Versatile Ring-Opening Copolymerization and Post-printing Functionalization of Lactone and poly(propylene fumarate) Block Copolymers: Resorbable Building Blocks for Additive Manufacturing

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Contents

Materials

All reagents were purchased from Sigma-Aldrich, with the exception of 2,6-di-tert-4-methylphenol, which was purchased from Acros. $Mg(BHT)_2(THF)_2$ was synthesized according to a previously reported procedure.[1] *ε*-heptalactone[2], *γmε*CL[2], and *ϑ*-propargyl-*ε*-nonalactone[3-4] were synthesized using Baeyer-Villager oxidation reactions according to modified versions of previously reported procedures. All solvents were purchased from Fisher and dried using an Innovative Technology Inc. Pure Solv MD-3 solvent purification system. Benzyl alcohol, propylene oxide, *δ*-valerolactone, *ε*-caprolactone, and *ε*-decalactone were dried over calcium hydride overnight prior to vacuum distillation. ω-pentadecalactone was dissolved in 75 wt.% toluene and dried over 3 Å molecular sieves. Maleic anhydride was sublimated and then dried *in vacuo* over P_2O_5 for 5 d. All other reagents were used as received.

Instrumental Methods

Proton (^{1}H) NMR spectra were recorded using a Varian Mercury 500 spectrometer. Carbon (^{13}C) NMR spectra were recorded using a Varian NMRS 500 spectrometer. All chemical shifts were recorded in parts per million (ppm) relative to the reference peak of chloroform solvent at δ = 7.26 and 77.16 ppm for ^{1}H and ^{13}C NMR spectra, respectively. Dispersities were determined through size exclusion chromatography (SEC) using a Tosoh EcoSEC HLC-8320GPC on TSKgel GMH_{HR}-M columns in series with refractive index (RI) detection using a calibration curve determined from polystyrene standards with tetrahydrofuran (THF) as the eluent flowing at 1.0 mL min^{-1} and a sample concentration of 10 mg mL^{-1}. DSC heating and cooling curves were obtained using a TA Instruments DSC 2910. Heating and cooling curves were run in triplicate in series under a nitrogen atmosphere at a heating rate of ±10 °C per min in a 40 µL aluminium crucible. The stamp was 3D printed using an Envisiontec™ Micro Plus Advantage® continuous digital light processing (cDLP) printer.

Synthesis of *ε*-heptalactone and *γ*-methyl-*ε*-caprolactone

A single neck round bottom flask containing 250 mL methylene chloride was cooled in an ice bath prior to addition of 223 mmol of either 2-methylcyclohexanone or 4-methylcyclohexanone and 275 mmol of *m*-chloroperoxybenzoic acid. After refluxing for 3 days, the reaction mixture was cooled in an ice bath and filtered over Celite, then washed with 10% $Na_2S_2O_3$ solution, saturated Na_2CO_3 solution, and brine (3X each). The organic layer was then dried with $MgSO_4$ and filtered prior to removal of solvent *via* rotary evaporation. Both products were dried over calcium hydride overnight and distilled under vacuum prior to use.

ε-heptalactone:

^{1}H NMR (500 MHz, 303 K, $CDCl_3$): δ = 4.44 (m, $CH_2(CH_3)O$), 2.64 (m, $C(=O)CH_2$), 1.73 (m, $CH_2CH(CH_3)$), 1.42 (m, $CH_2CH_2CH(CH_3)$).

γ-methyl-ε-caprolactone:
^{1}H NMR (500 MHz, 303 K, $CDCl_3$): δ = 4.23 (m, CH_2O), 2.75 (m, C(=O)CH_2), 1.73 (m, CH_2CH(CH_3)), 1.40 (m, CH_2CH(CH_3)), 0.96 (m, CH_2CH(CH_3)).

Synthesis of *ϑ*-propargyl-*ε*-nonalactone

30.0 mL cyclohexanone (28.4 g, 289 mmol), 28.5 mL pyrrolidine (24.7 g, 347 mmol), and 55.0 mg p-toluenesulfonic acid monohydrate (0.289 mmol) were dissolved in 60 mL toluene in a round bottom flask equipped with a Dean-Stark apparatus and reflux condenser. The solution was stirred at 150 ^oC for 16 h. The resulting solution was cooled to room temperature then washed with water and brine (3X each) prior to drying with $MgSO_4$ and solvent removal under reduced pressure. The product was purified by fractional distillation under vacuum (31.4 g, b.p. = 107-114 ^oC/16 mbar) to give a pale yellow oil. This was then dissolved in dry MeCN in a two neck round bottom flask then equipped with a reflux condenser prior to drop-wise addition of 26.8 mL propargyl bromide (80% in toluene, 37.0 g, 249 mmol). The reaction was stirred under reflux overnight then cooled to room temperature prior to removal of solvent under reduced pressure. 220 mL deionized water was added to the residue and the solution was then stirred under reflux for 1 h. The product was extracted with Et_2O then washed with brine (3X) and dried over $MgSO_4$. Fractional distillation under vacuum yielded an isomeric mixture of *ϑ*-propargyl-*ε*-nonalactone and *α*-propargyl-*ε*-caprolactone as a colorless oil (12.9 g, 94.7 mmol, b.p. = 93-95 ^oC / 16mbar). Next, 160 mL of methylene chloride was cooled in an ice bath prior to addition of the *ϑ*-propargyl-*ε*-nonalactone and *α*-propargyl-*ε*-caprolactone mixture (12.9 g, 94.7 mmol) and *m*-chloroperoxybenzoic acid (24.5 g, 142.1 mmol). The reaction mixture was refluxed for 48 h and filtered after cooling to room temperature. The product was washed with a concentrated, aqueous sodium sulfite solution (3X) and dried over $MgSO_4$ prior to removal of solvent using rotary evaporation. The final product was dried over calcium hydride overnight and distilled under vacuum before use.

General synthesis of lactone homopolymers

Using standard glovebox techniques, an ampoule was filled with a 2 M solution of $Mg(BHT)_2(THF)_2$ (586.8 mg, 0.97 mmol), benzyl alcohol (0.1 mL, 0.97 mmol), and ε-caprolactone (5.35 mL, 48.3 mmol) in toluene. The sealed ampoule was heated at 80 °C. The resultant polymer was recovered by precipitation in hexanes.

Characterization of lactone homopolymers

Lactone monomer (L)	Time (h)	Target DP	Actual DP	M_n (kDa) NMR	$Đ_M$ SEC
*δ*VL	1	50	51	5.1	1.14
*ε*CL	1	50	49	5.6	1.12
*ε*HL	24	50	43	5.6	1.14
*γ*m*ε*CL	1	50	50	6.5	1.11
*ε*DL	24	50	52	8.9	1.06

ωPDL	1	50	62	14.9	1.41

General synthesis of poly(lactone-*b*-propylene maleate) copolymers

Using standard glovebox techniques, an ampoule was filled with a 2 M solution of $Mg(BHT)_2(THF)_2$ (586.8 mg, 0.97 mmol), benzyl alcohol (01. mL, 0.97 mmol), and *ε*-caprolactone (5.35 mL, 48.3 mmol) in toluene. The sealed ampoule was heated at 80 °C. After a defined period of time, a 2 M solution of propylene oxide (3.38 mL, 48.3 mmol) and maleic anhydride (4.74 g, 48.3 mmol) in toluene was added to the reaction ampoule in a N_2 environment. The resealed ampoule was heated back to 80 °C for 5 d. The resultant polymer was recovered by precipitation in hexanes.

P(δVL-b-PM):

^{1}H NMR (500 MHz, 303 K, $CDCl_3$): δ = 7.33 (m, Ar), 6.24 (m, OC(=O)*H*=C*H*(=O)O), 5.24 (m, CH_2C*H*(CH_3)O), 5.10 (s, C=OOCH_2Ar), 4.23 (m, PO CH_2OC=O), 4.06 (m, δVL CH_2OC=O), 2.31 (s, δVL CH_2C=OO), 1.30 (m, PO CH_2CH(CH_3)O), 1.66 (all remaining hydrogens) ppm. ^{13}C NMR (125MHz, 303K, $CDCl_3$): δ = 173.32 (δVL*-δVL, O*C*OCH_2), 173.12 (δVL*-PO, O*C*OCH_2), 165.15 (MAn*-δVL, O*C*OCH_2), 164.77 and 164.49 (MAn*-PO, O*C*OCH_2), 130.54 and 130.00 (MAn*-PO, O(O)C**C*H=CH), 129.40 and 129.13 (MAn*-PO, O(O)C*CH=*C*H), 128.33 and 128.31 (εCL-MAn*, O(O)C*C*H=CH), 69.26 (MAn*-PO, O*C*H(CH_3)CH_2), 66.56 (MAn*-PO, O*C*H(CH_3)CH_2), 64.01 (δVL*- δVL, O*C*H_2), 33.81 (δVL*-δVL, OCO*C*H_2), 28.22 (δVL, OCH_2*C*H_2), 21.55 (δVL, OCOCH_2*C*H_2) and 16.34 (PO, CH_2CH(*C*H_3)O) ppm. SEC (THF): M_n = 6.5 kDa, M_w = 8.3 kDa, $Đ_M$ = 1.85. Yield: 89%.

P(εHL-b-PM):

^{1}H NMR (500 MHz, 303 K, $CDCl_3$): δ = 7.32 (m, Ar), 6.23 (m, OC(=O)*H*=C*H*(=O)O), 5.22 (m, CH_2C*H*(CH_3)O), 5.07 (s, C=OOCH_2Ar), 4.85 (m, εHL CH_2OC=O), 4.23 (m, PO CH_2OC=O), 2.23 (s, CH_2C=OO), 1.16 (m, εHL CH_3), 1.63-1.22 (all remaining hydrogens) ppm. ^{13}C NMR (125MHz, 303K, $CDCl_3$): δ = 173.10 (εHL*-εHL, OCOCH_2), 165.02 (MAn*-εHL, O*C*OCH_2), 164.63 and 164.39 (MAn*-PO, O*C*OCH_2), 130.40 and 129.91 (MAn*-PO, O(O)C**C*H=CH), 129.77 and 129.24 (MAn*-PO, O(O)C*CH=*C*H), 125.43 (εHL-MAn*, O()OC*C*H=CH), 77.53, 70.37 (εHL*-εHL, O*C*H_2), 69.12 (MAn*-PO, O*C*H(CH_3)CH_2), 66.33 (MAn*-PO, O*C*H(CH_3)CH_2), 35.51 (εHL*-εHL, *C*$H_2$$CH_2$COO), 34.44 (εHL, CH_2*C*H_2CH(CH_3)), 16.17 (PO, CH_2CH(*C*H_3)O), 19.89 (εHL, *C*H_3CH(CH_2)$_2$), 30.29 and 24.89 (all remaining carbons) ppm. SEC (THF): M_n = 4.5 kDa, M_w = 9.8 kDa, $Đ_M$ = 1.80. Yield: 92%.

P(γmεCL-b-PM):

^{1}H NMR (500 MHz, 303 K, $CDCl_3$): δ = 7.32 (m, Ar), 6.26 (m, OC(=O)*H*=C*H*(=O)O), 5.26 (m, CH_2C*H*(CH_3)O), 5.11 (s, C=OOCH_2Ar), 4.26 (m, PO CH_2OC=O), 4.10 (m, γmεCL CH_2OC(=O)), 2.29 (s, CH_2C=OO), 1.16 (m, γmεCL CH(CH_3)), 1.63-1.22 (all remaining hydrogens) ppm. ^{13}C NMR (125MHz, 303K, $CDCl_3$): δ = 173.53 (γmεCHL*- γmεCHL, OCOCH_2), 164.44 (MAn*- γmεCHL, O*C*OCH_2), 164.19 and 163.82 (MAn*-PO, O*C*OCH_2), 130.29 and 129.94 (MAn*-PO, O(O)C**C*H=CH), 129.04 and 128.77 (MAn*-PO, O(O)C*CH=*C*H), 125.24 (γmεCHL -MAn*, O()OC*C*H=CH), 77.34, 69.12 (γmεCHL *- γmεCHL, O*C*H_2), 68.10 (MAn*-PO, O*C*H(CH_3)CH_2), 66.36 (MAn*-PO, O*C*H(CH_3)CH_2), 35.02 (γmεCHL *-γmεCHL, *C*$H_2$$CH_2$COO), 34.56 (γmεCHL, CH_2*C*H_2CH(CH_3)), 16.13 (PO, CH_2CH(*C*H_3)O), 18.87 (γmεCHL, *C*H_3CH), 31.66 and 29.36 (all remaining carbons) ppm. SEC (THF): M_n = 7.4 kDa, M_w = 9.2 kDa, $Đ_M$ = 2.02. Yield: 87%.

P(ϑpεNL-b-PM):
^{1}H NMR (500 MHz, 303 K, $CDCl_3$): δ = 7.34 (m, Ar), 6.85 (m, OC(=O)*H*=C*H*(=O)O), 5.29 (m, CH_2C*H*(CH_3)O), 5.10 (s, C=OOCH_2Ar), 4.92 (m, C*H*(CH_2CCH)) 4.34 (m, PO CH_2OC=O), 4.05 (m, αpεCL, CH_2OC(=O)), 2.45 (m, CH_2CCH), 2.34 (s, CH_2C=OO), 2.01 (s, CC*H*), 1.65-1.39 (all remaining hydrogens) ppm. ^{13}C NMR (125MHz, 303K, $CDCl_3$): δ = 174.12 (αpεCL*- αpεCL, OCOCH_2), 173.42 (εCL*-εCL, OCOCH2), 172.87 (θpεNL*-θpεNL), 164.36 and 163.98 (MAn*-PO, O*C*OCH_2), 133.99 and 133.75 (MAn*-PO, O(O)C**C*H=CH), 133.50 and 133.26 (MAn*-PO, O(O)C*CH=*C*H), 81.21 (αpεCL and θpεNL, CH(*C*H_2CCH_3)), 78.57 (θpεNL, *C*H(CH_2CCH_3)), 71.25 (αpεCL, OC(=O)*C*), 70.53 (εCL, OC(=O)*C*), 70.07 (αpεCL and εCL, *C*OC(=O)), 69.22 (MAn*-PO, O*C*H(CH_3)CH_2), 67.89 (αpεCL and θpεNL, CH(CH_2C*C*H_3)), 66.57 (MAn*-PO, O*C*H(CH_3)CH_2), 16.33 (PO, CH_2CH(*C*H_3)O), 36.42-21.08 (all remaining carbons) ppm. SEC (THF): M_n = 7.4 kDa, M_w = 14.6 kDa, $Đ_M$ = 1.97. Yield: 86%.

P(εDL-b-PM):
^{1}H NMR (500 MHz, 303 K, $CDCl_3$): δ = 7.33 (m, Ar), 6.25 (m, OC(=O)*H*=C*H*(=O)O), 5.25 (m, CH_2C*H*(CH_3)O), 5.09 (s, C=OOCH_2Ar), 4.84 (m, εDL CH_2OC=O), 4.24 (m, PO CH_2OC=O), 2.26 (s, CH_2C=OO), 0.87 (m, εDL CH_3(CH_2)$_3$), 1.65-1.20 (all remaining hydrogens) ppm. ^{13}C NMR (125MHz, 303K, $CDCl_3$): δ = 173.41 (εDL*-εDL, OCOCH_2), 164.81 and 164.53 (MAn*-PO, O*C*OCH_2), 130.59 and 130.11 (MAn*-PO, O(O)C**C*H=CH), 129.96 and 129.47 (MAn*-PO, O(O)C*CH=*C*H), 125.65 (εDL-MAn*, O()OC*C*H=CH), 74.04 (εDL*-εDL, O*C*H_2), 69.30 (MAn*-PO, O*C*H(CH_3)CH_2), 66.58 (MAn*-PO, O*C*H(CH_3)CH_2), 34.64 (εDL*-εDL, OCO*C*H_2), 33.93 (εDL, CH_2*C*H_2CH(Bu)), 16.37 (PO, CH_2CH(*C*H_3)O), 14.12 (εDL, *C*H_3(CH_2)$_3$), 30.48, 27.60, 25.13 and 22.71 (all remaining carbons) ppm. SEC (THF): M_n = 2.6 kDa, M_w = 4.0 kDa, $Đ_M$ = 1.56. Yield: 85%.

P(PDL-b-PM):
^{1}H NMR (500 MHz, 303 K, $CDCl_3$): δ = 7.32 (m, Ar), 6.24 (m, OC(=O)*H*=C*H*(=O)O), 5.23 (m, CH_2C*H*(CH_3)O), 5.08 (s, C=OOCH_2Ar), 4.23 (m, PO CH_2OC=O), 4.02 (m, PDL CH_2OC=O), 2.25 (s, PDL CH_2C=OO), 1.60-1.23 (all remaining hydrogens) ppm. ^{13}C NMR (125MHz, 303K, $CDCl_3$): δ = 173.93 (PDL*- PDL, O*C*OCH_2), 173.63 (PDL*-PO, O*C*OCH_2), 165.12 (MAn*- PDL, O*C*OCH_2), 164.69 and 164.41 (MAn*-PO, O*C*OCH_2), 129.97 and 129.82 (MAn*-PO, O(O)C**C*H=CH), 129.35 and 129.27 (MAn*-PO, O(O)C*CH=*C*H), 128.55 and 128.18 (PDL-MAn*, O(O)C*C*H=CH), 69.18 (MAn*-PO, O*C*H(CH_3)CH_2), 66.45 (MAn*-PO, O*C*H(CH_3)CH_2), 64.13 (PDL*- PDL, O*C*H_2), 34.12 (PDL*- PDL, OCO*C*H_2), 30.34 (PDL, OCH_2*C*H_2), and 16.22 (PO, CH_2CH(*C*H_3)O) ppm. SEC (THF): M_n = 5.5 kDa, M_w = 7.8 kDa, $Đ_M$ = 1.41. Yield: 84%.

P(δVL-co-εCL-b-PM):
^{1}H NMR (500 MHz, 303 K, $CDCl_3$): δ = 7.32 (m, Ar), 6.24 (m, OC(=O)*H*=C*H*(=O)O), 5.21 (m, CH_2C*H*(CH_3)O), 5.08 (s, C=OOCH_2Ar), 4.26 (m, PO CH_2OC=O), 4.03 (m, CH_2OC=O), 2.28 (s, CH_2C=OO), 1.65-1.28 (all remaining hydrogens) ppm. ^{13}C NMR (125MHz, 303K, $CDCl_3$): δ = 173.49 (εCL*-εCL, O*C*OCH_2), 173.46 (εCL*-δVL, O*C*OCH_2), 173.25 (δVL*-εCL, O*C*OCH_2), 173.23 (δVL*-δVL, O*C*OCH_2), 173.01 (δVL*-PO or εCL*-PO, O*C*OCH_2), 165.06 (MAn*-δVL or MAn*-εCL, O*C*OCH_2), 164.68 and 164.40 (MAn*-PO, O*C*OCH_2), 130.54 and 130.00 (MAn*-PO, O(O)C**C*H=CH), 129.40 and 129.13 (MAn*-PO, O(O)C*CH=*C*H), 128.33 and 128.31 (εCL-MAn* or δVL-MAn*, O(O)C*C*H=CH), 69.26 (MAn*-PO, O*C*H(CH_3)CH_2), 66.56 (MAn*-PO, O*C*H(CH_3)CH_2), 64.01 (δVL or εCL, O*C*H_2), 33.81 (δVL or εCL, OCO*C*H_2), 28.22 (δVL or εCL, OCH_2*C*H_2), 21.55 (δVL or εCL, OCOCH_2*C*H_2) and 16.34 (PO, CH_2CH(*C*H_3)O) ppm. SEC (DMF): M_n = 1.6 kDa, M_w = 3.2 kDa, $Đ_M$ = 1.97. Yield: 82%.

General procedure for the isomerization of poly(lactone-*b*-propylene maleate)

Poly(*ε*-caprolactone)-*b*-(propylene maleate) (1.0 g, 12 mol. eq. olefin) was dissolved into chloroform (50 mL) and diethylamine (0.01 mL, 0.15 mol. eq. per alkene) was added. The solution was refluxed for 24 h under a nitrogen atmosphere. After cooling to room temperature, the organic solution was washed with a 0.5 M phosphate buffer solution (150 mL, pH = 6) prior to removal of solvent *via* rotary evaporation.

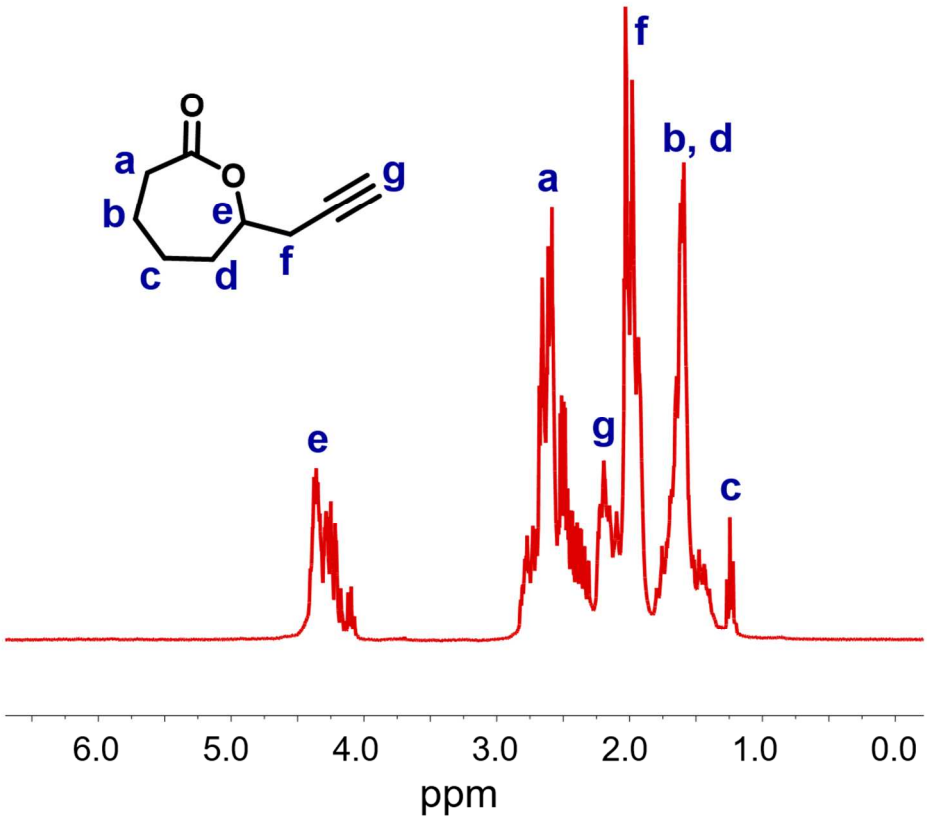

Figure 1: ^{1}H NMR spectra of an isomeric mixture of *α*-propargyl-*ε*-caprolactone and *ϑ*-propargyl-*ε*-nonalactone (500 MHz, $CDCl_3$, 303 K).

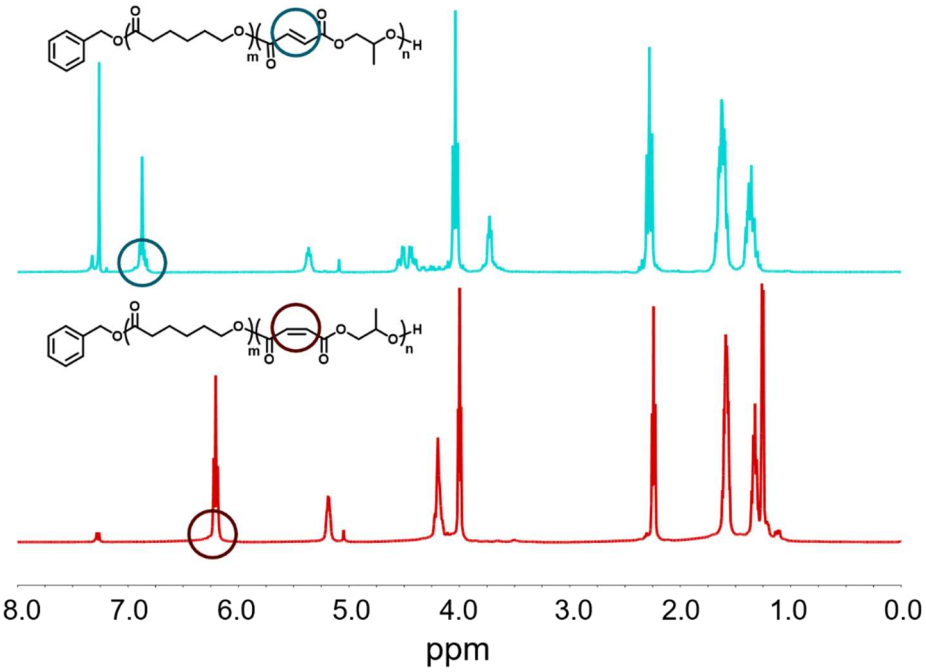

Figure 2: ^{1}H NMR spectra of DP 50 poly(*ε*-caprolactone-*b*-propylene maleate) (bottom) and poly(*ε*-caprolactone-*b*-propylene fumarate) (top) (500 MHz, $CDCl_3$, 303 K).

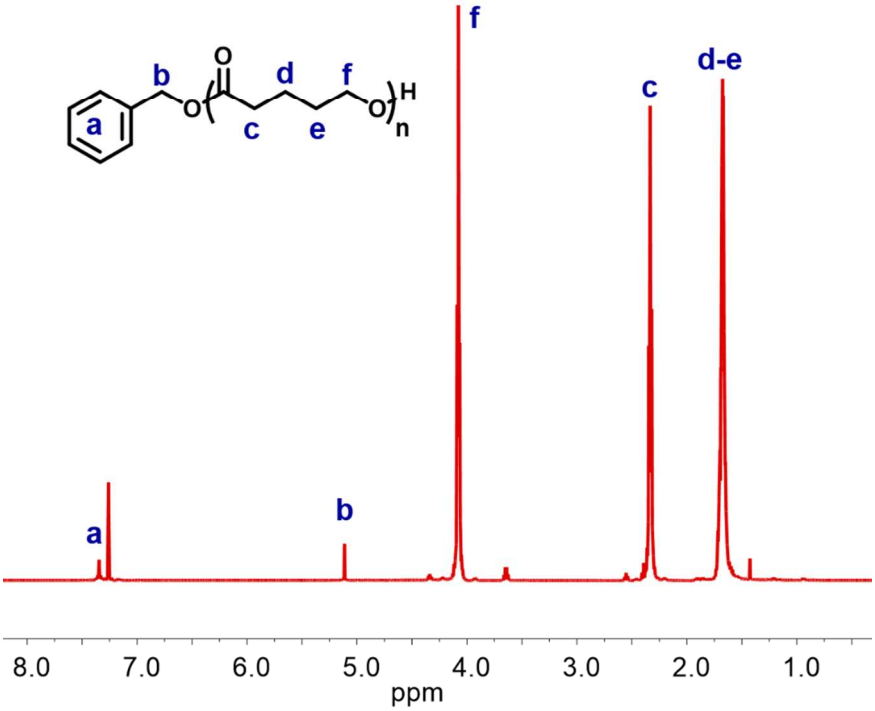

Figure 3: ^{1}H NMR spectra of poly(*δ*-valerolactone) (500 MHz, $CDCl_3$, 303 K).

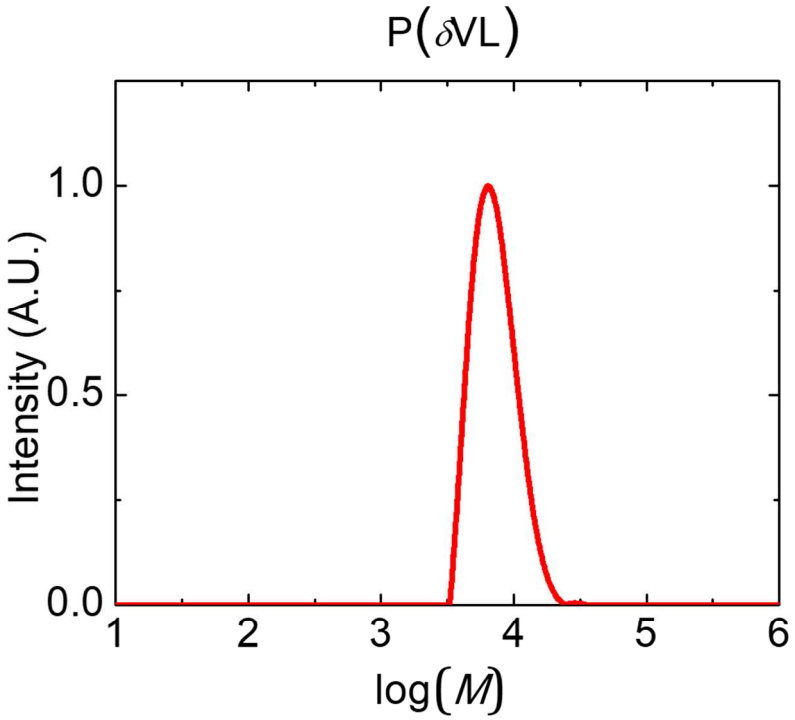

Figure 4: SEC chromatogram for poly(δ-valerolactone). The molecular mass determined against poly(styrene) standards.

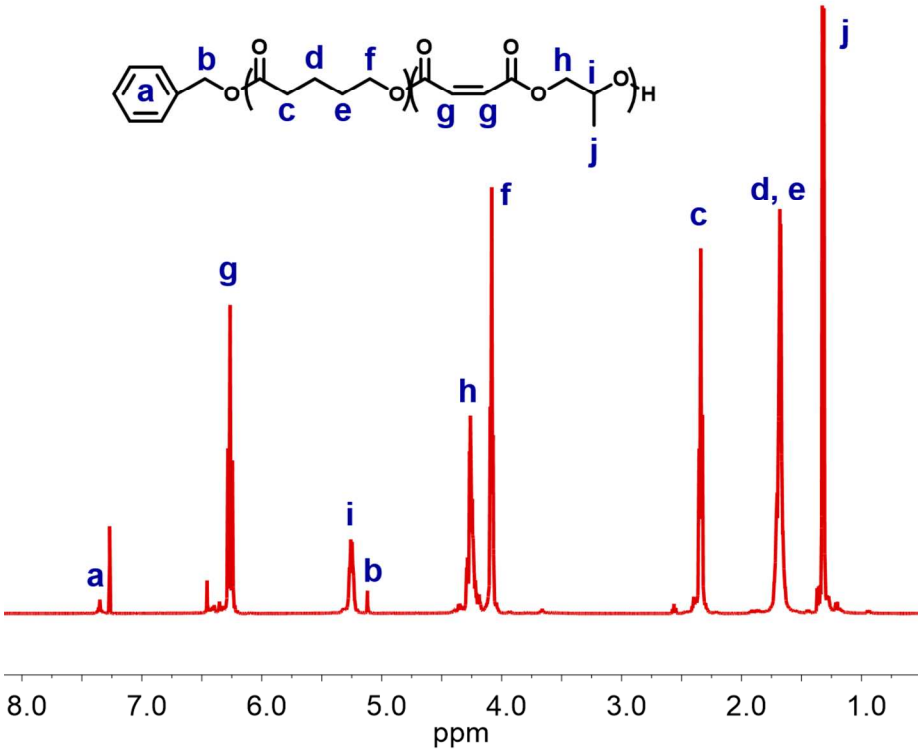

Figure 5: ^{1}H NMR spectra of poly(δ-valerolactone-*b*-propylene maleate) (500 MHz, CDCl3, 303 K).

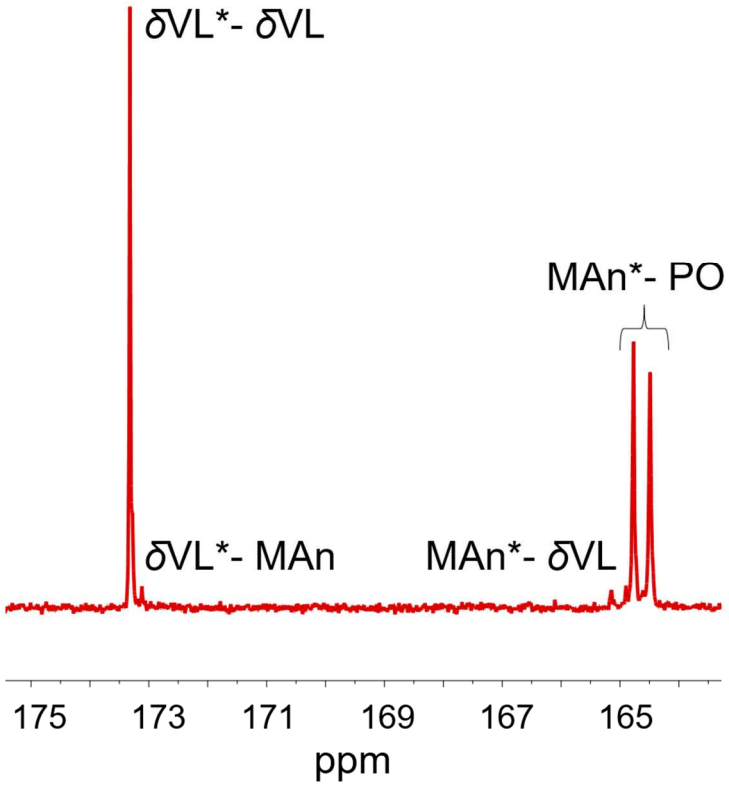

Figure 6: ^{13}C NMR spectra of the carbonyl diad region of poly(*δ*-valerolactone-*b*-propylene maleate) (125 MHz, CDCl3, 303 K).

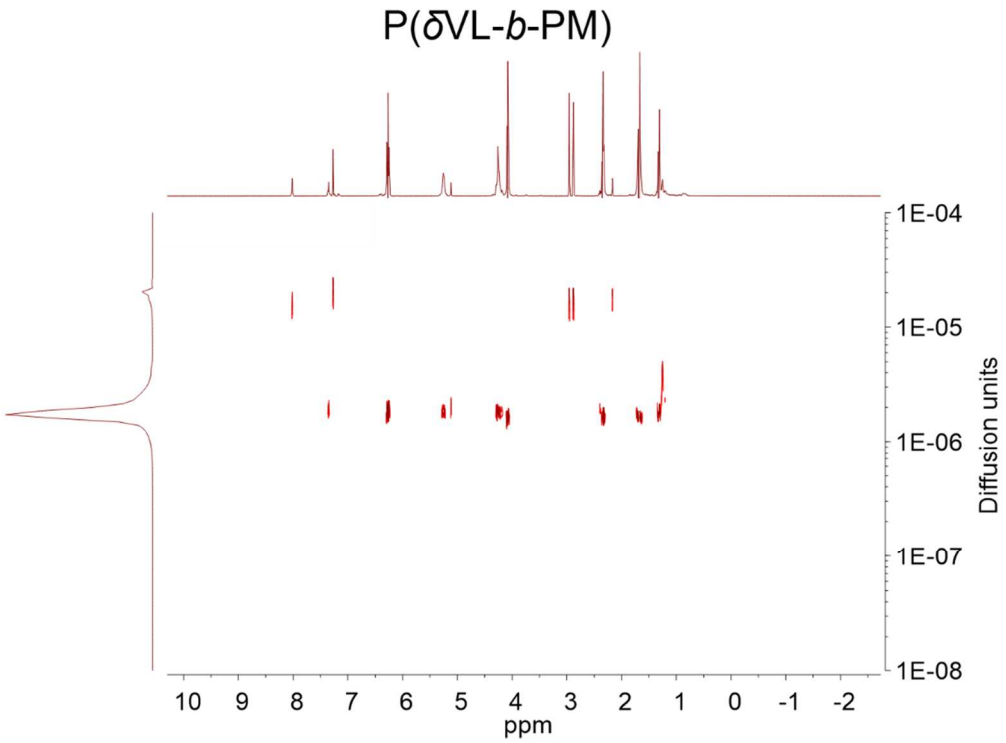

Figure 7: DOSY NMR spectra of poly(*δ*-valerolactone-*b*-propylene maleate) (500 MHz, 298 K, CDCl3).

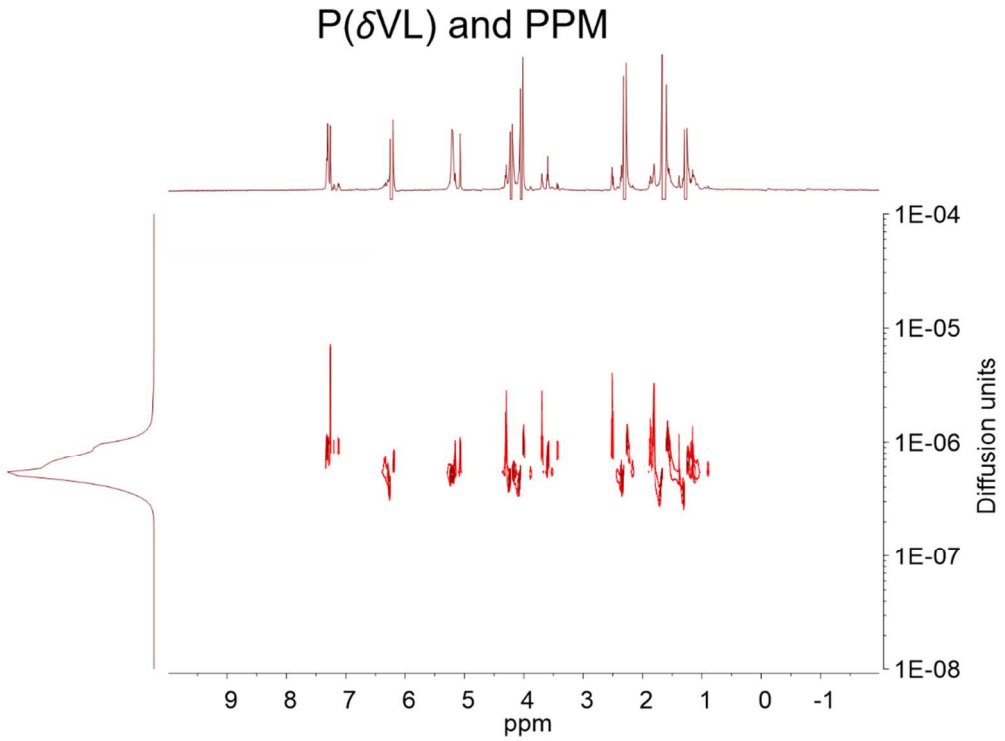

Figure 8: DOSY NMR spectra of poly(*δ*-valerolactone) and poly(propylene maleate) (500 MHz, 298 K, CDCl3).

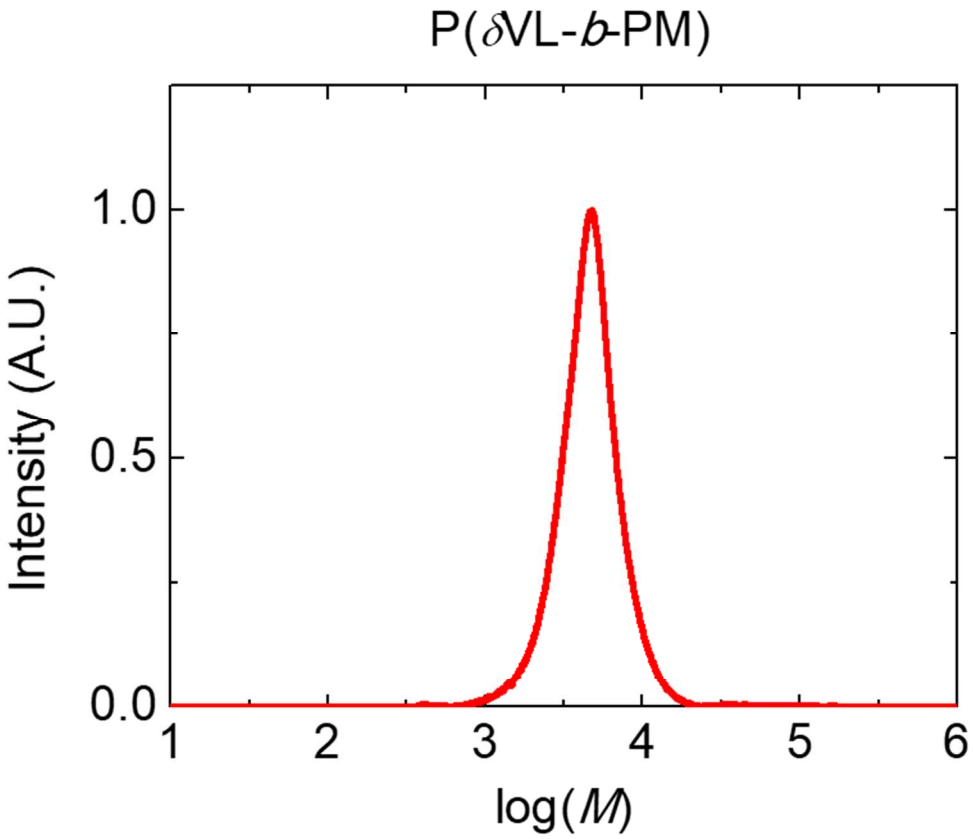

Figure 9: SEC chromatogram for poly(*δ*-valerolactone-*b*-propylene maleate). The molecular mass determined against poly(styrene) standards.

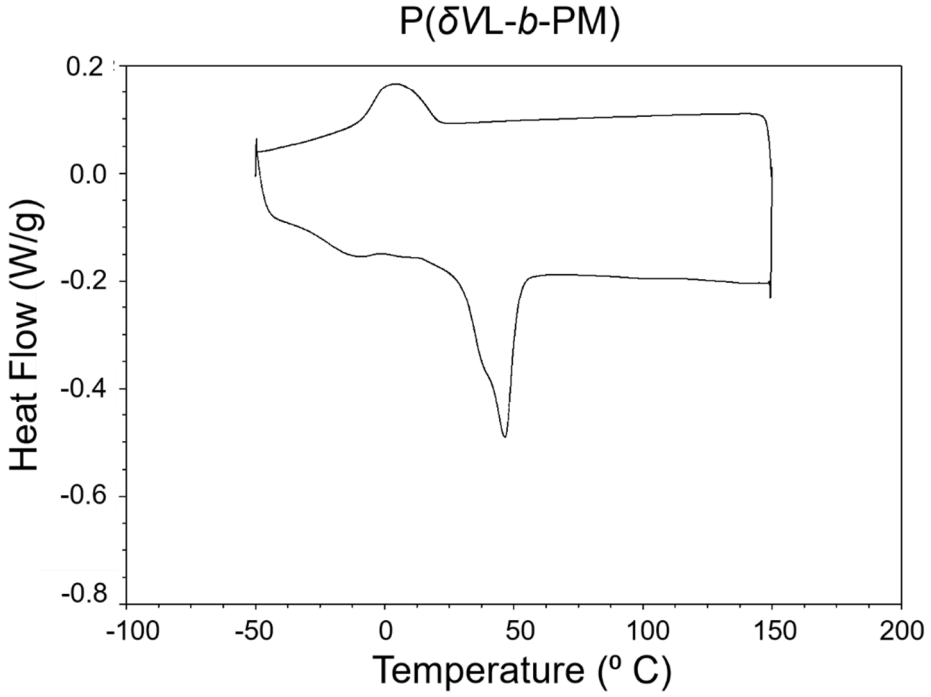

Figure 10: DSC thermograms (second heating curve, between -50 and 150 °C) for poly(*δ*-valerolactone-*b*-propylene maleate).

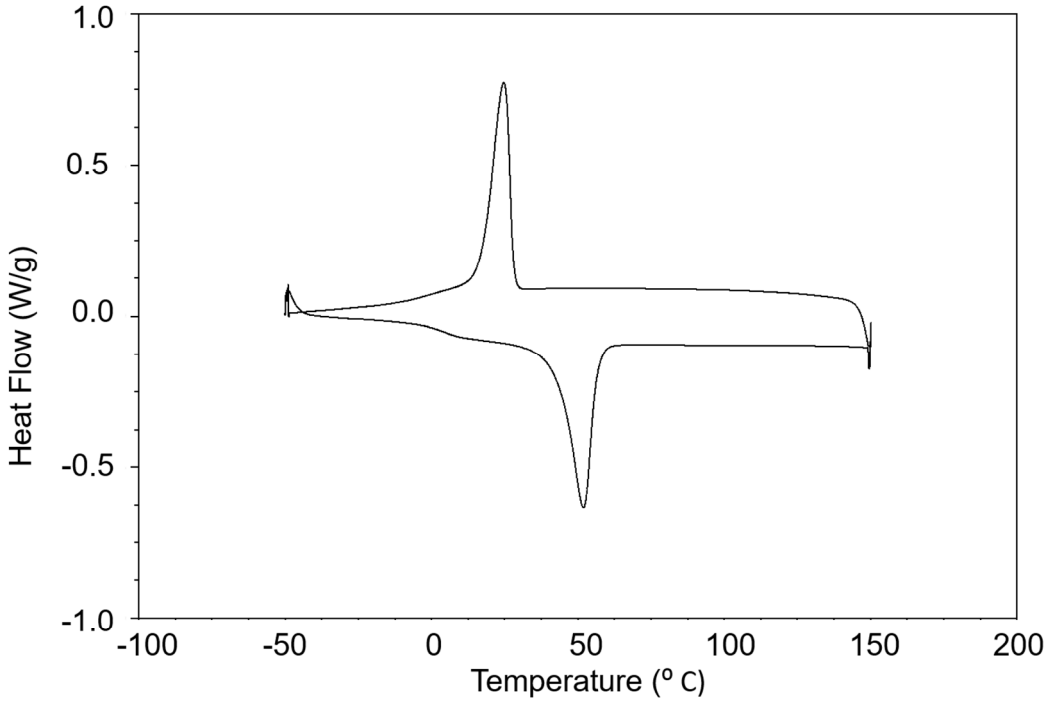

Figure 11: DSC thermograms (second heating curve, between -50 and 150 °C) for poly(*δ*-valerolactone) and poly(propylene maleate).

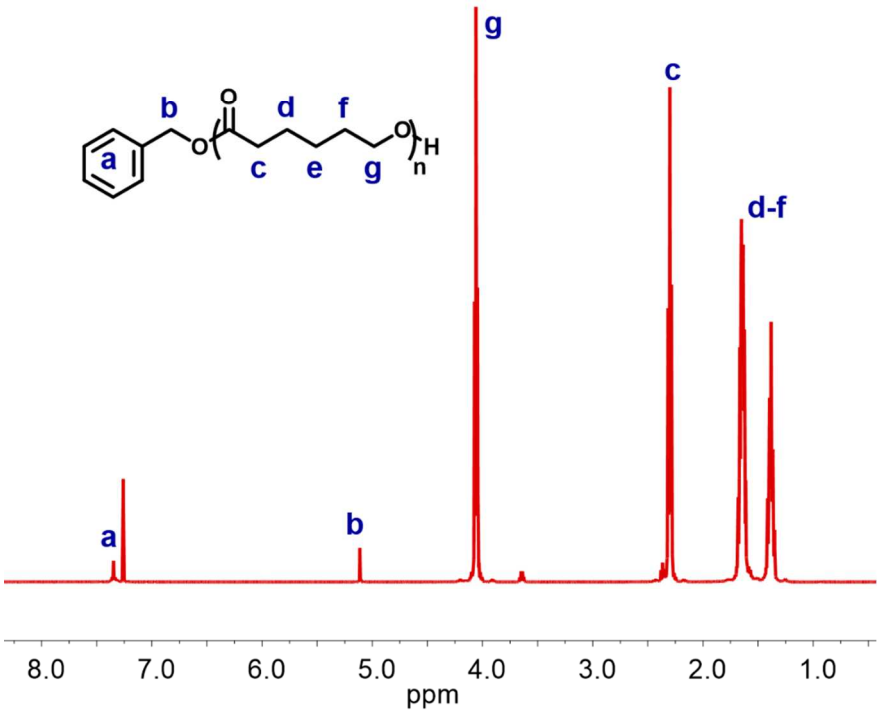

Figure 12: ^{1}H NMR spectra of poly(*ε*-caprolactone) (500 MHz, CDCl3, 303 K).

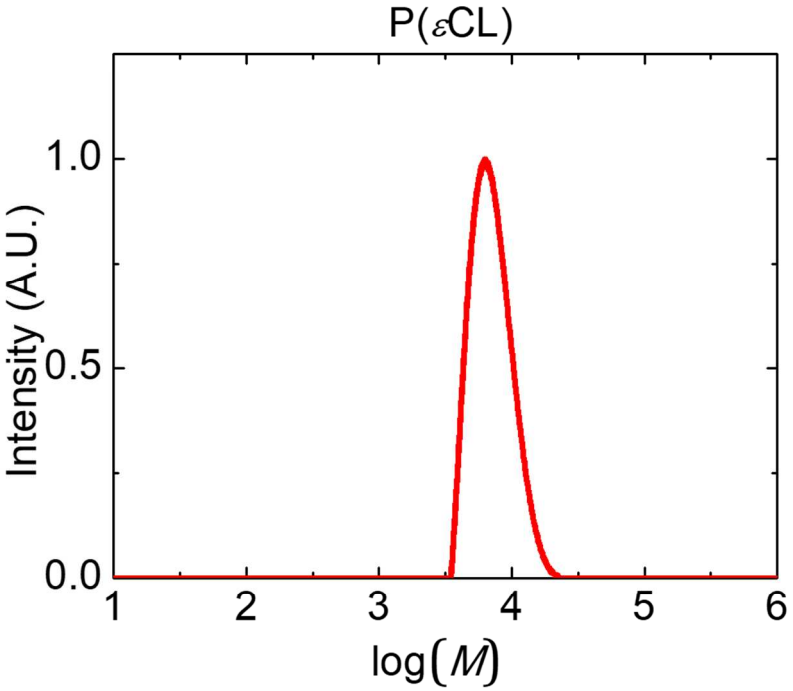

Figure 13: SEC chromatogram of poly(*ε*-caprolactone). The molecular mass determined against poly(styrene) standards.

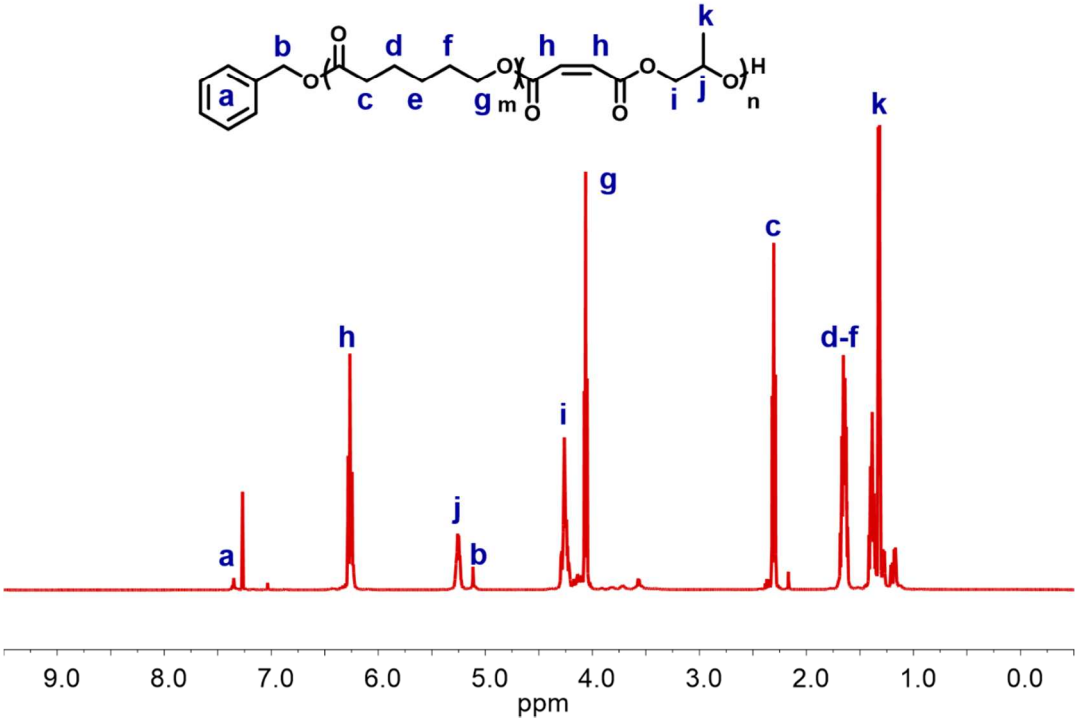

Figure 14: ^{1}H NMR spectra of poly(*ε*-caprolactone-*b*-propylene maleate) (500 MHz, CDCl3, 303 K).

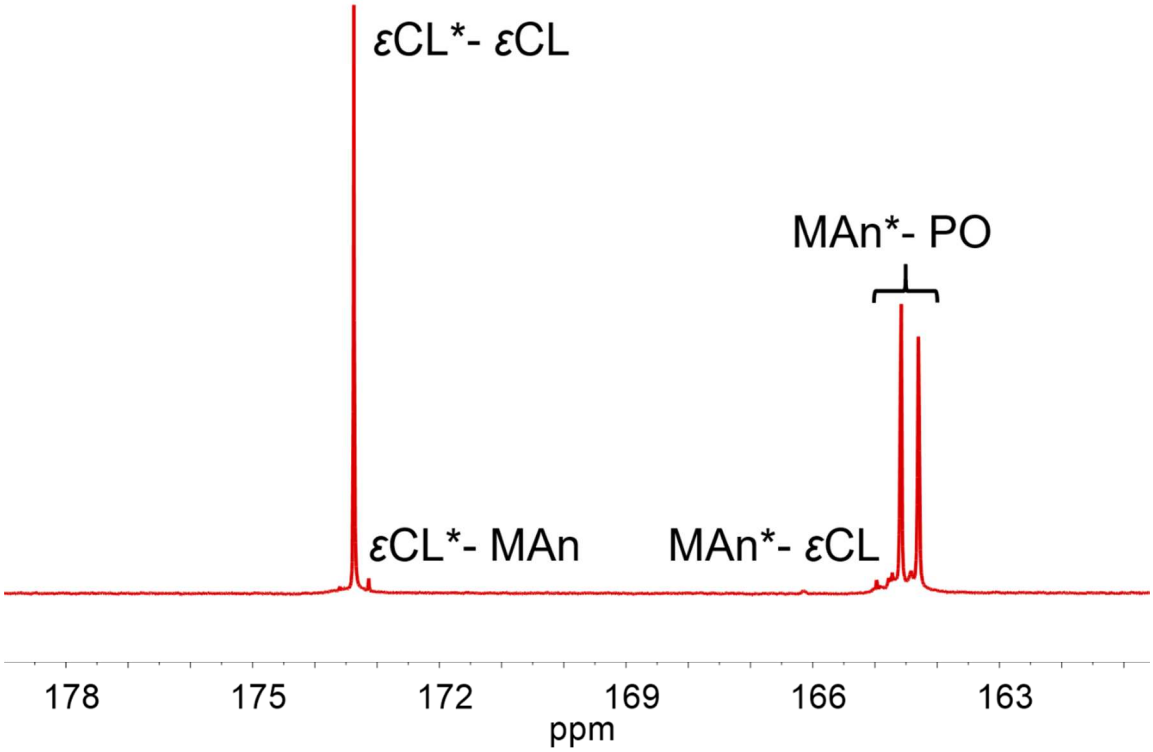

Figure 15: ^{13}C NMR spectra of the carbonyl diad region of poly(*ε*-caprolactone-*b*-propylene maleate) (125 MHz, CDCl3, 303 K).

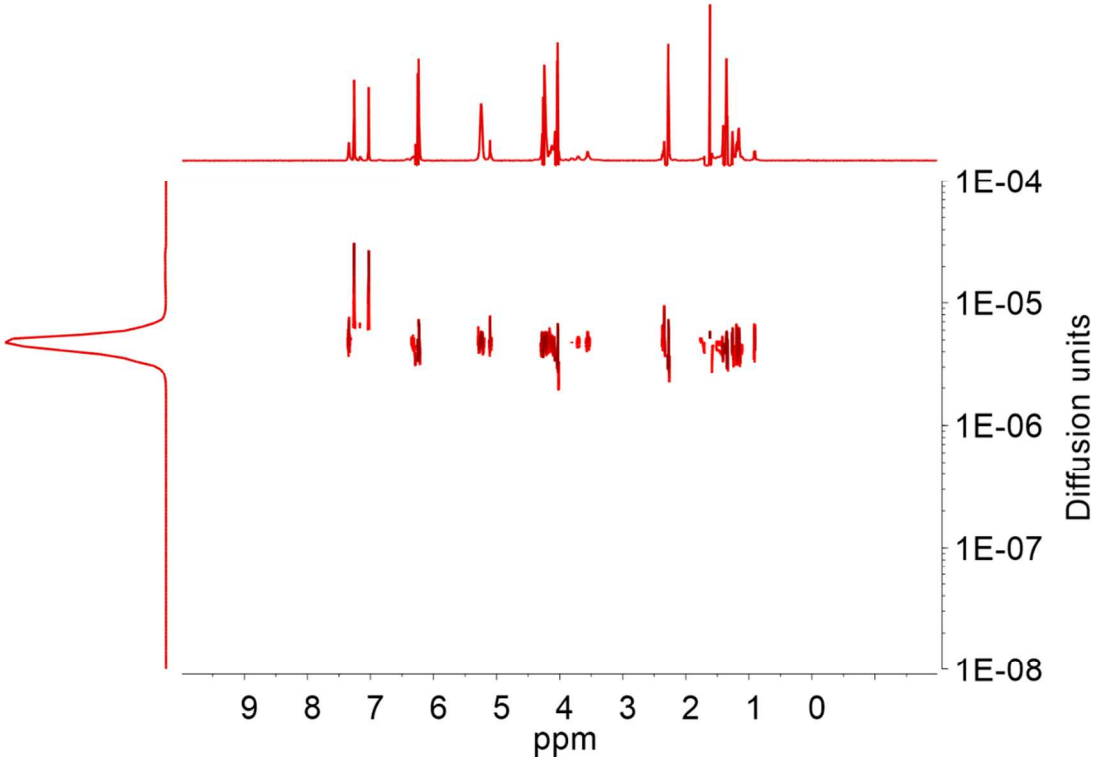

Figure 16: DOSY NMR spectra of poly(*ε*-caprolactone-*b*-propylene maleate) (500 MHz, 298 K, CDCl3).

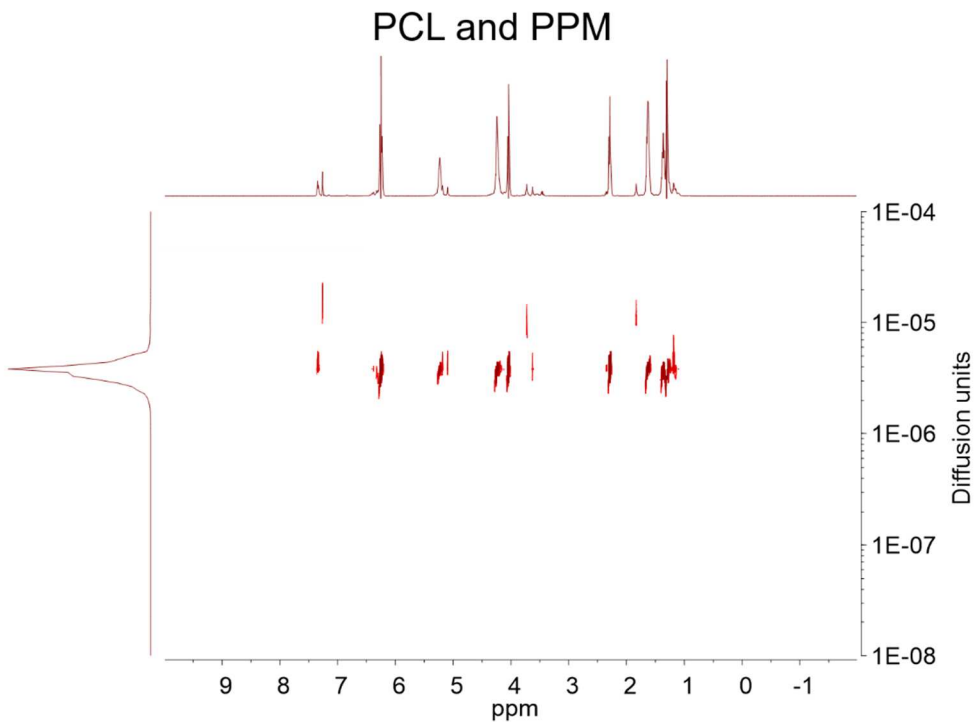

Figure 17: DOSY NMR spectra of poly(*ε*-caprolactone) and poly(propylene maleate) (500 MHz, 298 K, CDCl3).

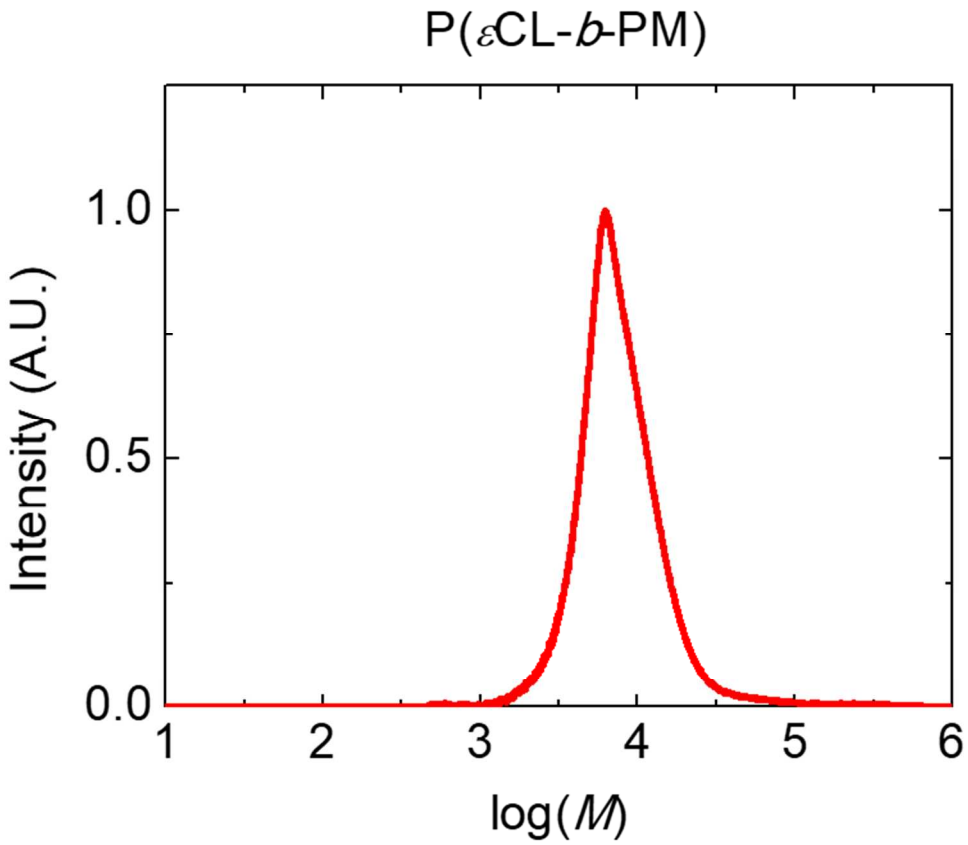

Figure 18: SEC chromatogram for poly(*ε*-caprolactone-*b*-propylene maleate). The molecular mass determined against poly(styrene) standards.

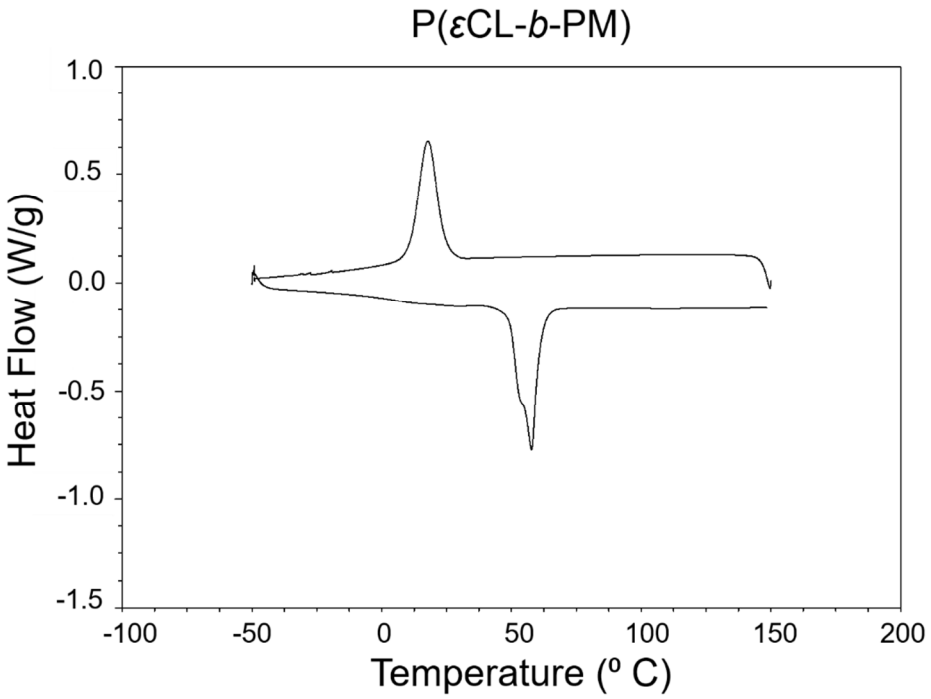

Figure 19: DSC thermograms (second heating curve, between -50 and 150 °C) for poly(*ε*-caprolactone-*b*-propylene maleate).

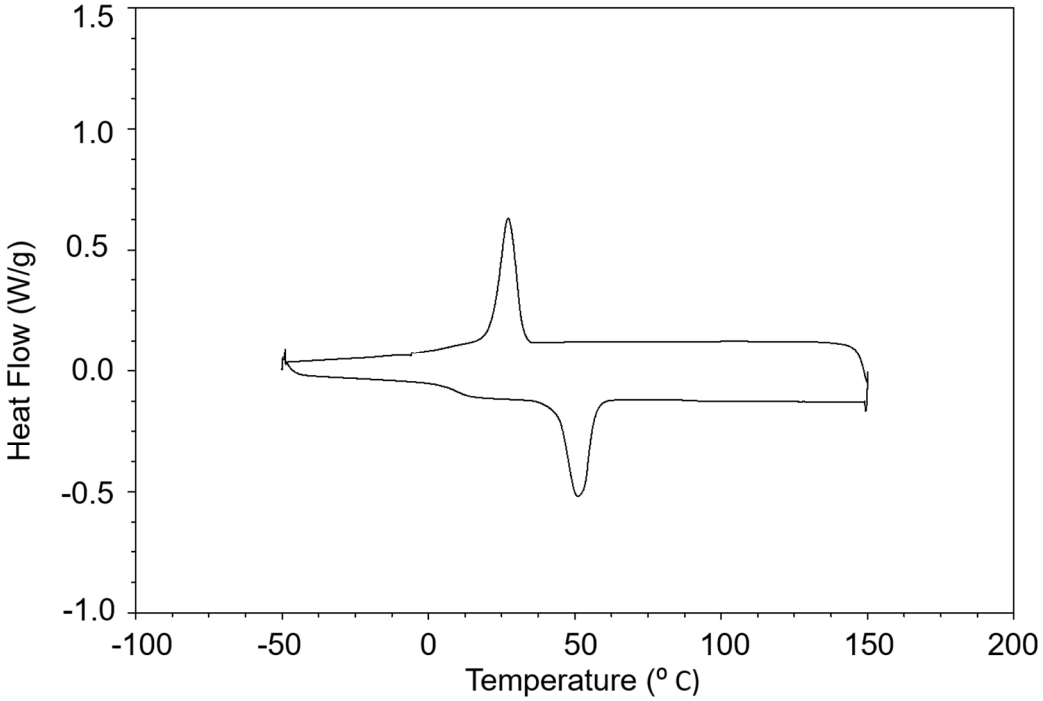

Figure 20: DSC thermograms (second heating curve, between -50 and 150 °C) for poly(*ε*-caprolactone) and poly(propylene maleate).

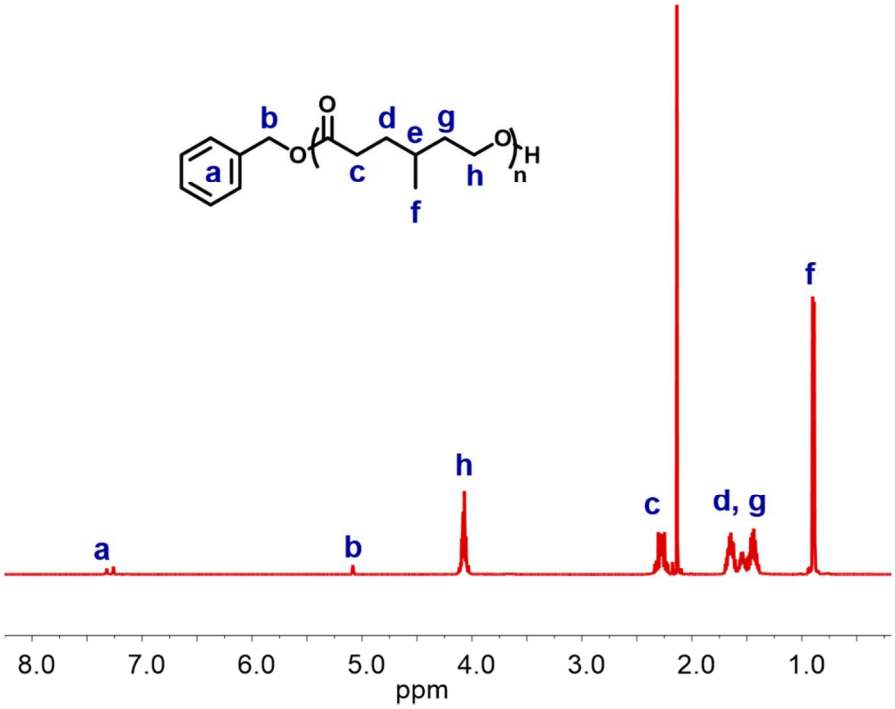

Figure 21: ^{1}H NMR spectra of poly(*γ*-methyl-*ε*-caprolactone) (500 MHz, CDCl3, 303 K).

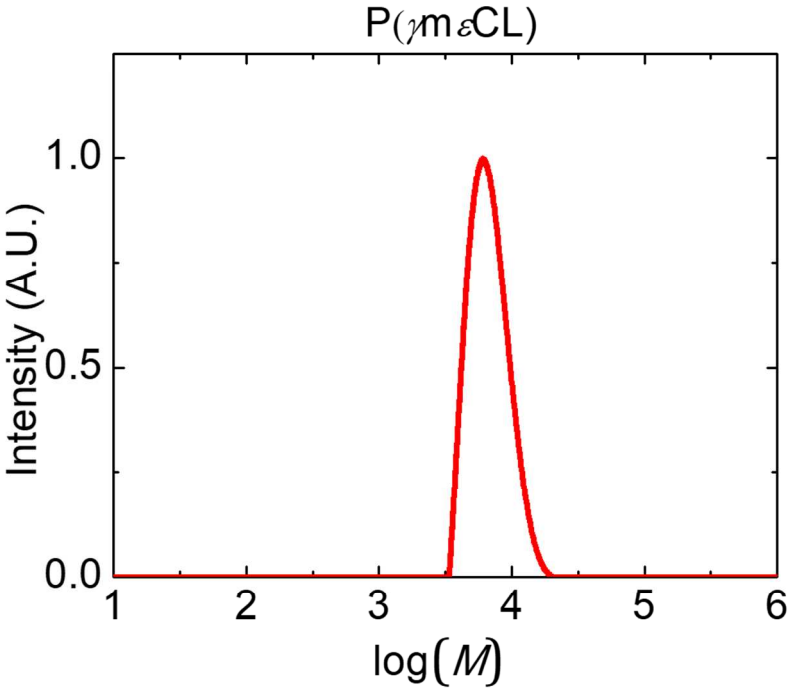

Figure 22: SEC chromatogram for poly(*γ*-methyl-*ε*-caprolactone). The molecular mass determined against poly(styrene) standards.

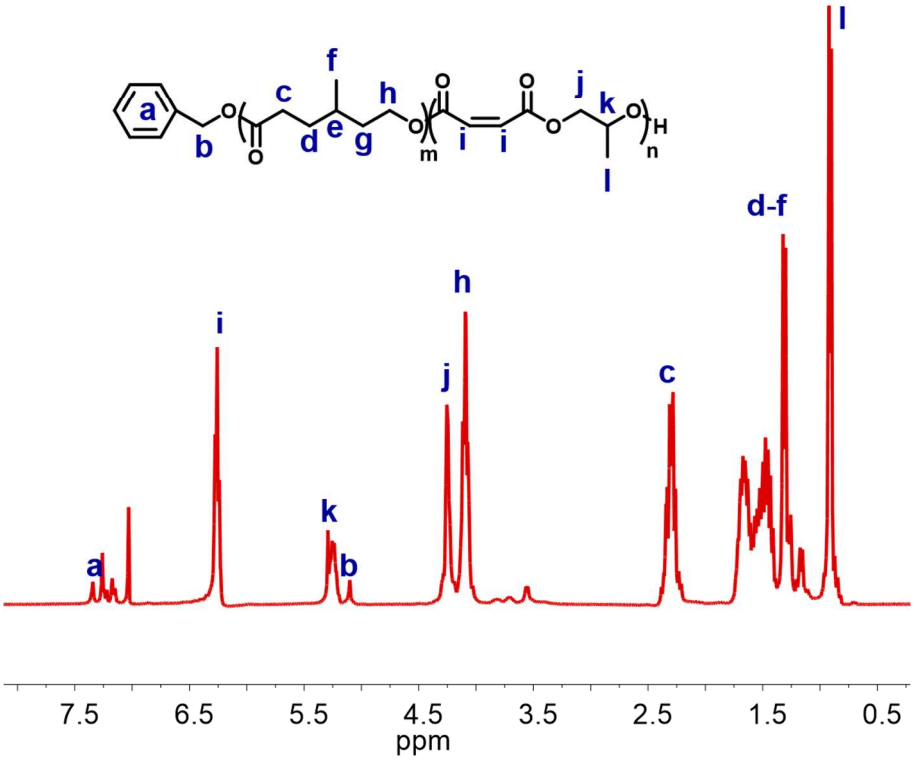

Figure 23: ^{1}H NMR spectra of poly(*γ*-methyl-*ε*-caprolactone-*b*-propylene maleate) (500 MHz, CDCl3, 303 K).

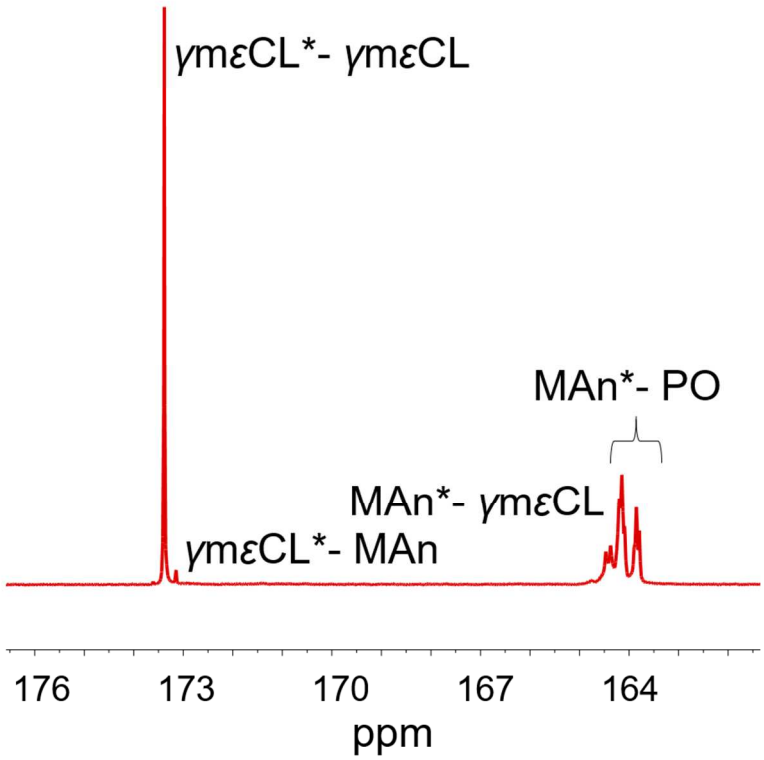

Figure 24: ^{13}C NMR spectra of the carbonyl diad region of poly(*γ*-methyl-*ε*-caprolactone-*b*-propylene maleate) (125 MHz, CDCl3, 303 K).

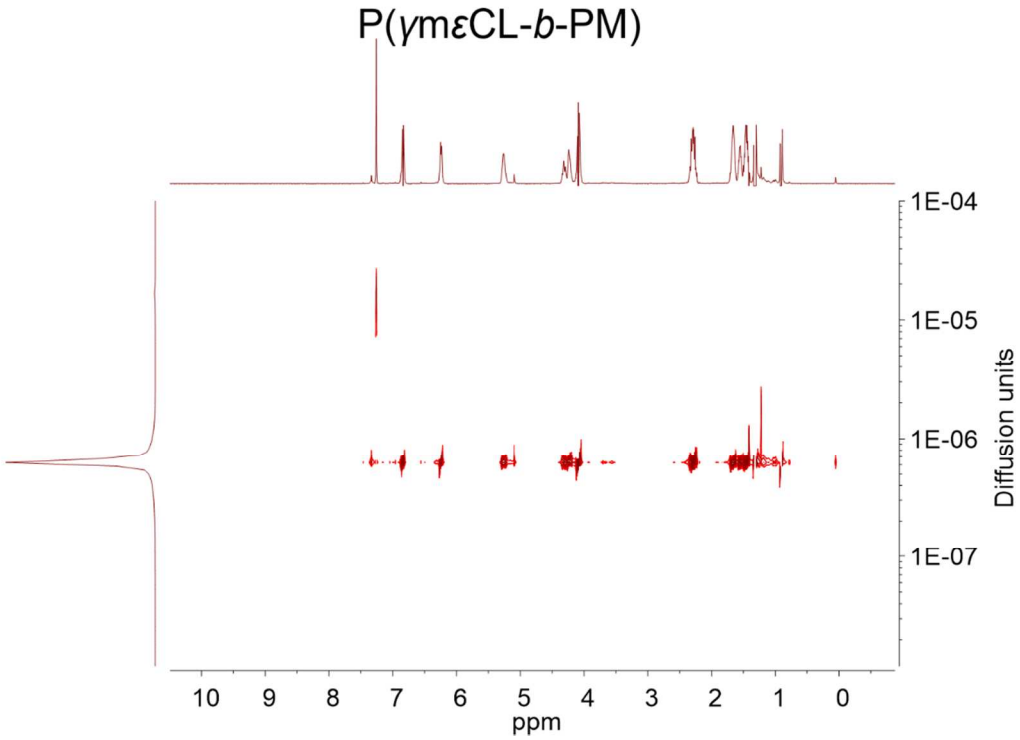

Figure 25: DOSY NMR spectra of poly(*γ*-methyl-*ε*-caprolactone-*b*-propylene maleate) (500 MHz, 298 K, CDCl3).

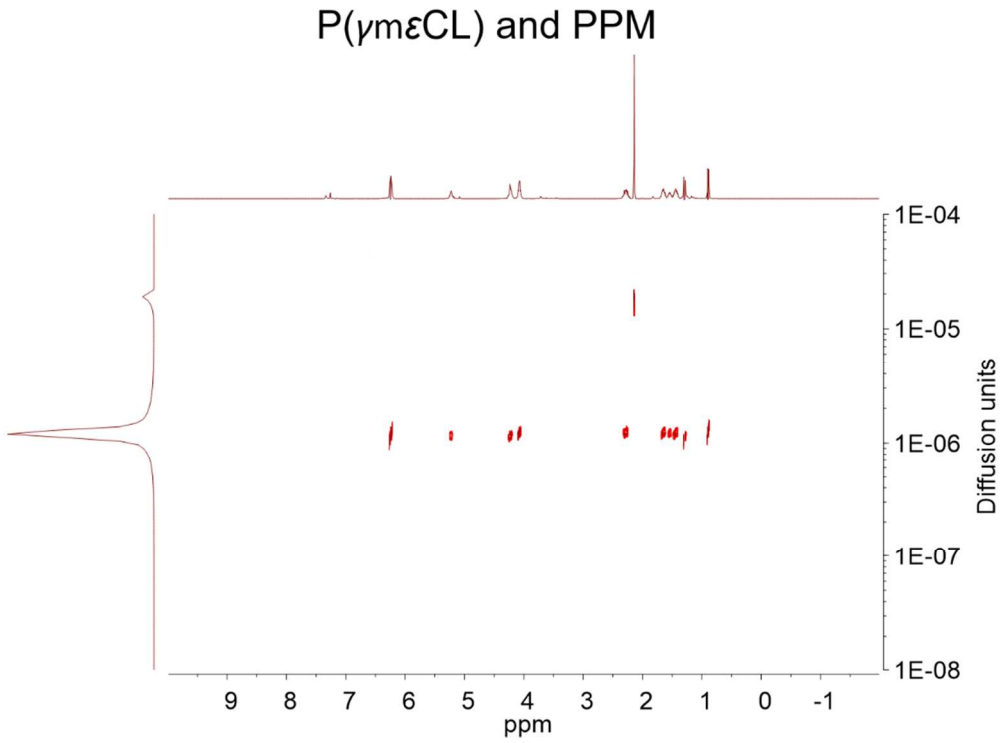

Figure 26: DOSY NMR spectra of poly(*γ*-methyl-*ε*-caprolactone) and poly(propylene maleate) (500 MHz, 298 K, CDCl3).

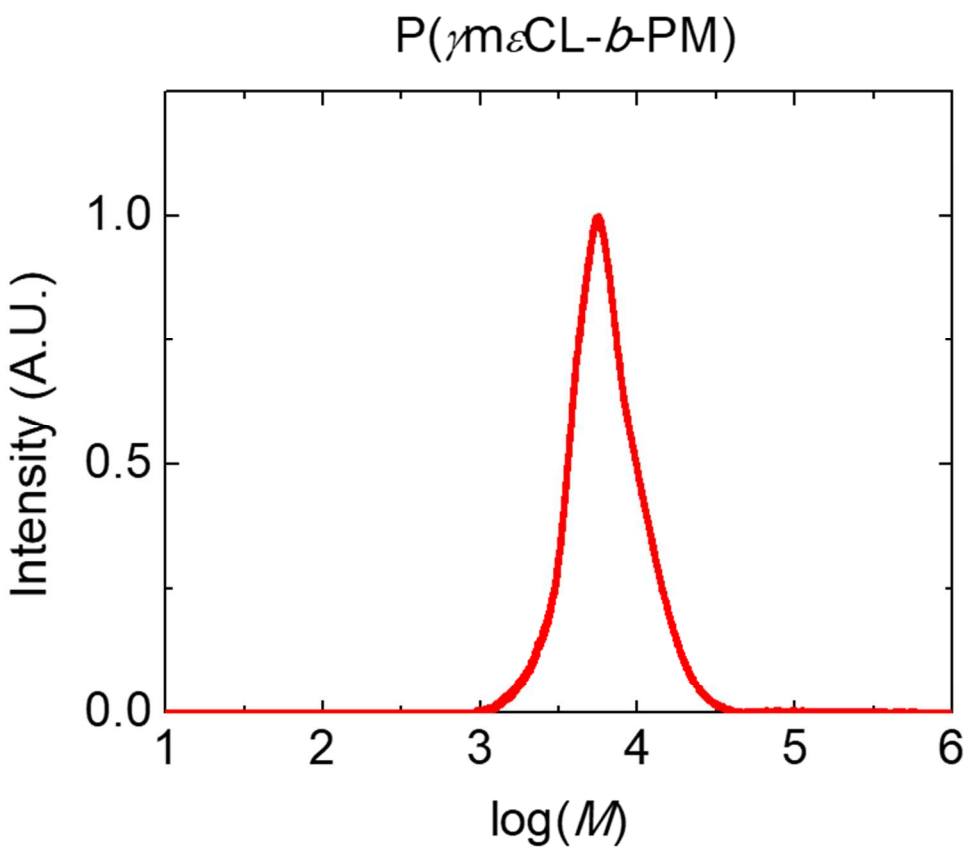

Figure 27: SEC chromatogram for poly(*γ*-methyl-*ε*-caprolactone-*b*-propylene maleate). The molecular mass determined against poly(styrene) standards.

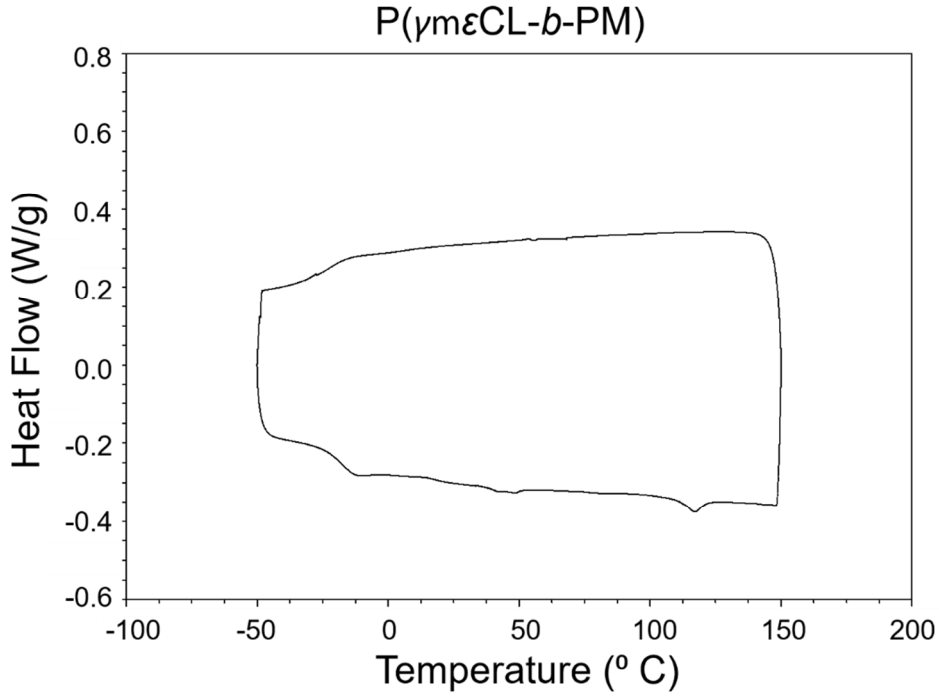

Figure 28: DSC thermograms (second heating curve, between -50 and 150 °C) for poly(*γ*-methyl-*ε*-caprolactone-*b*-propylene maleate).

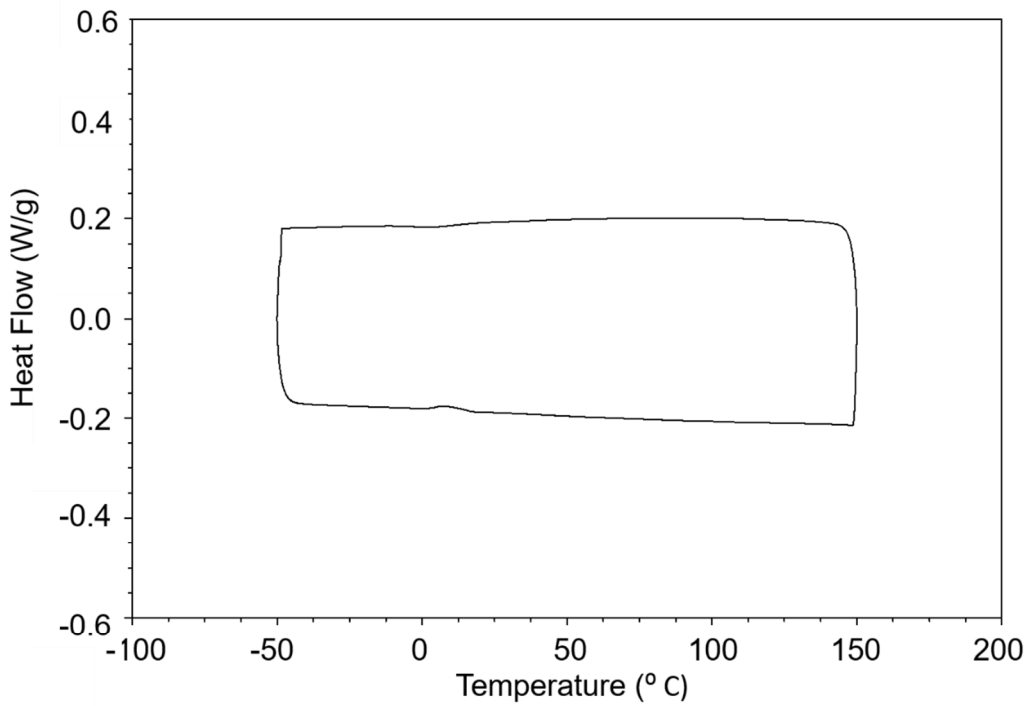

Figure 29: DSC thermograms (second heating curve, between -50 and 150 °C) for poly(*γ*-methyl-*ε*-caprolactone) and poly(propylene maleate).

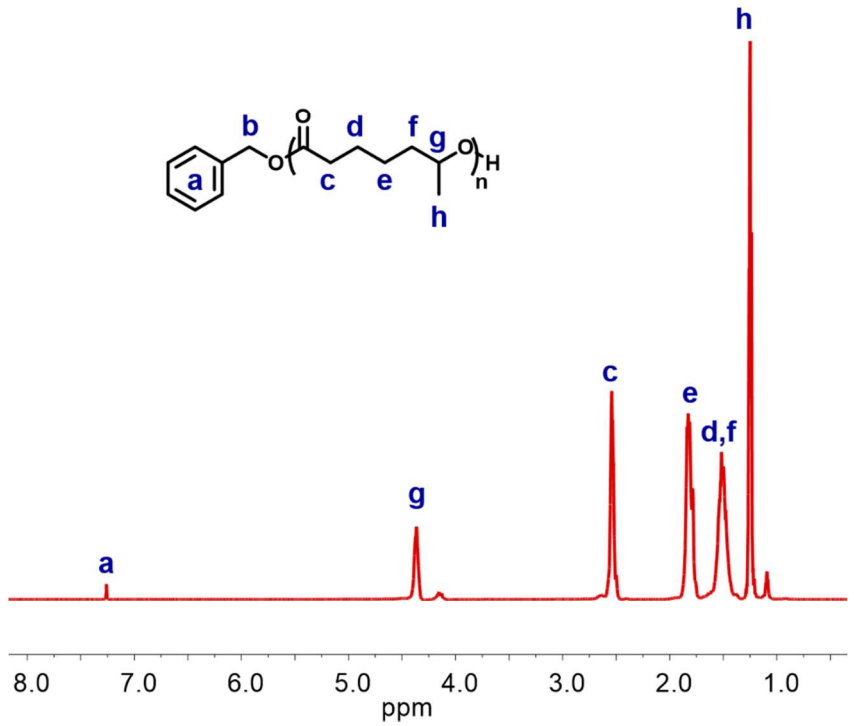

Figure 30: ^{1}H NMR spectra of poly(*ε*-heptalactone) (500 MHz, CDCl3, 303 K).

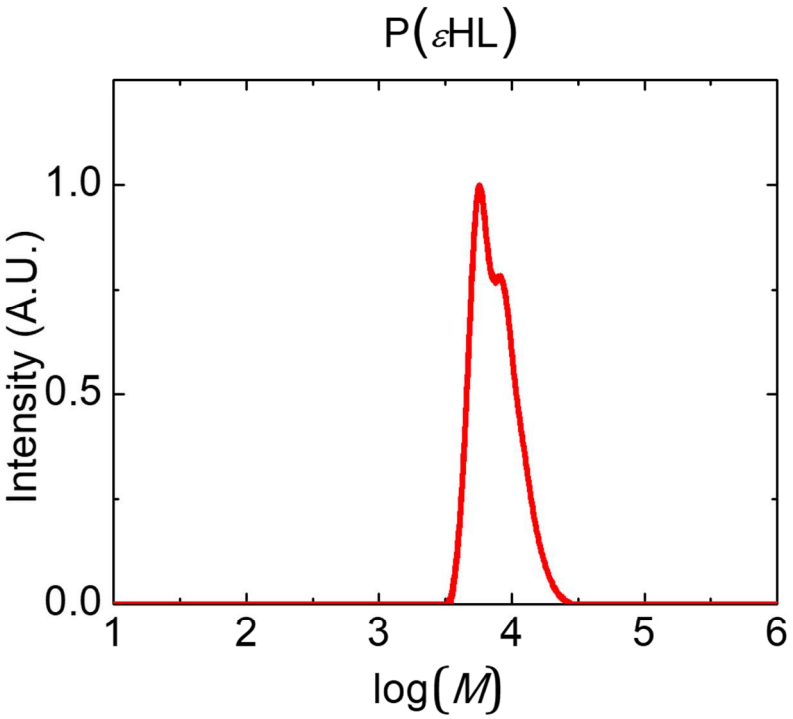

Figure 31: SEC chromatogram for poly(*ε*-heptalactone). The molecular mass determined against poly(styrene) standards.

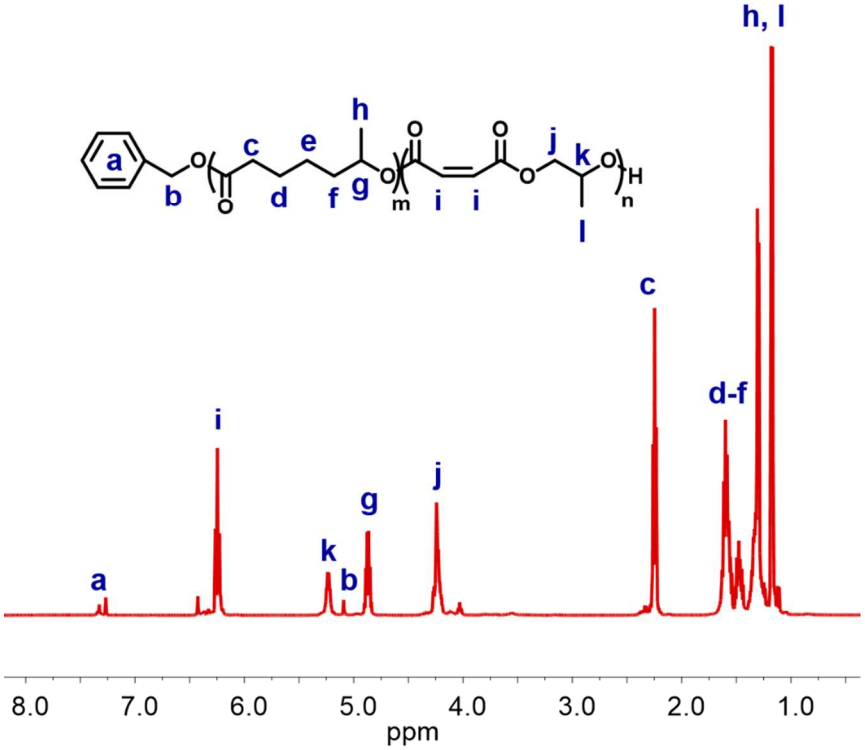

Figure 32: ^{1}H NMR spectra of poly(*ε*-heptalactone-*b*-propylene maleate) (500 MHz, CDCl3, 303 K).

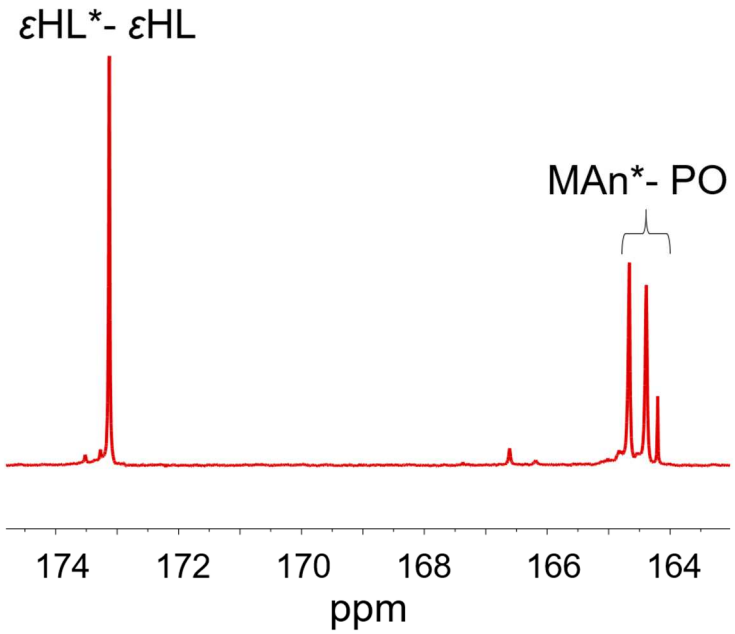

Figure 33: ^{13}C NMR spectra of the carbonyl diad region of poly(*ε*-heptalactone-*b*-propylene maleate) (125 MHz, CDCl3, 303 K).

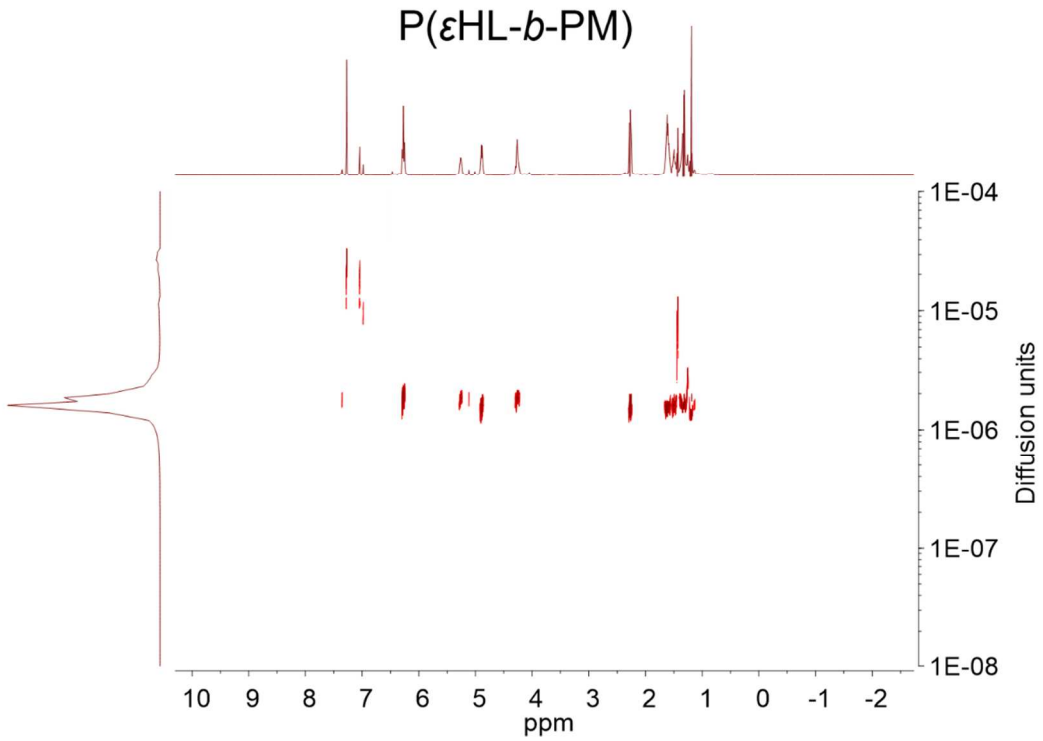

Figure 34: DOSY NMR spectra of poly(*ε*-heptalactone-*b*-propylene maleate) (500 MHz, 298 K, CDCl3).

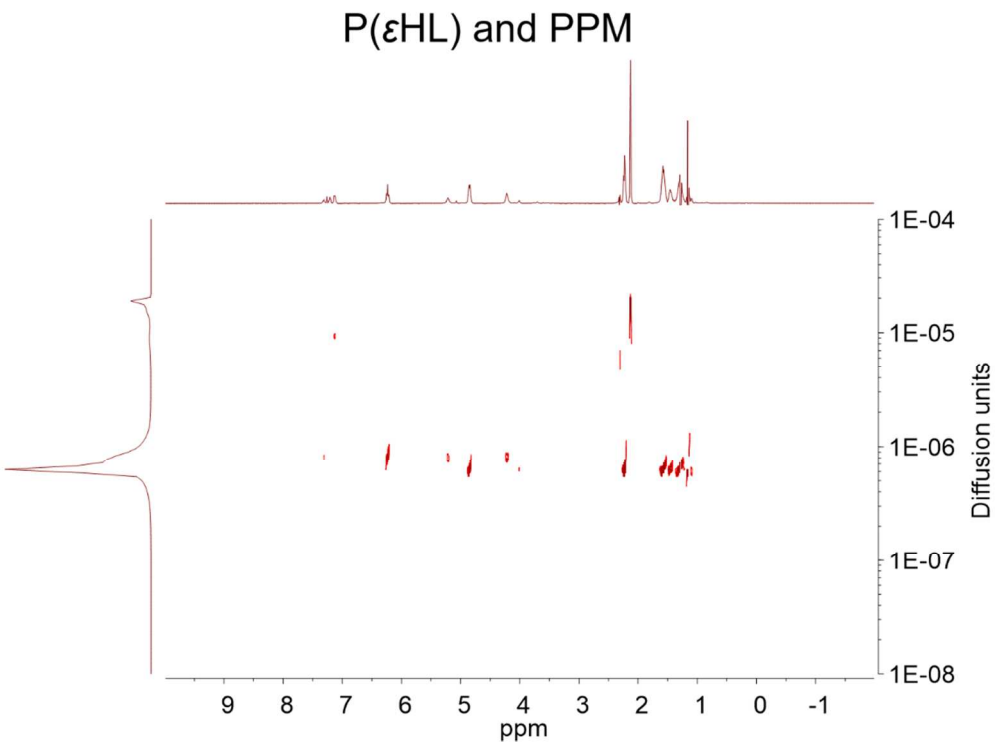

Figure 35: DOSY NMR spectra of poly(*ε*-heptalactone) and poly(propylene maleate) (500 MHz, 298 K, CDCl3).

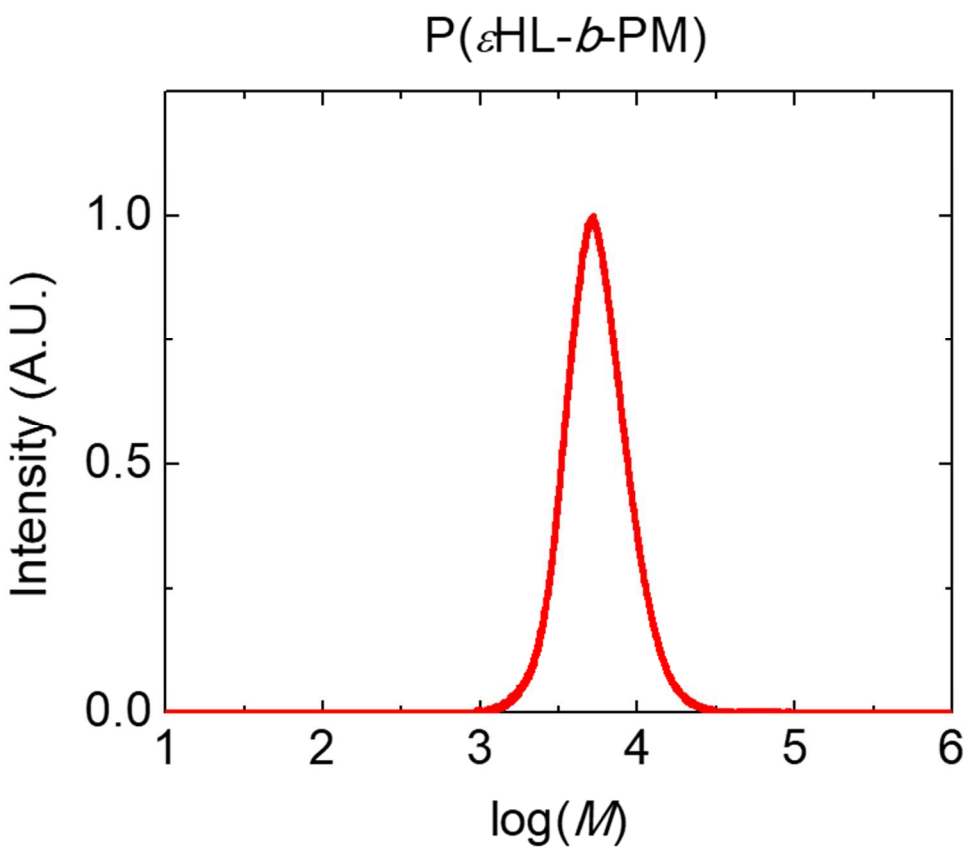

Figure 36: SEC chromatogram for poly(*ε*-heptalactone-*b*-propylene maleate). The molecular mass determined against poly(styrene) standards.

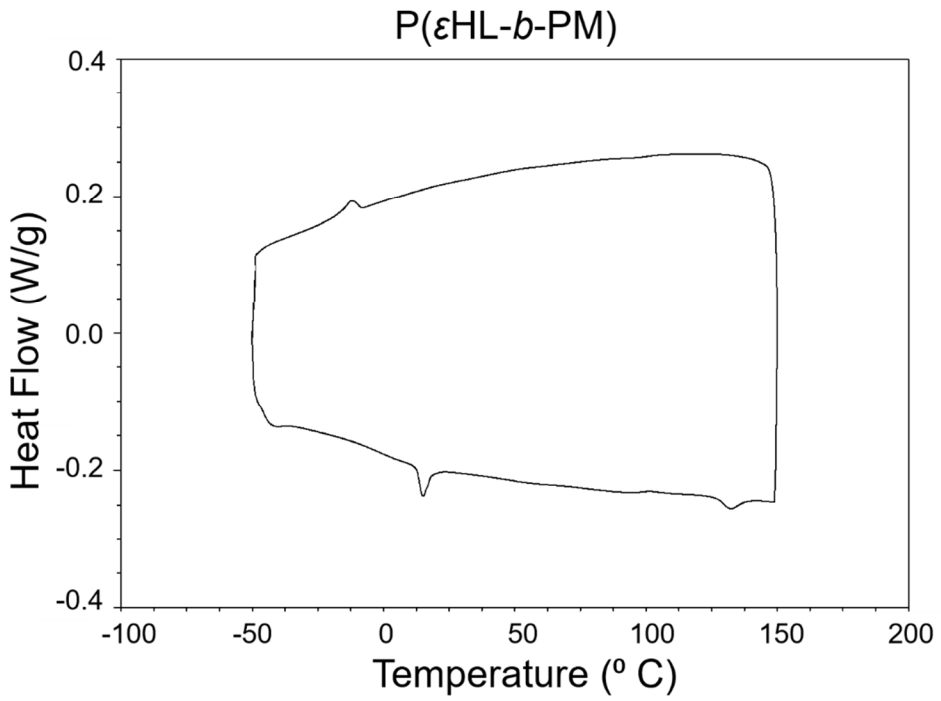

Figure 37: DSC thermograms (second heating curve, between -50 and 150 °C) for poly(*ε*-heptalactone-*b*-propylene maleate).

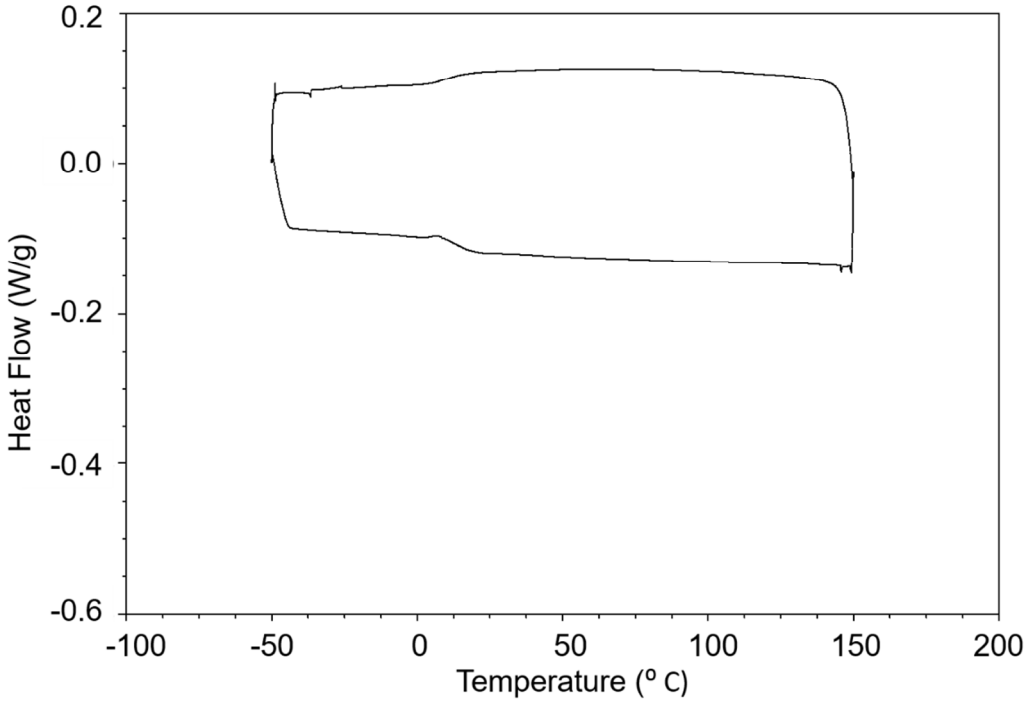

Figure 38: DSC thermograms (second heating curve, between -50 and 150 °C) for poly(*ε*-heptalactone) and poly(propylene maleate).

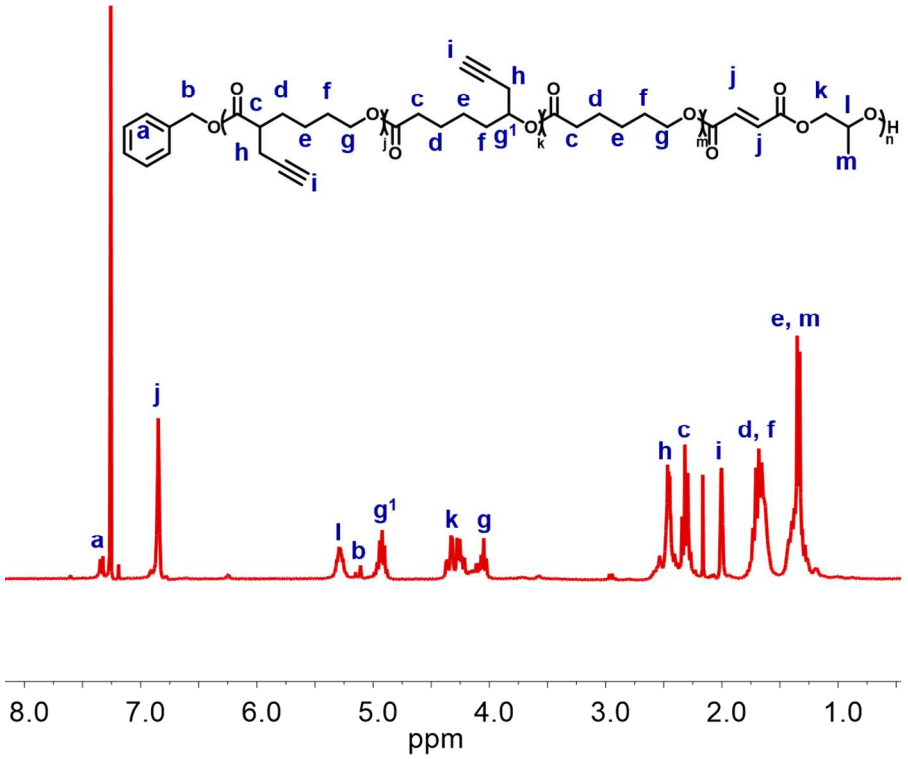

Figure 39: ^{1}H NMR spectra of poly(*ϑ*-propargyl-*ε*-nonalactone-*b*-*ε*-caprolactone-*b*-propylene maleate) (500 MHz, CDCl3, 303 K).

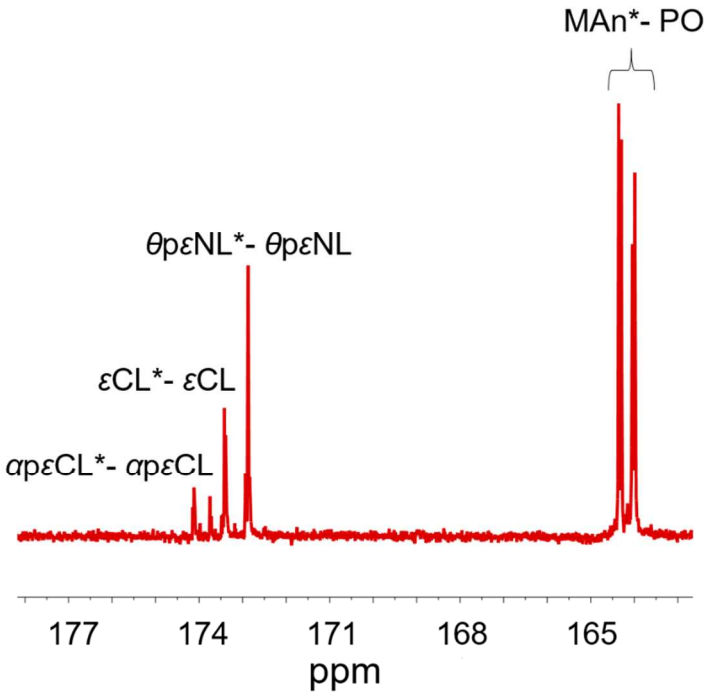

Figure 40: ^{13}C NMR spectra of the carbonyl diad region of poly(*ϑ*-propargyl-*ε*-nonalactone-*b*-*ε*-caprolactone-*b*-propylene maleate) (125 MHz, CDCl3, 303 K).

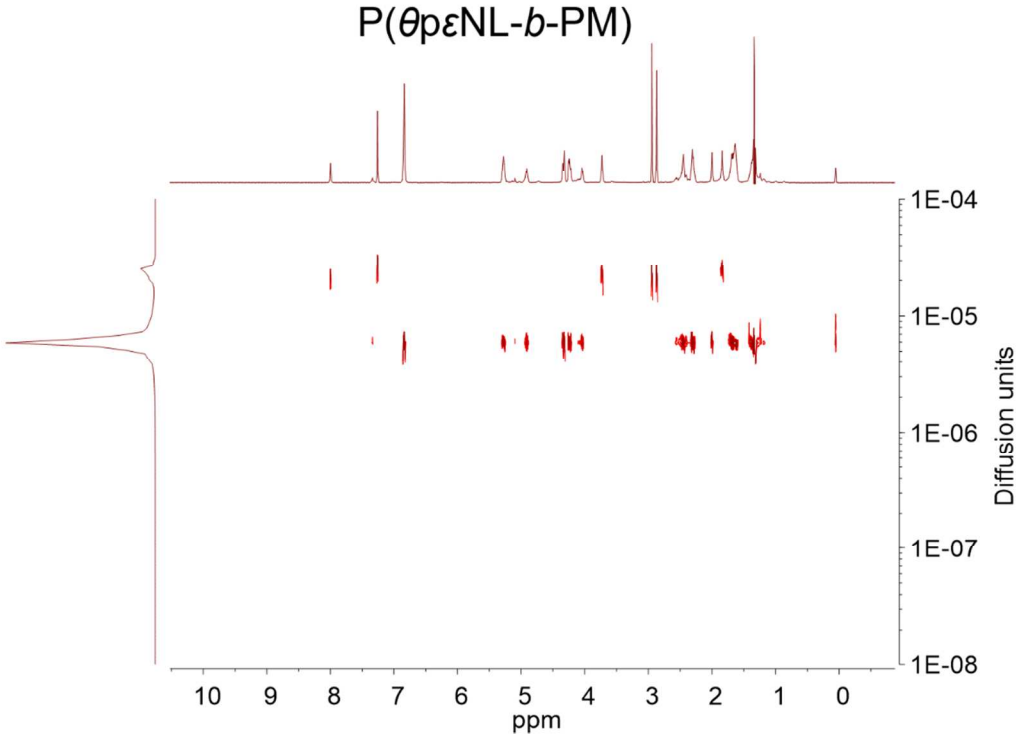

Figure 41: DOSY NMR spectra of poly(ϑ-propargyl-ε-nonalactone-*b*-ε-caprolactone-*b*-propylene maleate) (500 MHz, 298 K, CDCl3).

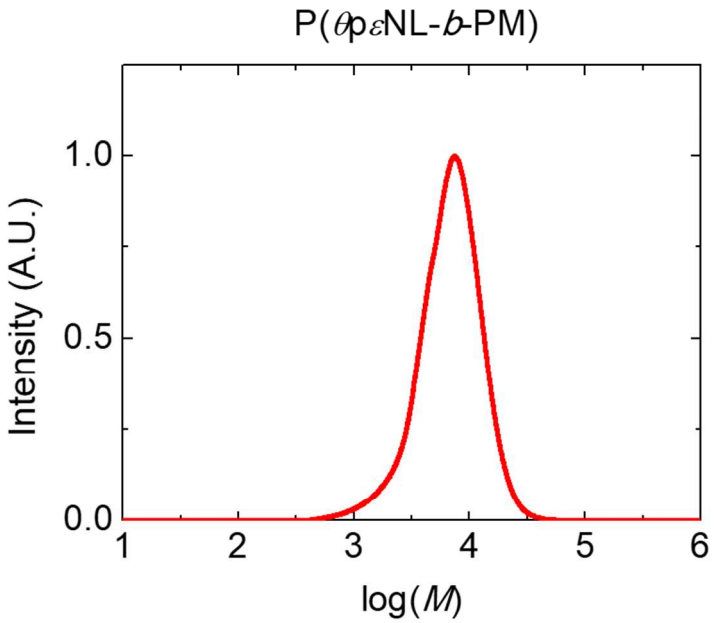

Figure 42: SEC chromatogram for poly(ϑ-propargyl-ε-nonalactone-*b*-ε-caprolactone-*b*-propylene maleate). The molecular mass determined against poly(styrene) standards.

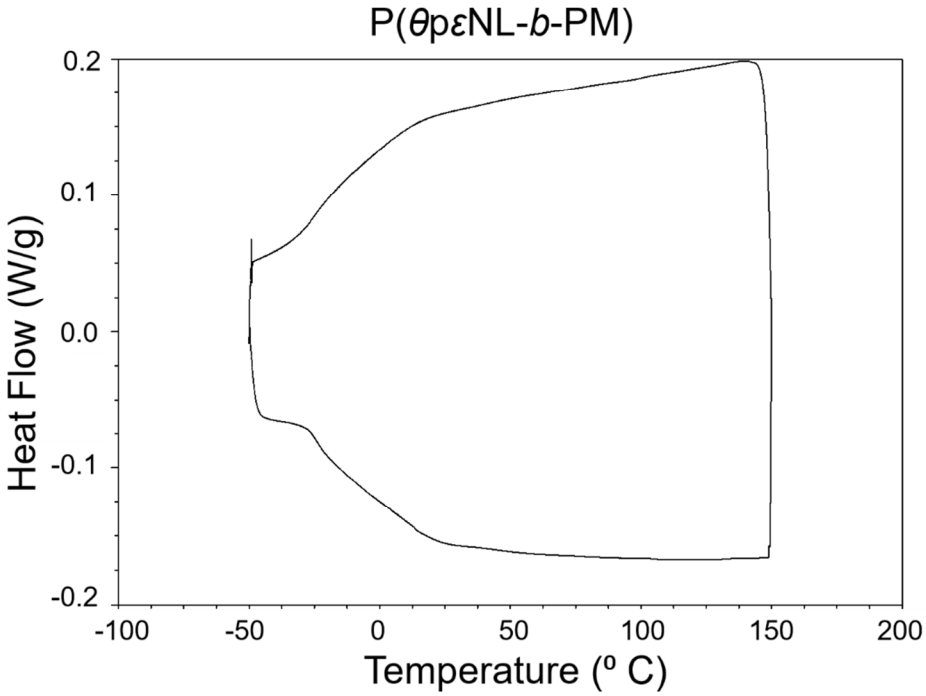

Figure 43: DSC thermograms (second heating curve, between -50 and 150 °C) for poly(*ϑ*-propargyl-*ε*-nonalactone-*b*-*ε*-caprolactone-*b*-propylene maleate).

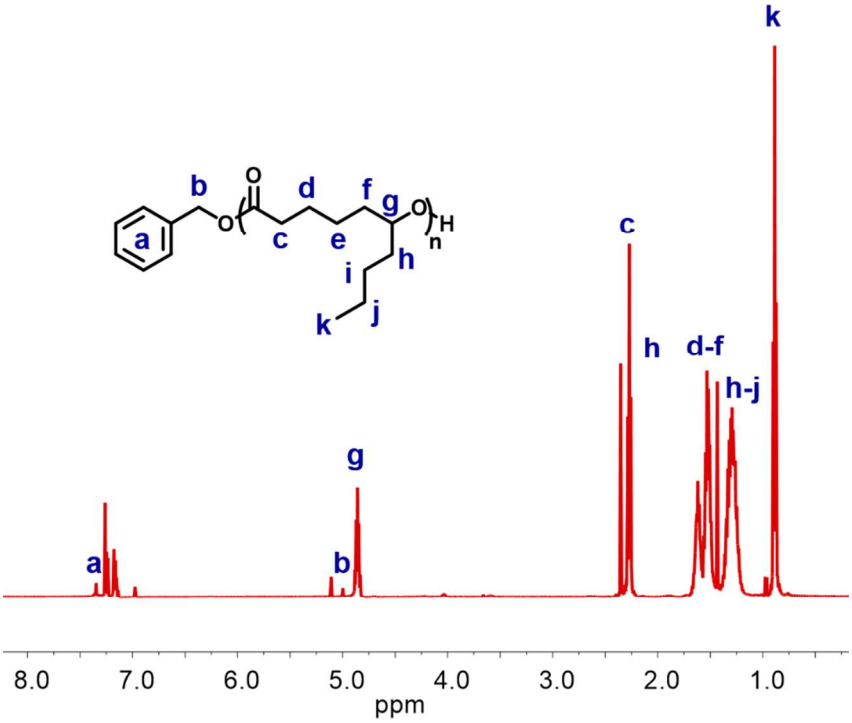

Figure 44: ^{1}H NMR spectra of poly(*ε*-decalactone) (500 MHz, CDCl3, 303 K).

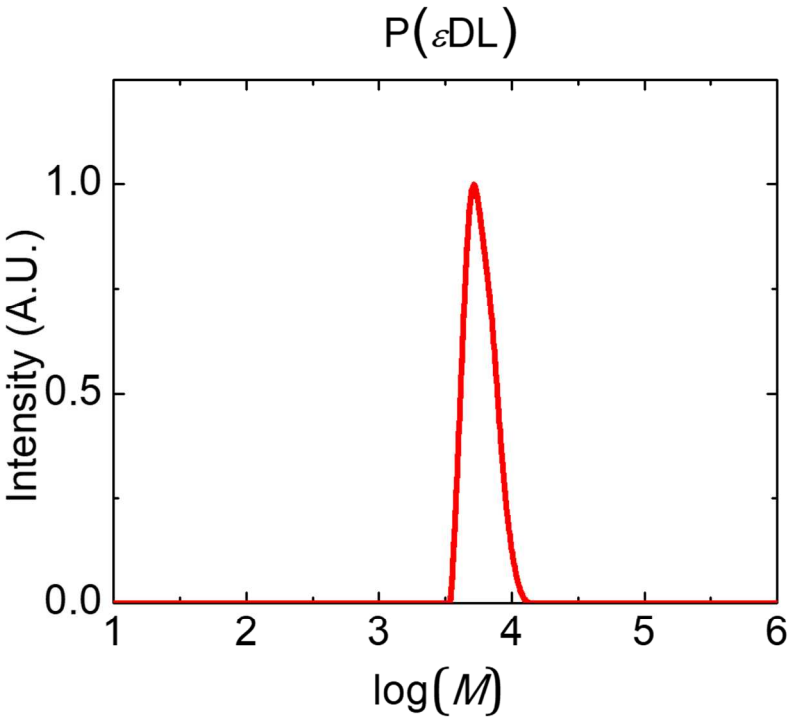

Figure 45: SEC chromatogram for poly(*ε*-decalactone). The molecular mass determined against poly(styrene) standards.

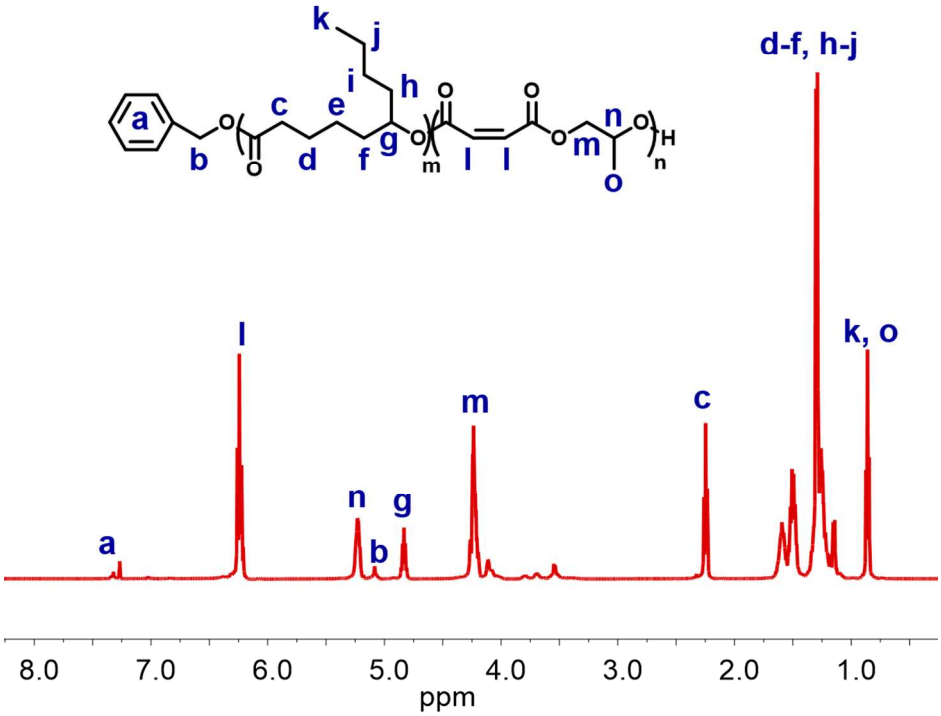

Figure 46: ^{1}H NMR spectra of poly(*ε*-decalactone-*b*-propylene maleate) (500 MHz, CDCl3, 303 K).

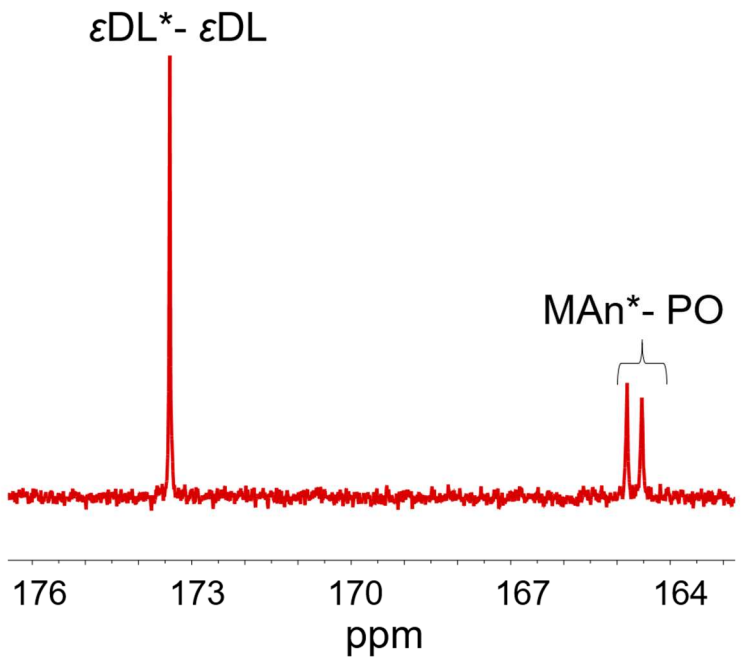

Figure 47: ^{13}C NMR spectra of the carbonyl diad region of poly(*ε*-decalactone-*b*-propylene maleate) (125 MHz, CDCl3, 303 K).

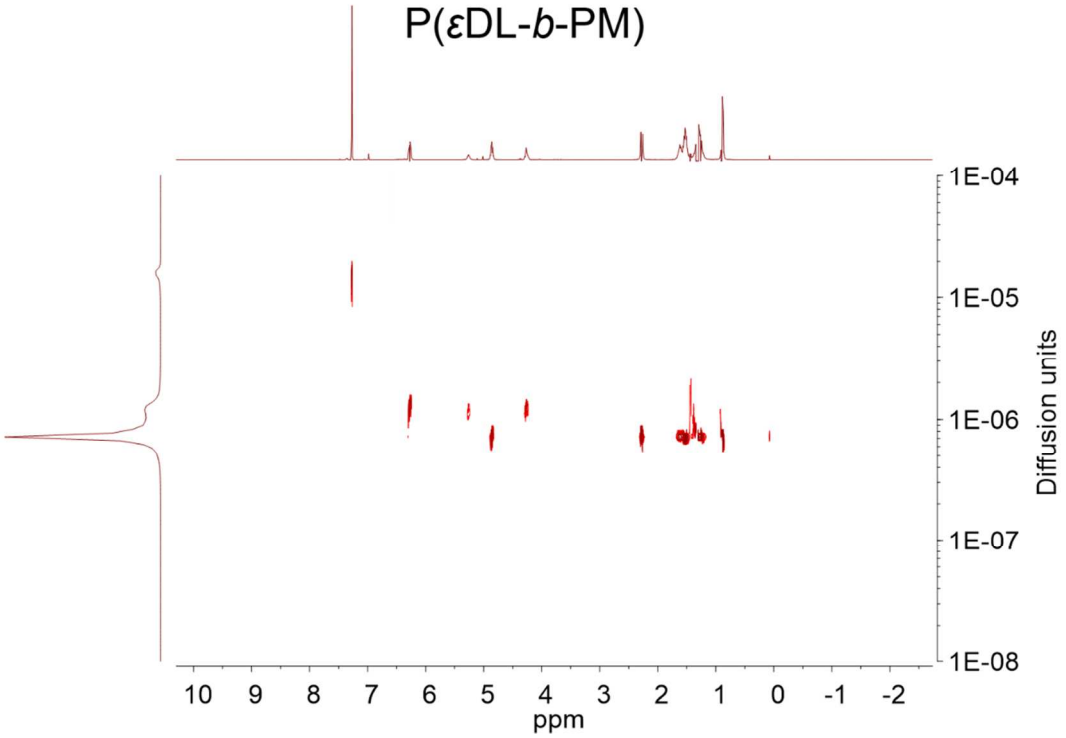

Figure 48: DOSY NMR spectra of poly(*ε*-decalactone-*b*-propylene maleate) (500 MHz, 298 K, CDCl3).

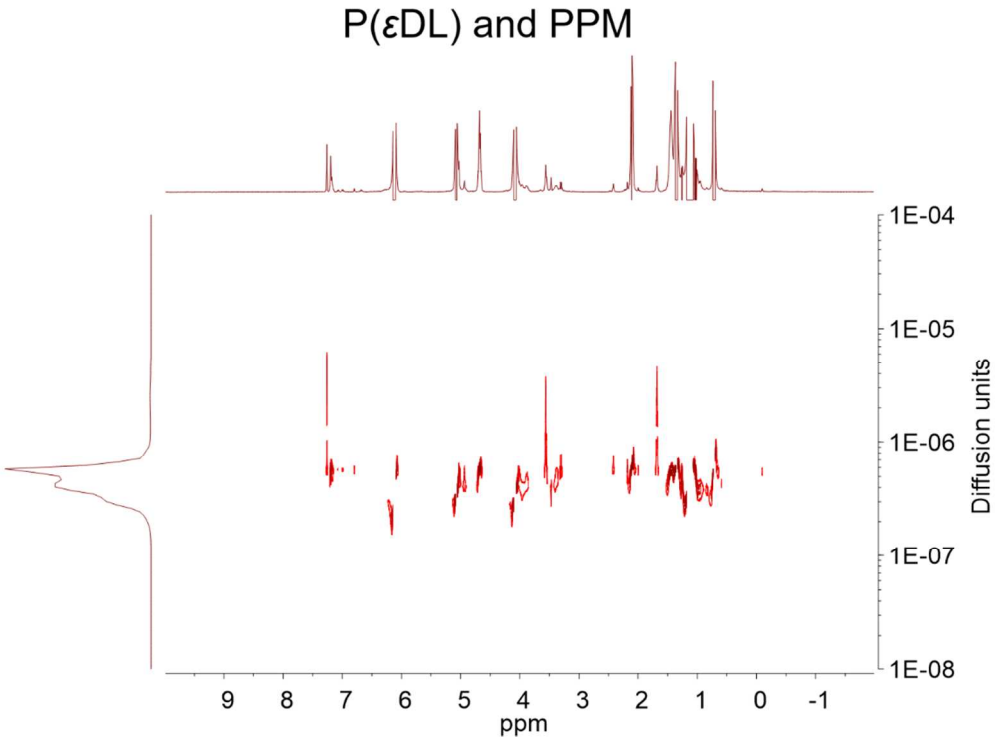

Figure 49: DOSY NMR spectra of poly(*ε*-decalactone) and poly(propylene maleate) (500 MHz, 298 K, CDCl3).

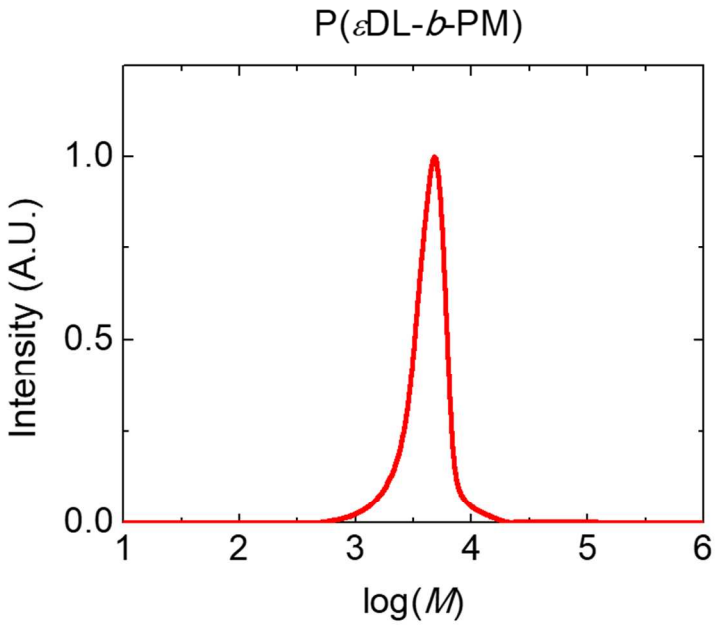

Figure 50: SEC chromatogram for poly(*ε*-decalactone-*b*-propylene maleate). The molecular mass determined against poly(styrene) standards.

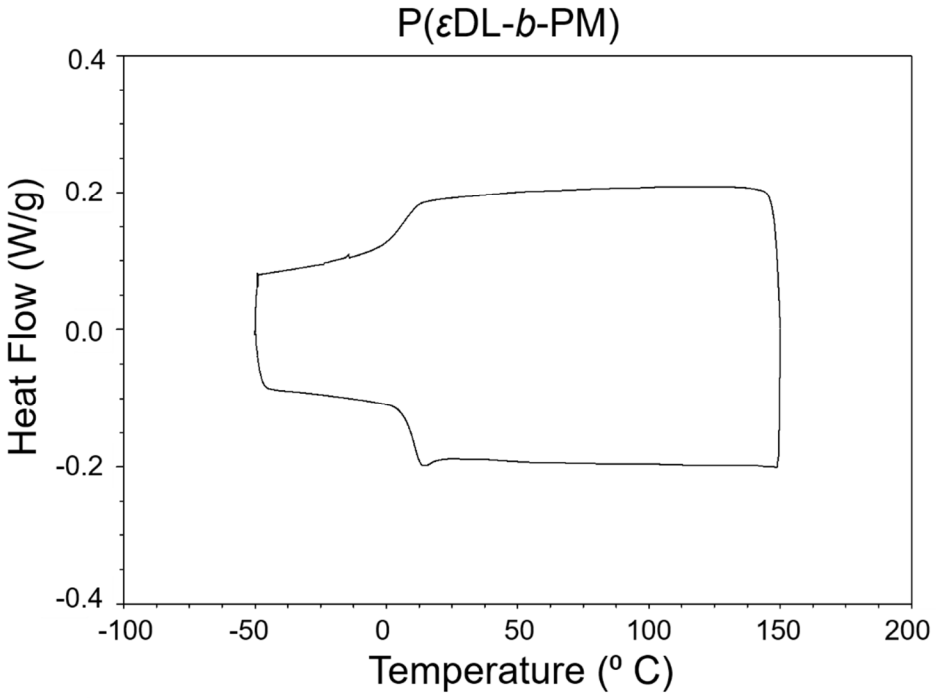

Figure 51: DSC thermograms (second heating curve, between -50 and 150 °C) for poly(*ε*-decalactone-*b*-propylene maleate).

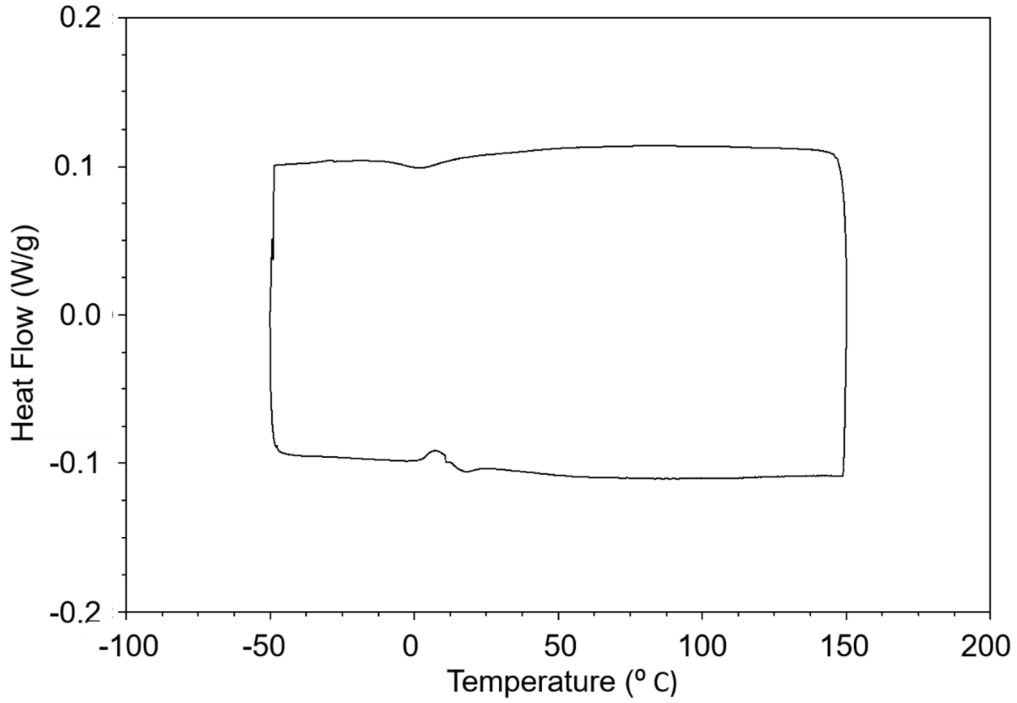

Figure 52: DSC thermograms (second heating curve, between -50 and 150 °C) for poly(*ε*-decalactone) and poly(propylene maleate).

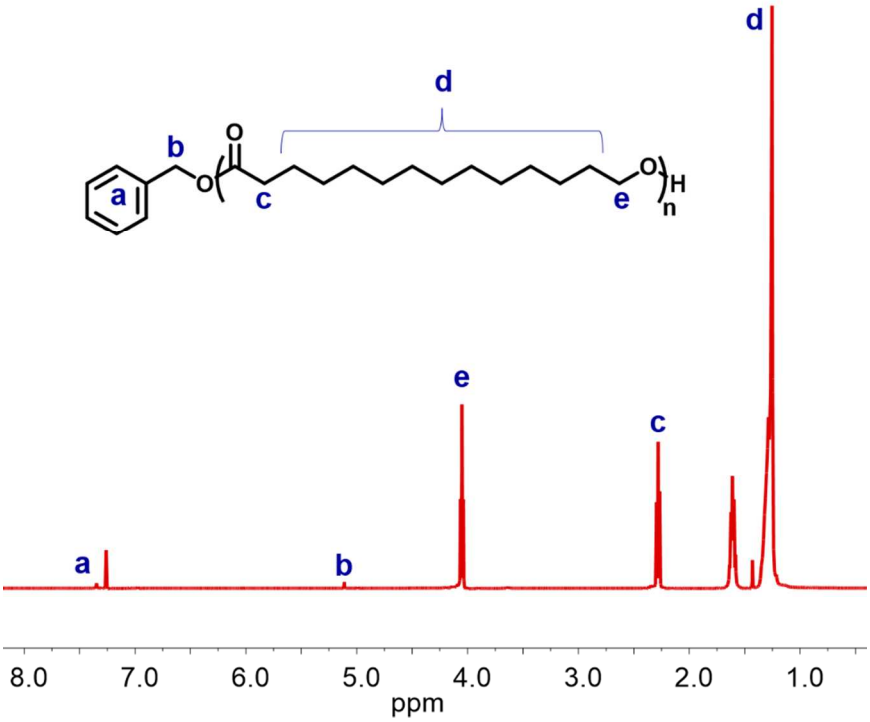

Figure 53: ^{1}H NMR spectra of poly(*ω*-pentadecalactone) (500 MHz, CDCl3, 303 K).

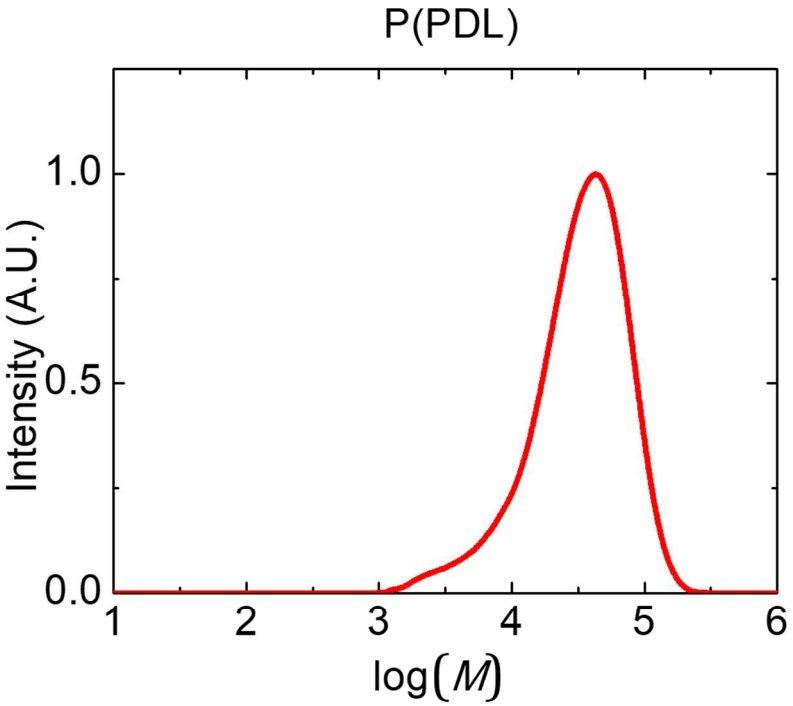

Figure 54: SEC chromatogram for poly(*ω*-pentadecalactone). The molecular mass determined against poly(styrene) standards.

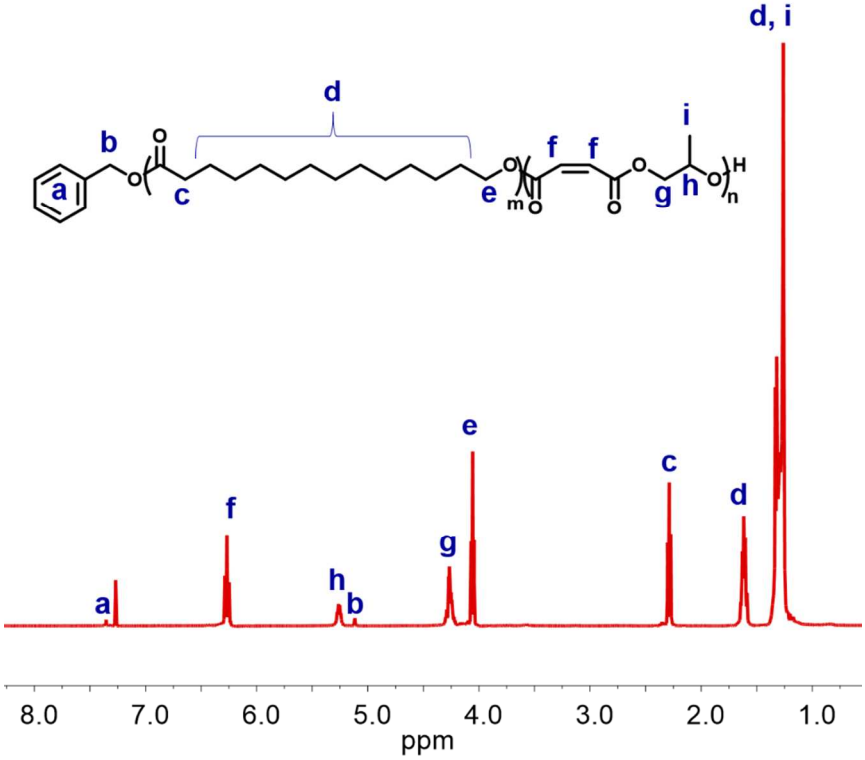

Figure 55: ^{1}H NMR spectra of poly(*ω*-pentadecalactone-*b*-propylene maleate) (500 MHz, CDCl3, 303 K).

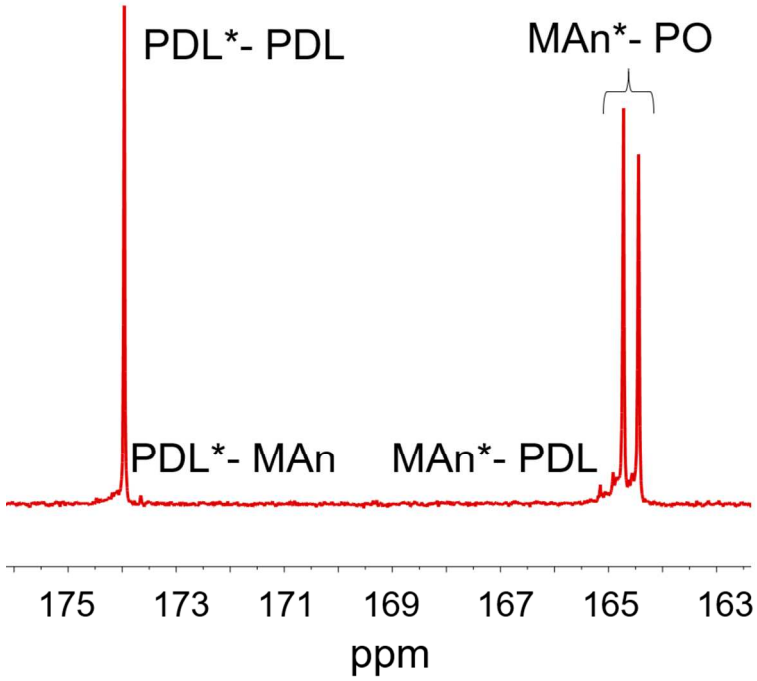

Figure 56: ^{13}C NMR spectra of the carbonyl diad region of poly(*ω*-pentadecalactone-*b*-propylene maleate) (125 MHz, CDCl3, 303 K).

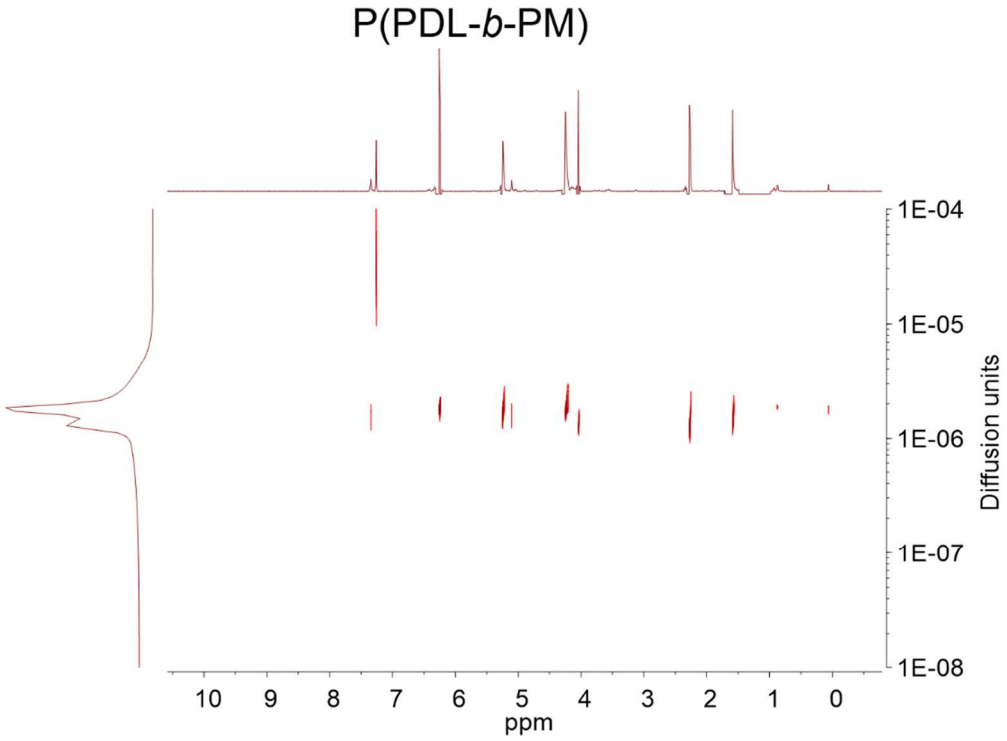

Figure 57: DOSY NMR spectra of poly(*ω*-pentadecalactone-*b*-propylene maleate) (500 MHz, 298 K, CDCl3).

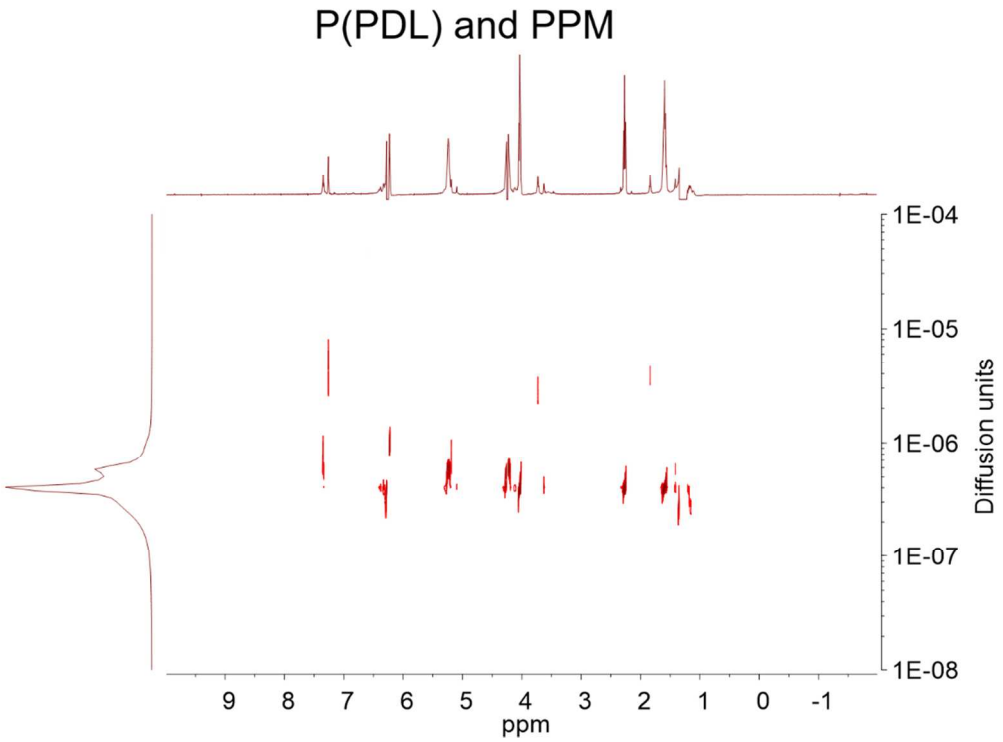

Figure 58: DOSY NMR spectra of poly(*ω*-pentadecalactone) and poly(propylene maleate) (500 MHz, 298 K, CDCl3).

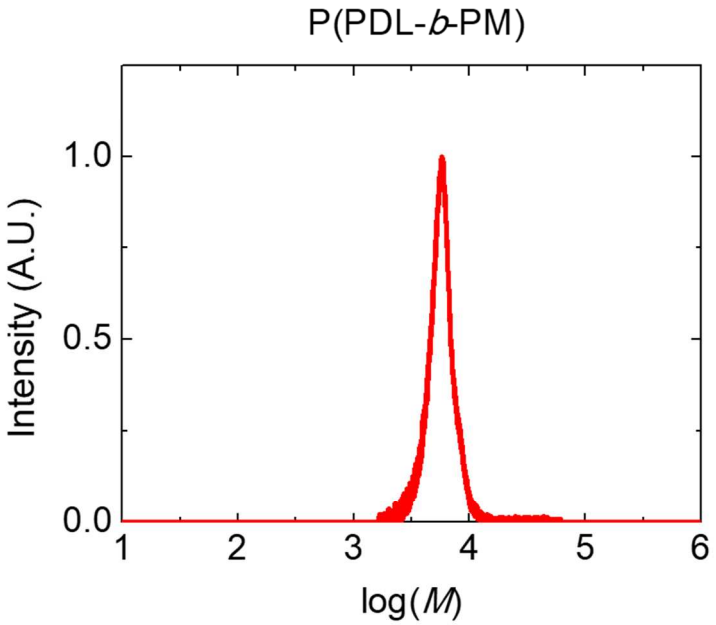

Figure 59: SEC chromatogram for poly(*ω*-pentadecalactone-*b*-propylene maleate). The molecular mass determined against poly(styrene) standards.

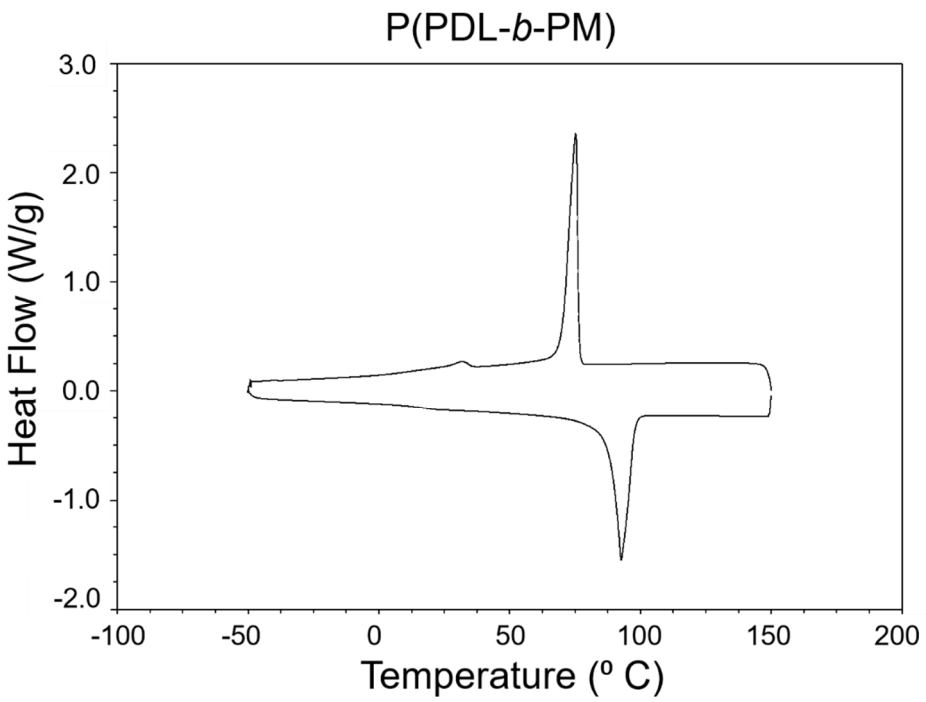

Figure 60: DSC thermograms (second heating curve, between -50 and 150 °C) for poly(*ω*-pentadecalactone-*b*-propylene maleate).

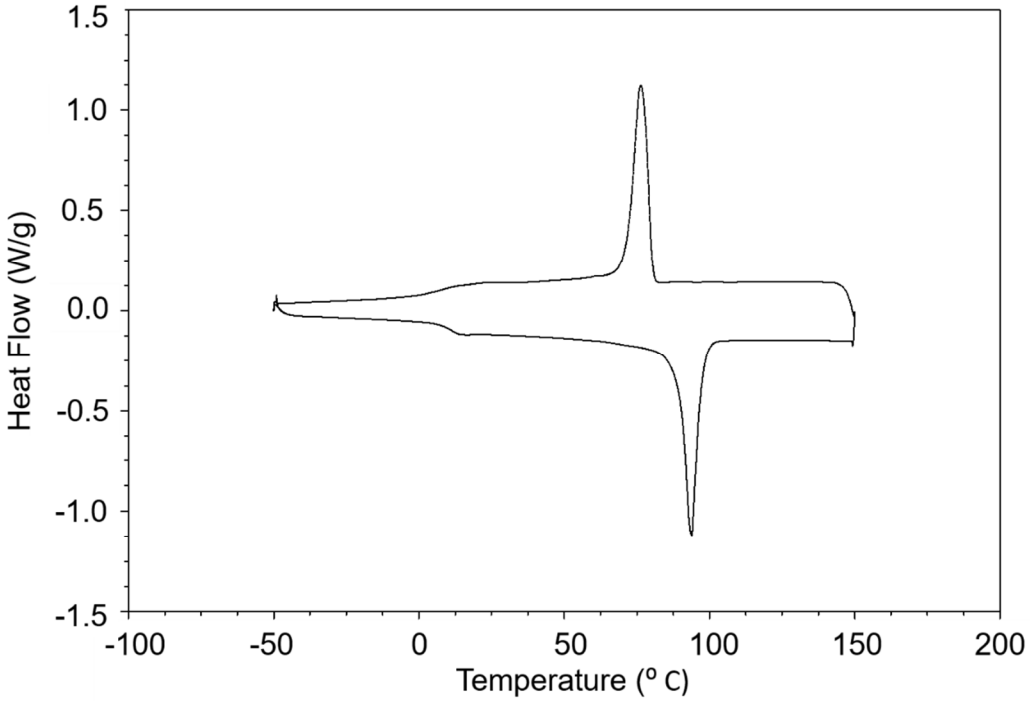

Figure 61: DSC thermograms (second heating curve, between -50 and 150 °C) for poly(*ω*-pentadecalactone) and poly(propylene maleate).

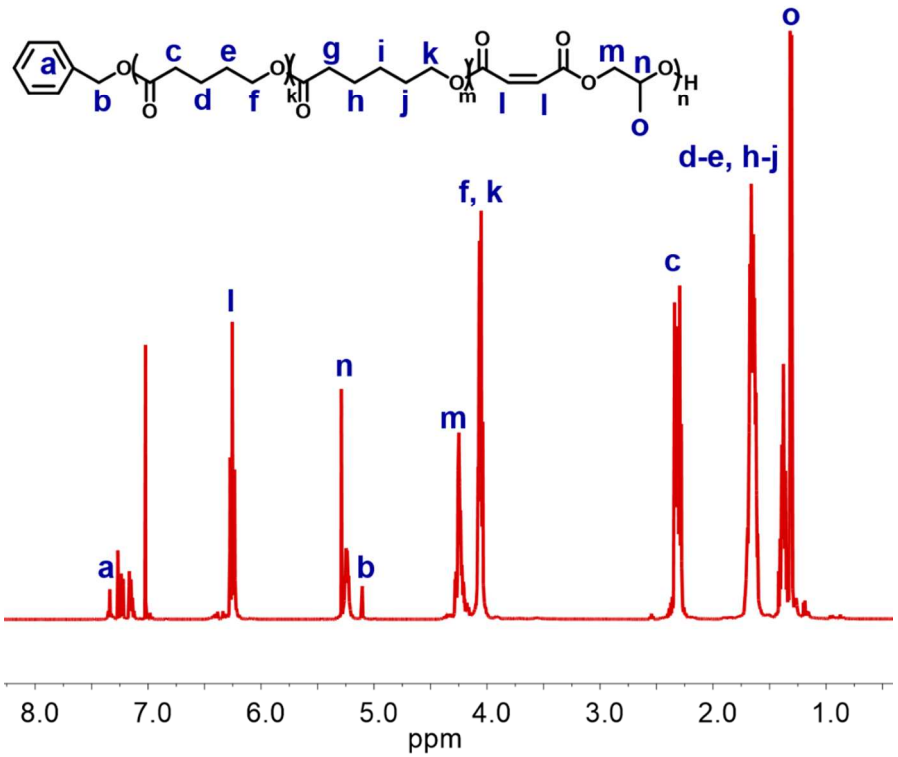

Figure 62: ^{1}H NMR spectra of poly(*δ*-valerolactone-*co*-*ε*-caprolactone-*b*-propylene maleate) (500 MHz, CDCl3, 303 K).

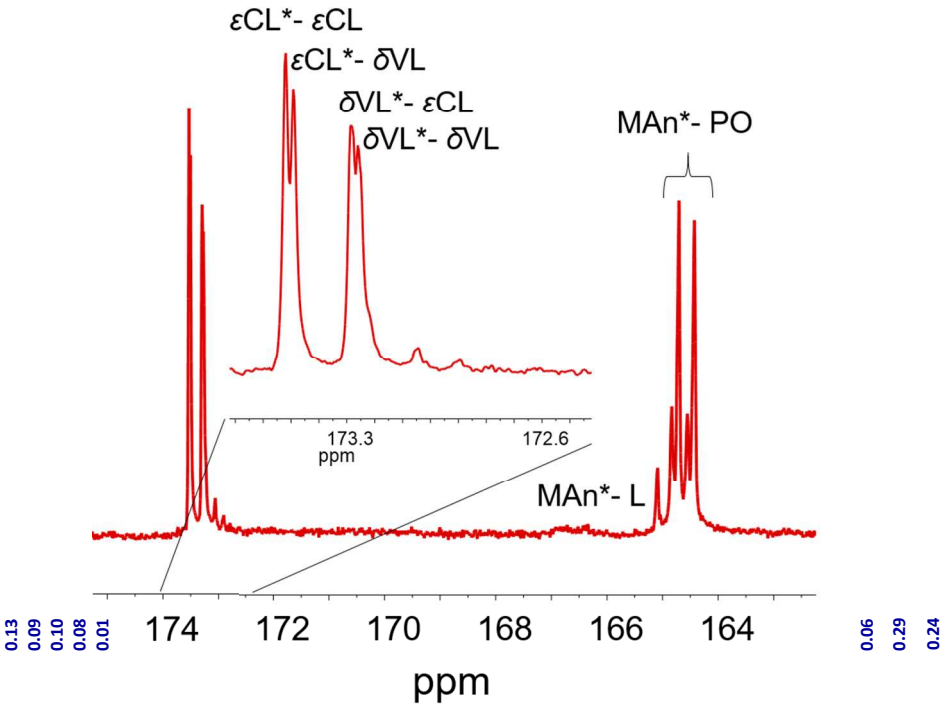

Figure 63: ^{13}C NMR spectra of the carbonyl diad region of poly(*δ*-valerolactone-*co*-*ε*-caprolactone-*b*-propylene maleate) (125 MHz, CDCl3, 303 K).

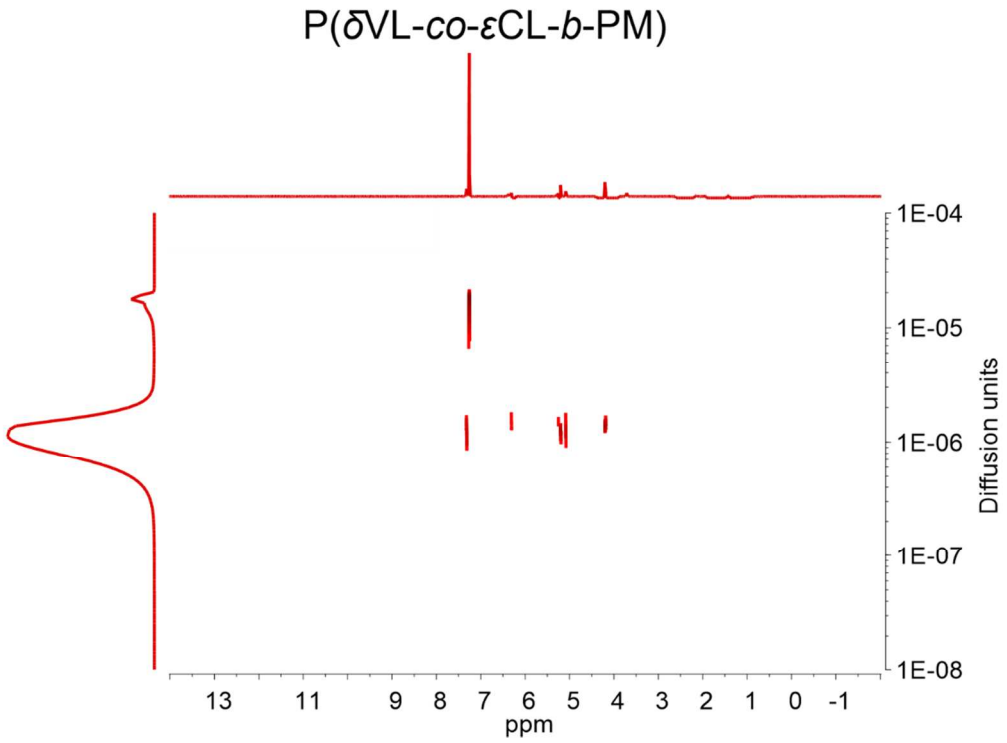

Figure 64: DOSY NMR spectra of poly(*δ*-valerolactone-*co*-*ε*-caprolactone-*b*-propylene maleate) (500 MHz, 298 K, CDCl3).

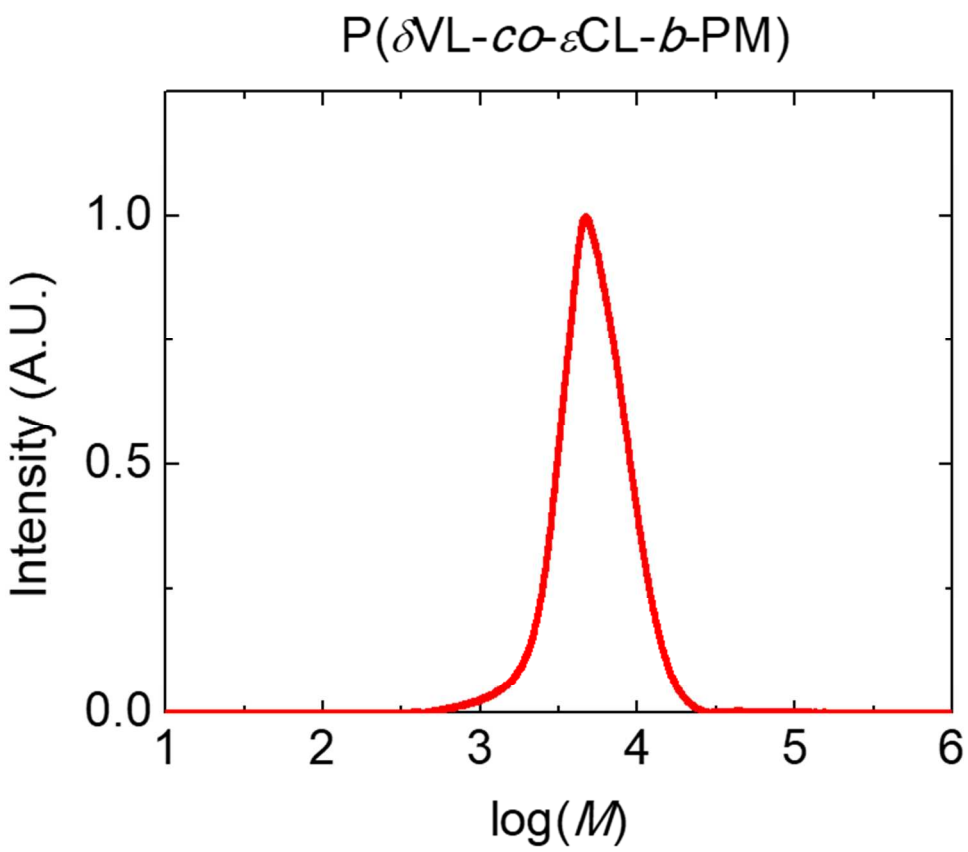

Figure 65: SEC chromatogram for poly(*δ*-valerolactone-*co*-*ε*-caprolactone-*b*-propylene maleate). The molecular mass determined against poly(styrene) standards.

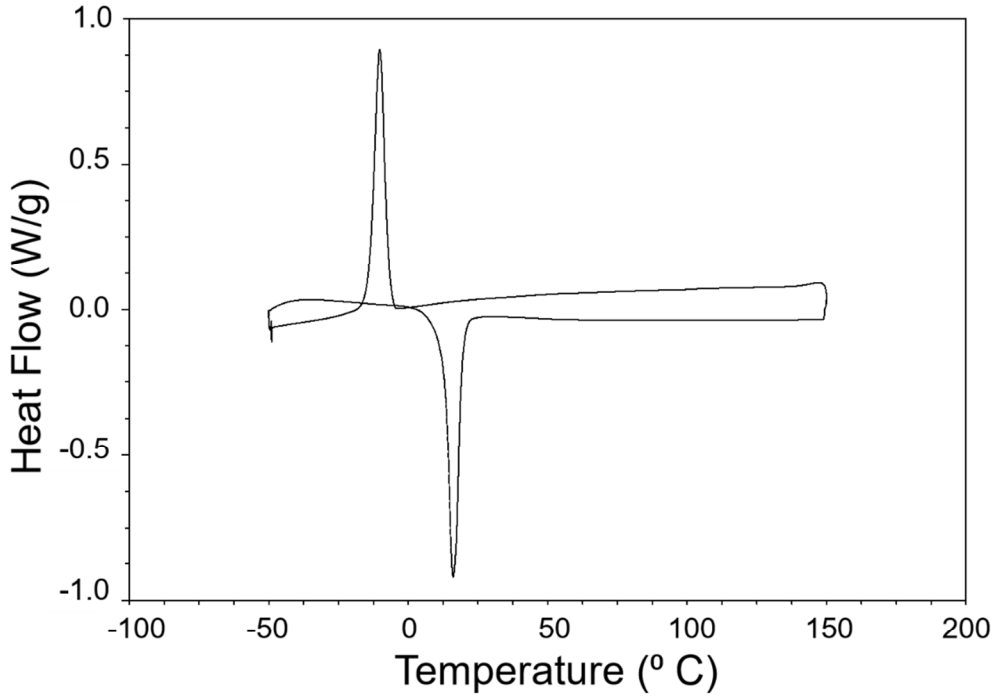

Figure 66: DSC thermograms (second heating curve, between -50 and 150 °C) for poly(*δ*-valerolactone-*co*-*ε*-caprolactone-*b*-propylene maleate).

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