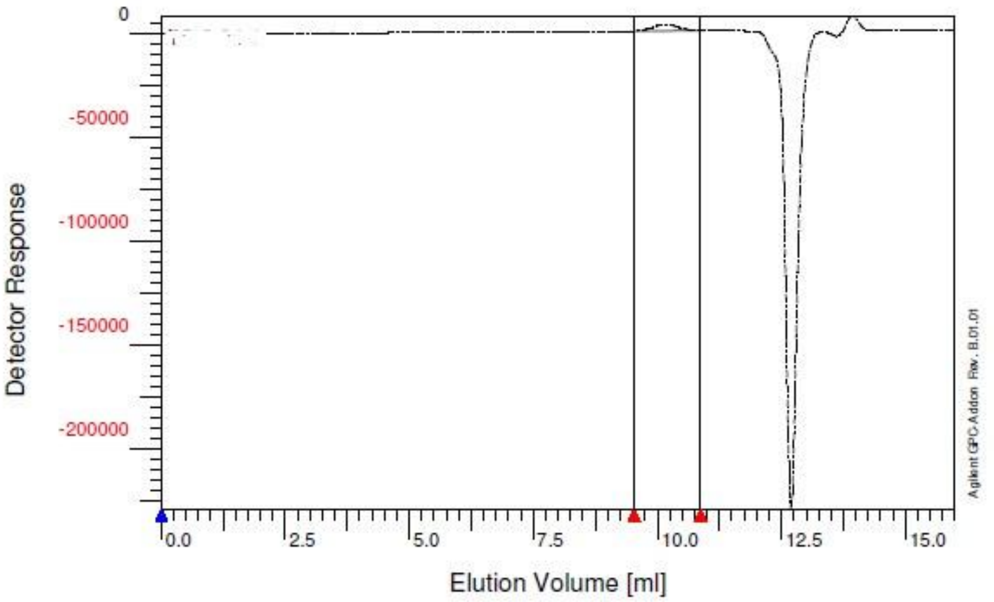


Figure S48: IR (neat) spectrum for **P7**.



Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mp (g/mol)	Đ
4.2804e3	4.6450e3	5.0360e3	4.5129e3	1.0852

Figure S49: GPC analysis for **P7**.

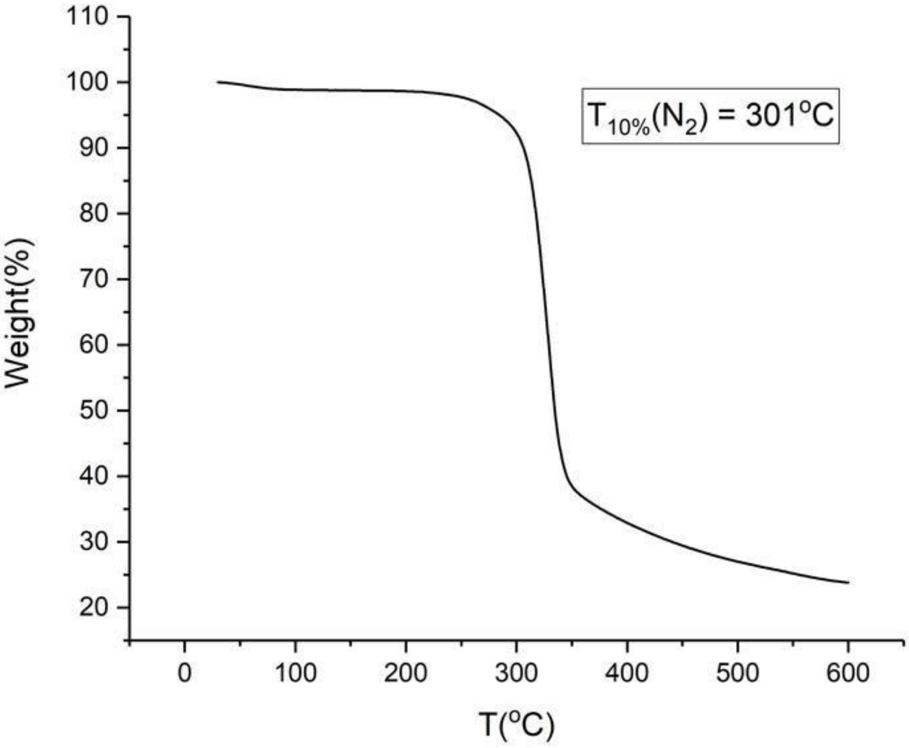
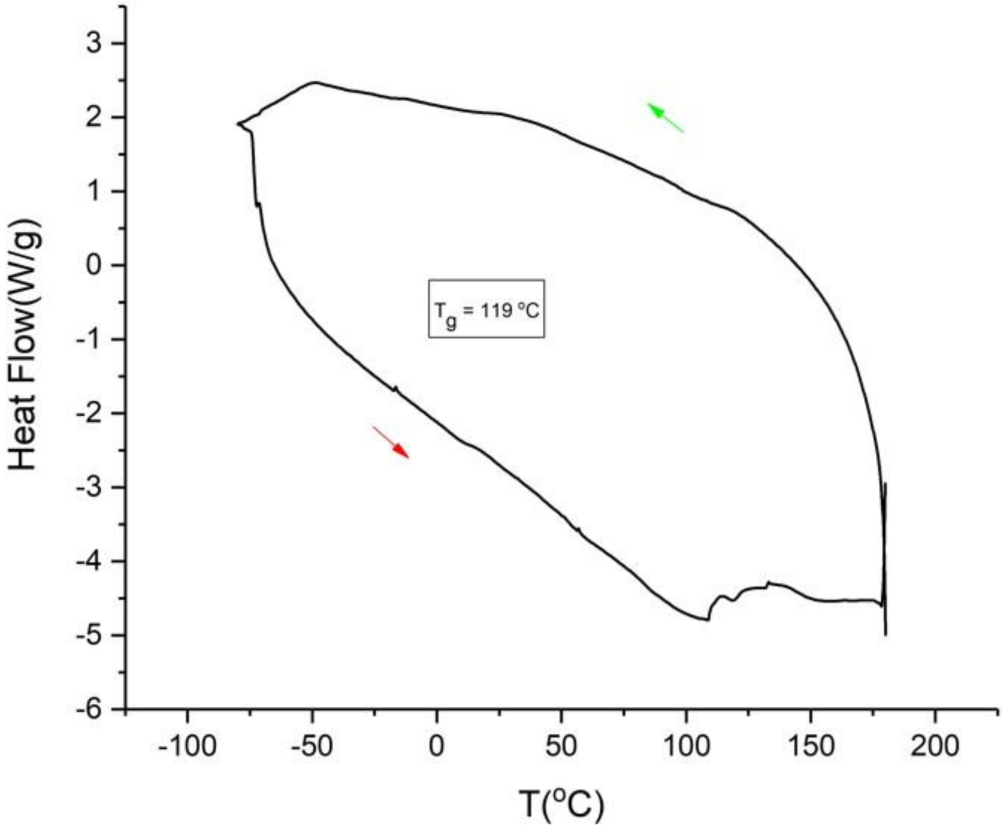
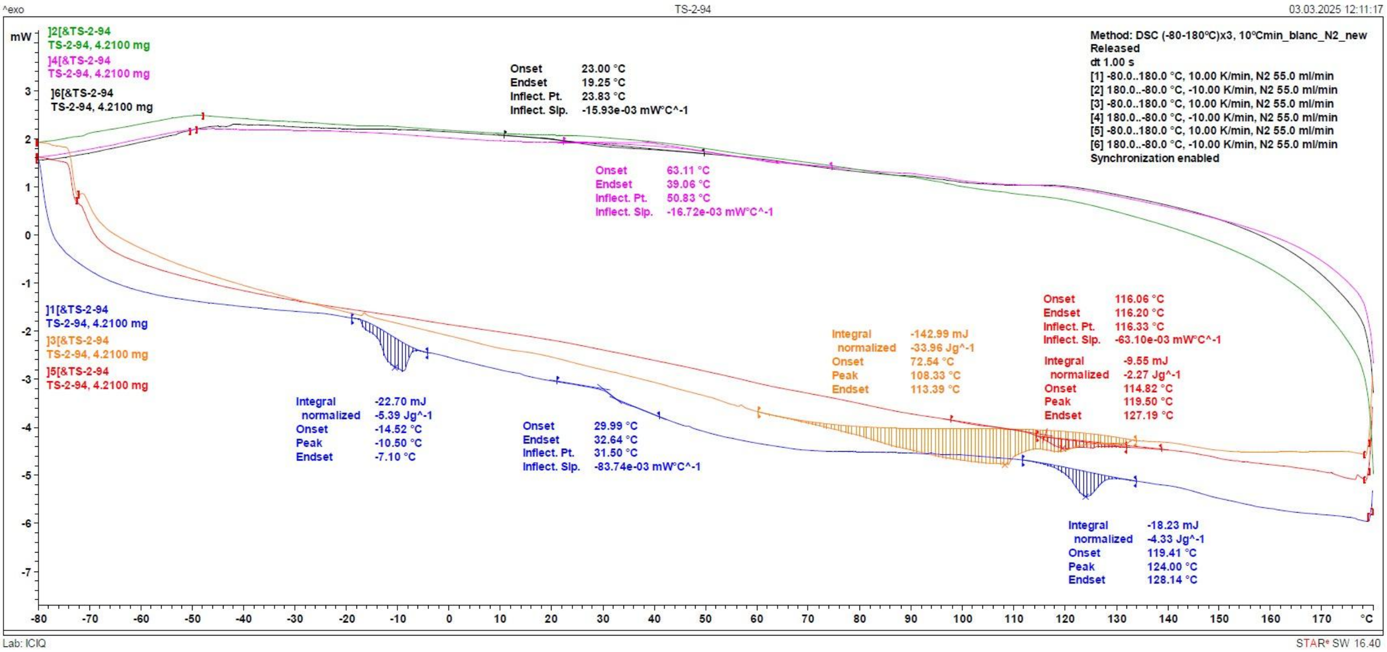


Figure S50: TGA analysis for **P7**.





Method: DSC (-80-180ºC)x3, 10ºCmin_blanc_N2_new
Released
dt 1.00 s
[1] -80.0..180.0 °C, 10.00 K/min, N2 55.0 ml/min
[2] 180.0..-80.0 °C, -10.00 K/min, N2 55.0 ml/min
[3] -80.0..180.0 °C, 10.00 K/min, N2 55.0 ml/min
[4] 180.0..-80.0 °C, -10.00 K/min, N2 55.0 ml/min
[5] -80.0..180.0 °C, 10.00 K/min, N2 55.0 ml/min
[6] 180.0..-80.0 °C, -10.00 K/min, N2 55.0 ml/min
Synchronization enabled

Figure S51: DSC analysis (second heating/cooling) for **P7**. Below the **full data** set is shown. Please note that the thermal transition appears more like a T_m rather a T_g thus pointing at a semicrystalline material.

H_d + H_e

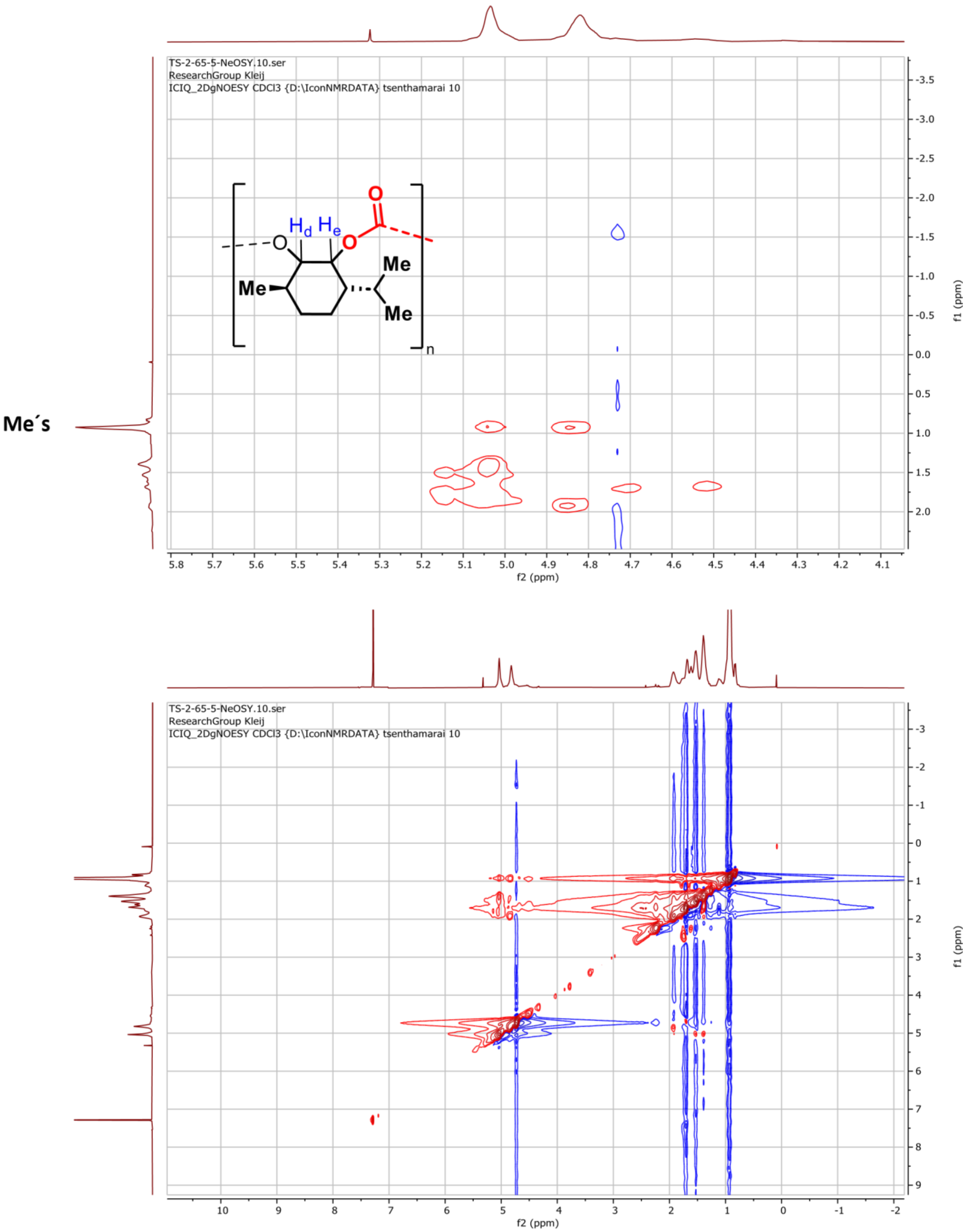
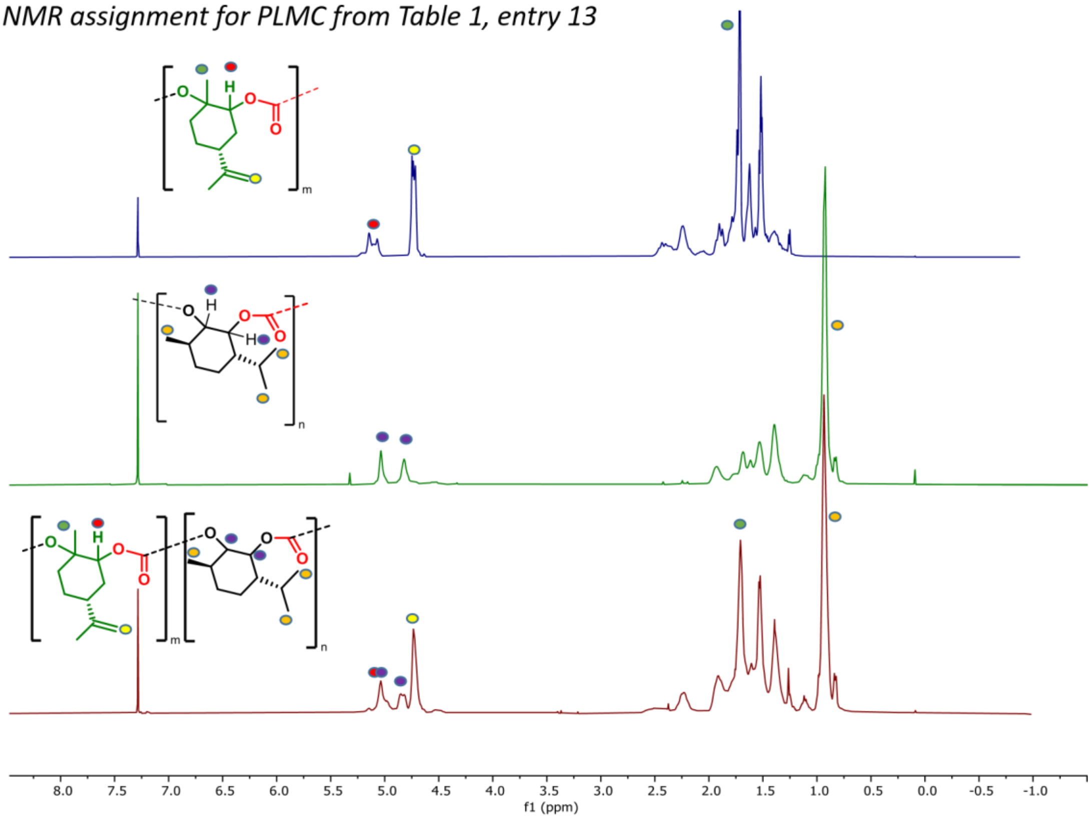


Figure S52: Below, full NOESY spectrum (CDCl$_3$, 400 MHz) of poly(menthene carbonate). Top: zoomed region showing the cross-peaks between the three **Me**-groups of the menthene fragment and the cyclohexyl **H$_d$** and **H$_e$**.

^{1}H NMR assignment for PLMC from Table 1, entry 13



^{13}C NMR assignment for PLMC from Table 1, entry 13

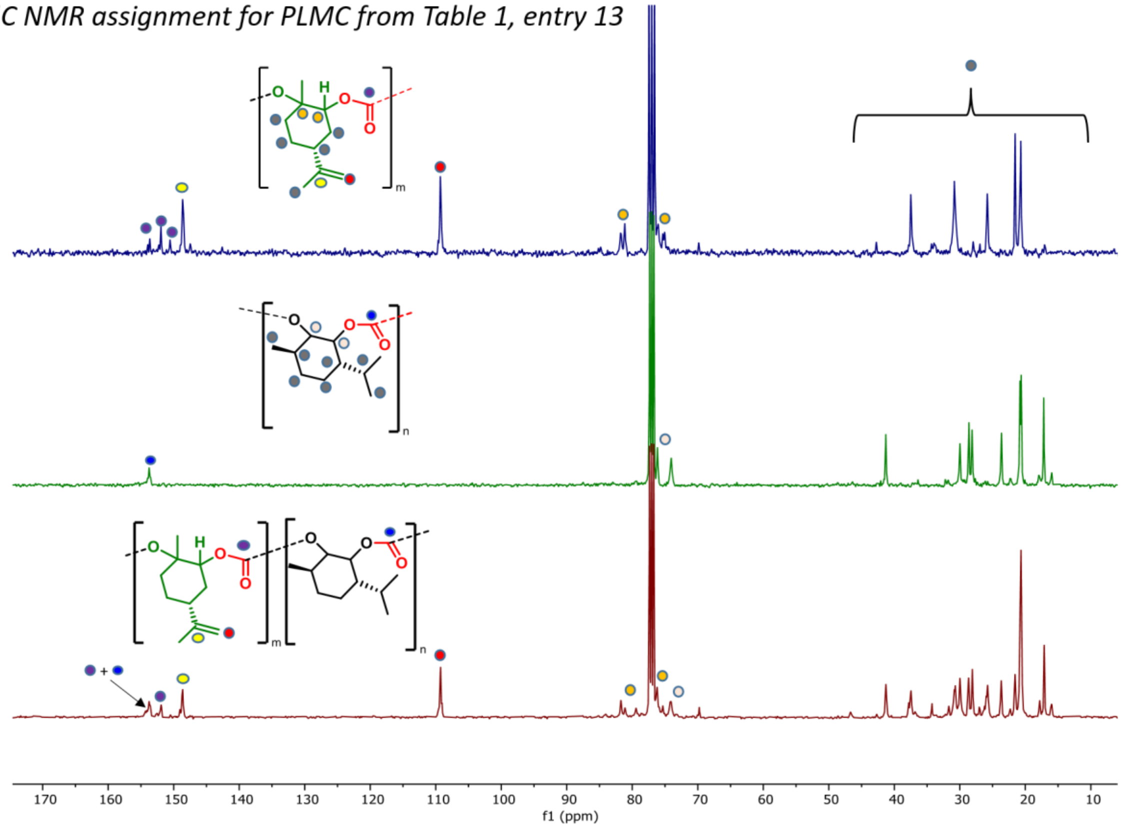


Figure S53: Assignment of all relevant H- and C-centers of the PLMC from Table 1 (entry 13) in the recorded ^{1}H (<u>TOP</u>) and ^{13}C NMR spectrum (<u>BOTTOM</u>) showing PLC and PMC reference data.