

Electronic Supplementary Information

Physical Properties and Hydrolytic Degradability of Polyethylene-Like Polyacetals and Polycarbonates

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1. General Methods and Materials

All reactions were performed under inert gas atmosphere using glove box or standard Schlenk techniques. Work up of polymerization experiments and degradation studies were performed under air. Ethanol and methanol were distilled from magnesium turnings prior to use; THF and toluene were distilled from sodium and stored under inert gas conditions. All other solvents were used in technical grade as received.

Carbon monoxide (3.7) and hydrogen gas (5.0) were supplied by Air Liquide. Methyl oleate (92.5%, Dakolub MB9001 high oleic sunflower oil methyl ester) was supplied by Dako AG, ethyl erucate (95%) by TCI Europe. Diethoxymethane, dimethyl carbonate, potassium carbonate, tetrabromomethane, $[(PCy_3)_2Cl_2Ru=CHPh]$ (Grubbs 1st generation catalyst) and ethyl vinyl ether were supplied by Sigma Aldrich. *para*-Toluene sulfonic acid monohydrate was supplied by Merck. Triphenylphosphine and potassium *tert*-butoxide were purchased from Acros. 10-Undecenol was supplied by ACME Synthetic Chemicals (Mumbai, India). Octadecane-1,18-dioic acid was kindly donated by Emery Oleochemicals. All deuterated solvents for NMR spectroscopy were supplied by Eurisotop.

Dichlorobis[2-(diphenylphosphino)ethylamin]ruthenium was prepared as reported.^[1]

Dimethyl nonadecanedioate and diethyl tricosanedioate were prepared by isomerizing alkoxyacylation of methyl oleate and ethyl erucate, respectively, by reported procedures.^[2]

Nuclear magnetic resonance (NMR) spectra were recorded on a Varian Inova 400 and a Bruker Avance 400 spectrometer. ¹H and ¹³C chemical shifts were referenced to the solvent signals. High-temperature NMR measurements of polymers were performed in 1,1,2,2-tetrachloroethane-*d*₂ at 130 °C.

Differential scanning calorimetry (DSC) measurements were performed on a Netzsch Phoenix 204 F1 instrument with heating and cooling rates of 10 °C min⁻¹. All data reported were collected from the second heating cycles.

Gel permeation chromatography (GPC) measurements were carried out on a Polymer Laboratories PL-GPC 50 with two PLgel 5 μm MIXED-C columns in THF at 40 °C against polystyrene standards with refractive index detection. High temperature GPC measurements were carried out in 1,2,4-trichlorobenzene at 160 °C at a flow rate of 1 mL min⁻¹ on a Polymer Laboratories 220 instrument equipped with Olexis columns and differential refractive index, viscosity, and light-scattering (15° and 90°) detectors. Data reported were determined directly against linear PE standards.

Infra red (IR) spectra were recorded on a Perkin-Elmer Spectrum 100 instrument with an ATR unit.

Wide angle X-Ray diffraction (WAXD) was performed on a Bruker AXS D8 Advance diffractometer using CuKα₁ radiation. Diffraction patterns were recorded in the range 10 to 60 degrees 2θ, at 25 °C.

2. Synthesis of Long-Chain Polyacetals and Polycarbonates

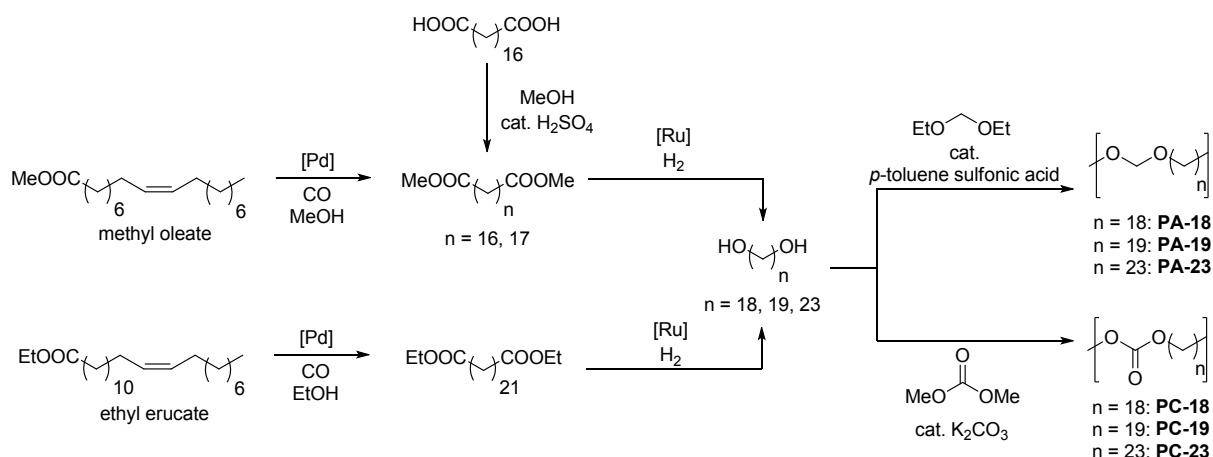
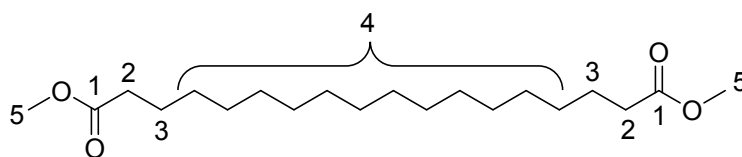


Figure S1. Synthesis of polyacetals (**PA-18**, **PA-19**, **PA-23**) and polycarbonates (**PC-18**, **PC-19**, **PC-23**)

Monomer Synthesis

Synthesis of Dimethyl 1,18-octadecanedioate

In a 500 mL three-necked round bottom flask equipped with a condenser, octadecane-1,18-dioic acid (41.9 g, 133 mmol) was heated under reflux in 200 mL of methanol p.a. with 10 drops of sulfuric acid for 40 minutes. The solution was cooled to room temperature and a solid precipitated, which was separated by filtration. The residue was recrystallized from methanol to yield dimethyl-1,18-octadecanedioate as a colorless solid (39.4 g, 115 mmol, 87%).

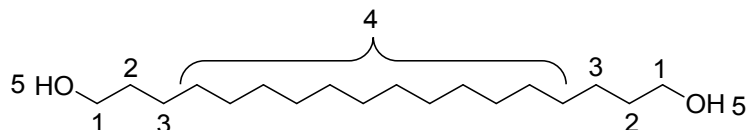


¹H NMR (CDCl₃, 400 MHz, 25°C): δ (ppm) = 3.66 (s, 6H, H-5), 2.30 (t, ³J_{H-H} = 7.6 Hz, 4H, H-2), 1.61 (p, ³J_{H-H} = 7.3 Hz, 4H, H-3), 1.28-1.25 (m, 24H, H-4). ¹³C NMR (CDCl₃, 400 MHz, 25°C): δ (ppm) = 174.5 (C-1), 51.6 (C-5), 34.3 (C-2), 29.8- 29.3 (C-4), 25.1 (C-3).

Synthesis of Octadecane-1,18-diol^[2]

Dichlorobis[2-(diphenylphosphino)ethylamin]ruthenium^[1] (30 mg, 0.048 mmol) and sodium methanolate (120 mg, 2.22 mmol) were weighed into a 200 mL Schlenk tube, and dissolved in 70 mL of dry THF. The solution was cannula transferred into a Schlenk tube charged with dimethyl 1,18-octadecanedioate (10.5 g, 30.7 mmol). The mixture was cannula transferred into a mechanically stirred 250 mL steel pressure reactor with a glass inlay under inert gas conditions. The reactor was

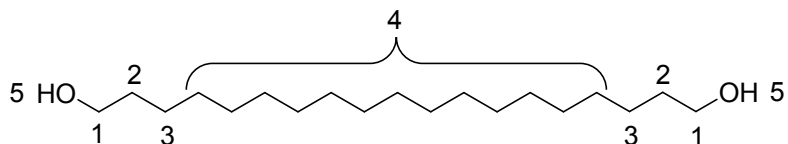
pressurized with 80 bar of hydrogen gas and heated to 90 °C. After 22 h, the reactor was cooled to room temperature and vented. The precipitated colorless solid was dissolved in hot THF and filtered over celite. Recrystallization from THF yielded octadecane-1,18-diol as a colorless solid (5.3 g, 18.5 mmol, 60 %).



^1H NMR ($\text{C}_2\text{D}_2\text{Cl}_4$, 400 MHz, 130°C): δ (ppm) = 3.58 (t, $^3J_{\text{H-H}} = 6.6$ Hz, 4H, H-1), 1.54 (p, $^3J_{\text{H-H}} = 6.7$ Hz, 4H, H-2), 1.36-1.28 (m, 28H, H-3, H-4), 1.04 (s, 2H, H-5). ^{13}C NMR ($\text{C}_2\text{D}_2\text{Cl}_4$, 400 MHz, 130°C): δ (ppm) = 63.2 (C-1), 33.2 (C-2), 29.7-30.0 (C-4), 26.0 (C-3).

Synthesis of Nonadecane-1,19-diol^[2]

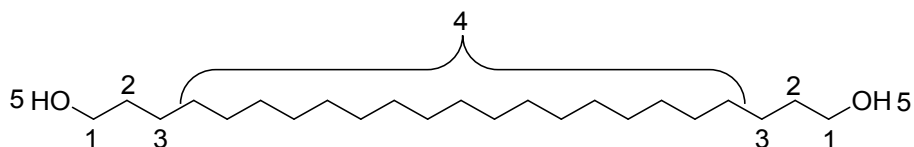
Nonadecane-1,19-diol was prepared from dimethyl 1,19-nonadecanedioate (12.0 g, 33.7 mmol) as described for octadecane-1,18-diol to yield a colorless solid (7.0 g, 24.5 mmol, 73 %).



^1H NMR ($\text{C}_2\text{D}_2\text{Cl}_4$, 400 MHz, 130°C): δ (ppm) = 3.58 (t, $^3J_{\text{H-H}} = 6.6$ Hz, 4H, H-1), 1.54 (p, $^3J_{\text{H-H}} = 6.8$ Hz, 4H, H-2), 1.36-1.28 (m, 30H, H-3, H-4). ^{13}C NMR ($\text{C}_2\text{D}_2\text{Cl}_4$, 400 MHz, 130°C): δ (ppm) = 63.2 (C-1), 33.2 (C-2), 29.7-30.0 (C-4), 26.0 (C-3).

Synthesis of Tricosane-1,23-diol^[2]

Tricosane-1,23-diol was prepared from diethyl 1,23-tricosanedioate (14.0 g, 31.8 mmol) as described for octadecane-1,18-diol to yield a colorless solid (9.6 g, 27.0 mmol, 85 %).

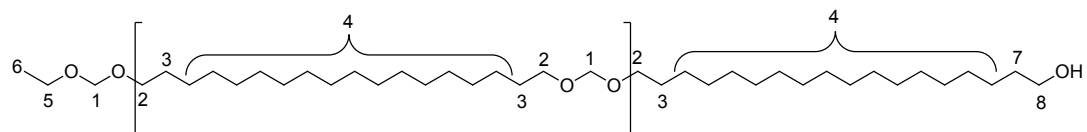


^1H NMR ($\text{C}_2\text{D}_2\text{Cl}_4$, 400 MHz): δ (ppm) = 3.58 (t, $^3J_{\text{H-H}} = 6.6$ Hz, 4H, H-1), 1.54 (p, $^3J_{\text{H-H}} = 6.7$ Hz, 4H, H-2, 130°C), 1.36-1.28 (m, 38H, H-3, H-4), 1.07 (s, 2H, H-5). ^{13}C NMR ($\text{C}_2\text{D}_2\text{Cl}_4$, 400 MHz, 130°C): δ (ppm) = 63.2 (C-1), 33.2 (C-2), 29.8-30.0 (C-4), 26.0 (C-3).

Synthesis of Polyacetals

Polyacetal-18

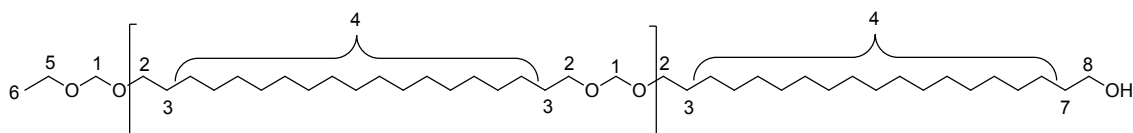
PA-18 was prepared in a 100 mL double-necked Schlenk tube equipped with a mechanical stirrer (helical agitator) for efficient mixing of the polymer melt. Under an argon atmosphere, the Schlenk tube was charged with octadecane-1,18-diol (1.0 g, 3.5 mmol), *p*-toluenesulfonic acid (9.9 mg, 0.05 mmol) and diethoxy methane (2.5 mL, 20.0 mmol). The reaction mixture was heated to 80 °C under stirring for 30 min. During the next 3 h, an argon flow was applied several times for ca. five seconds to remove side products. The temperature was increased to 90 °C and every 30 min the Schlenk tube was frequently evacuated for one min. After further 1.5 h, the reaction apparatus was completely evacuated (to a reduced pressure of 0.1 mbar) and heated to 115 °C. After 30 min, another portion of *p*-toluenesulfonic acid (9.9 mg, 0.05 mmol) was added. After 1.5 h the temperature was raised to 150 °C and the polymerization was continued under reduced pressure over night. The reaction apparatus was cooled to room temperature, vented and the polymer obtained was dissolved in boiling chloroform and precipitated in ice-cold methanol. The precipitate was isolated by filtration, washed with methanol and acetone and dried in vacuum to yield **PA-18** as a slightly beige solid (0.7 g, 67 %).



^1H NMR (CDCl_3 , 400 MHz): δ (ppm) = 4.64 (s, 2H, H-1), 3.61 (t, $^3J_{\text{H-H}} = 6.7$ Hz, H-8), 3.57 (q, $^3J_{\text{H-H}} = 7.1$ Hz, H-5), 3.50 (t, $^3J_{\text{H-H}} = 6.7$ Hz, 4 H, H-2), 1.56 (p, 4H, H-3), 1.34-1.23 (m, 28H, H-4), 1.20 (t, $^3J_{\text{H-H}} = 7.1$ Hz H-6). ^{13}C NMR (CDCl_3 , 400 MHz): δ (ppm) = 95.5 (C-1), 68.1 (C-2), 63.3 (C-8), 30.0-26.0 (C-3, C-4).

Polyacetal-19

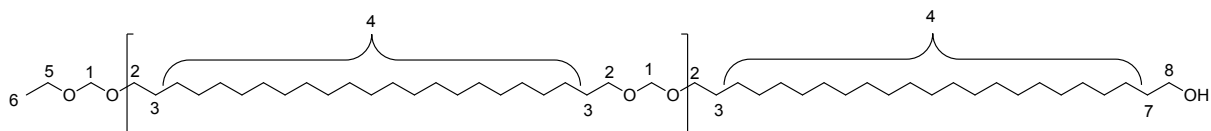
PA-19 was prepared similar to the procedure given for **PA-18**. Nonadecane-1,19-diol (0.8 g, 2.5 mmol), *p*-toluenesulfonic acid (4.7 mg, 0.025 mmol) and diethoxy methane (1.9 mL, 15.0 mmol) were employed. **PA-19** was received as a slightly beige solid (0.5 g, 64%).



^1H NMR (CDCl_3 , 400 MHz): δ (ppm) = 4.66 (s, 2H, H-1), 3.63 (t, $^3J_{\text{H-H}} = 6.7$ Hz, H-8), 3.59 (q, $^3J_{\text{H-H}} = 7.1$ Hz, H-5), 3.52 (t, $^3J_{\text{H-H}} = 6.7$ Hz, 4 H, H-2), 1.57 (p, 4H, H-3), 1.34-1.25 (m, 30H, H-4), 1.20 (m, H-6). ^{13}C NMR (CDCl_3 , 400 MHz): δ (ppm) = 95.5 (C-1), 68.1 (C-2), 63.3 (C-8), 30.0-26.5 (C-3, C-4).

Polyacetal-23

PA-23 was prepared similar to the procedure given for **PA-18**. Tricosane-1,23-diol (2.0 g, 5.6 mmol), *p*-toluenesulfonic acid (16.0 mg, 0.084 mmol) and diethoxy methane (4.0 mL, 32.0 mmol) were employed. **PA-23** was obtained as a brittle material (1.7 g, 80%).

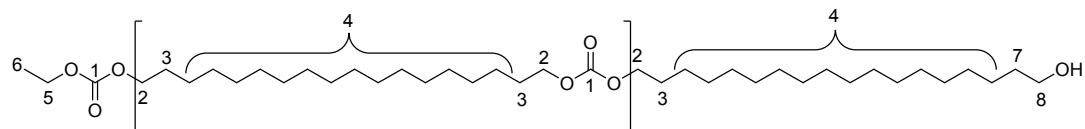


^1H NMR ($\text{C}_2\text{D}_2\text{Cl}_4$, 400 MHz, 130°C): δ (ppm) = 4.64 (s, 2H, H-1), 3.63 (t, $^3J_{\text{H-H}} = 6.7$ Hz, H-8), 3.58 (q, $^3J_{\text{H-H}} = 7.1$ Hz, H-5, H-8), 3.50 (t, $^3J_{\text{H-H}} = 6.7$ Hz, 4 H, H-2), 1.56 (q, 4H, H-3), 1.34-1.23 (m, 38H, H-4), 1.20 (t, $^3J_{\text{H-H}} = 7.1$ Hz, H-6). ^{13}C NMR ($\text{C}_2\text{D}_2\text{Cl}_4$, 400 MHz, 130°C): δ (ppm) = 95.6 (C-1), 68.3 (C-2), 63.1 (C-8), 30.0-25.9 (C-3, C-4).

Synthesis of Polycarbonates

Polycarbonate-18

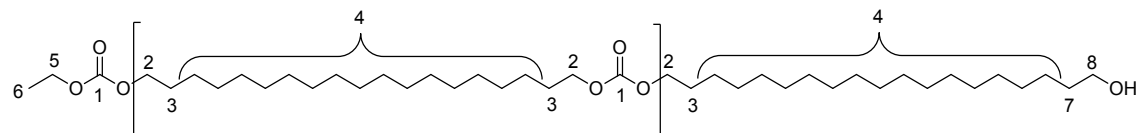
PC-18 was prepared in a 100 mL double-neck Schlenk tube equipped with a mechanical stirrer (helical agitator) for efficient mixing of the polymer melt. Under an argon atmosphere, the polymerization apparatus was charged with octadecane-1,18-diol (5.0 g, 17.5 mmol), K_2CO_3 (121 mg, 0.88 mmol) and dimethyl carbonate (14.8 mL, 175.0 mmol). The mixture was heated to 110°C . To relieve the pressure in the Schlenk tube, it was evacuated for 5 sec periodically. After 3.5 h, the reaction mixture was completely evacuated (applying a reduced pressure of 0.1 mbar). After further 1.5 h, the reaction temperature was raised to 220°C over night. The reaction mixture was cooled to room temperature and the polymer was removed from the Schlenk tube. **PC-18** was received as a beige solid (4.5 g, 83%).



^1H NMR ($\text{C}_2\text{D}_2\text{Cl}_4$, 400 MHz): δ (ppm) = 4.01 (t, $^3J_{\text{H-H}} = 6.8$ Hz, 4H, H-2), 3.68 (s, H-5), 3.52 (t, $^3J_{\text{H-H}} = 6.6$ Hz, H-7), 1.57 (p, 4H, H-3), 1.42 (m, H-6), 1.22-1.16 (m, 28H, H-4). ^{13}C NMR ($\text{C}_2\text{D}_2\text{Cl}_4$, 400 MHz): δ (ppm) = 155.6 (C-1), 68.4 (C-2), 30.0-26.0 (C-3, C-4).

Polycarbonate-19

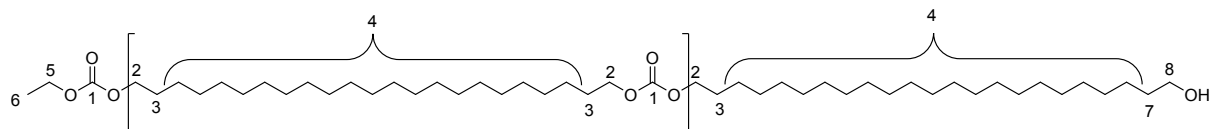
Polycarbonate-19 was prepared similar to the procedure given for polycarbonate-18. Therefore nonadecane-1,19-diol (5.0 g, 16.7 mmol), K_2CO_3 (115 mg, 0.84 mmol) and dimethyl carbonate (14.0 mL, 166.5 mmol) were used. Polycarbonate-19 was received as a beige solid (4.1 g, 76%).



1H NMR ($C_2D_2Cl_4$, 400 MHz): δ (ppm) = 4.01 (t, $^3J_{H-H}$ = 6.8 Hz, 4H, H-2), 3.52 (t, $^3J_{H-H}$ = 6.7 Hz, H-7), 1.57 (p, 4H, H-3), 1.46 (m, H-6) 1.22-1.17 (m, 30H, H-4). ^{13}C NMR ($C_2D_2Cl_4$, 400 MHz): δ (ppm) = 155.6 (C-1), 68.4 (C-2), 30.0-26.0 (C-3, C-4).

Polycarbonate-23

Polycarbonate-23 was prepared similar to the procedure given for polycarbonate-18. Therefore tricosane-1,23-diol (5.0 g, 14.0 mmol), K_2CO_3 (97 mg, 0.70 mmol) and dimethyl carbonate (12.0 mL, 140.3 mmol) were used. Polycarbonate-18 was received as a beige solid (4.3 g, 81%).



1H NMR ($C_2D_2Cl_4$, 400 MHz): δ (ppm) = 4.09 (t, $^3J_{H-H}$ = 6.7 Hz, 4H, H-2), 3.73 (s, H-5), 3.58 (t, $^3J_{H-H}$ = 6.5 Hz, H-7), 1.65 (p, 4H, H-3), 1.54 (m, H-6), 1.55-1.27 (m, 38H, H-4). ^{13}C NMR ($C_2D_2Cl_4$, 400 MHz): δ (ppm) = 155.5 (C-1), 68.2 (C-2), 29.8-25.9 (C-3, C-4).

Molecular Weight Estimation by ^1H NMR Spectroscopy

Polyacetals

The degree of polymerization (DP_n) and the molecular weight (M_n) was calculated from the ratio of the ^1H NMR proton signal intensities of the end groups (E_1 - E_3) compared to the proton signal intensity of the acetal group of the polymer chain (P) in the ^1H NMR spectra. There are two types of end groups present:

E_1 hydroxyl end group (3.63 ppm, t, 2H)

$E_2; E_3$ ethoxyacetal end group (3.60 ppm, q, 2H; 1.22 ppm, t, 3H)

$$\text{DP}_n = \frac{2 \times \int P}{\int E_1 + \int E_2}$$

The number-average degree of polymerization (DP_n) was calculated according to:

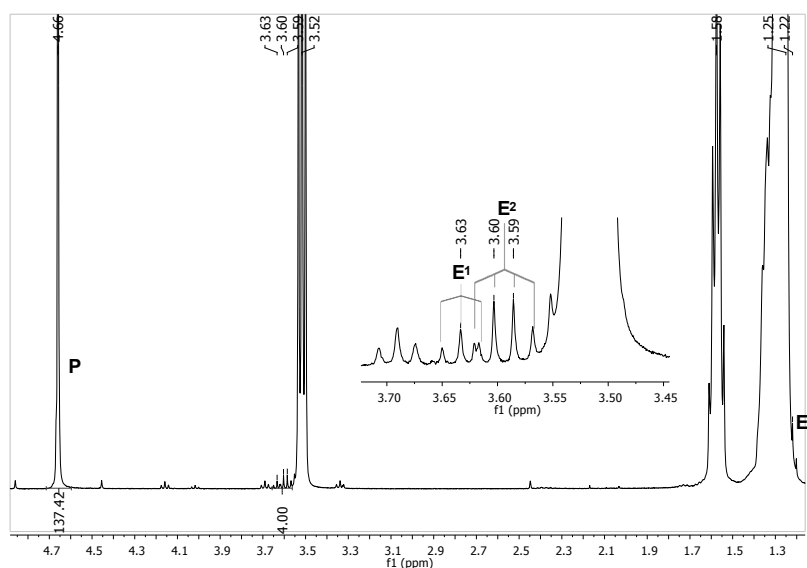


Figure S2. Molecular weight estimation for polyacetals by ^1H NMR spectroscopy.

Polycarbonates

The degree of polymerization (DP_n) and the molecular weight (M_n) was calculated from the ratio of the ^1H NMR proton signal intensities of the end groups (E_1 - E_3) compared to the proton signal intensity of the methylene group adjacent to the carbonate group in the polymer chain (P). There are two types of end groups present:

E_1 methyl carbonate end group (3.77 ppm, s, 3H)

$E_2; E_3$ hydroxyl end group (3.63 ppm, t, 2H, 1.55 ppm, m, 2H)

The number-average degree of polymerization (DP_n) was calculated according to:

$$\text{DP}_n = \frac{\int P}{\frac{2}{3} \int E_1 + \int E_2}$$

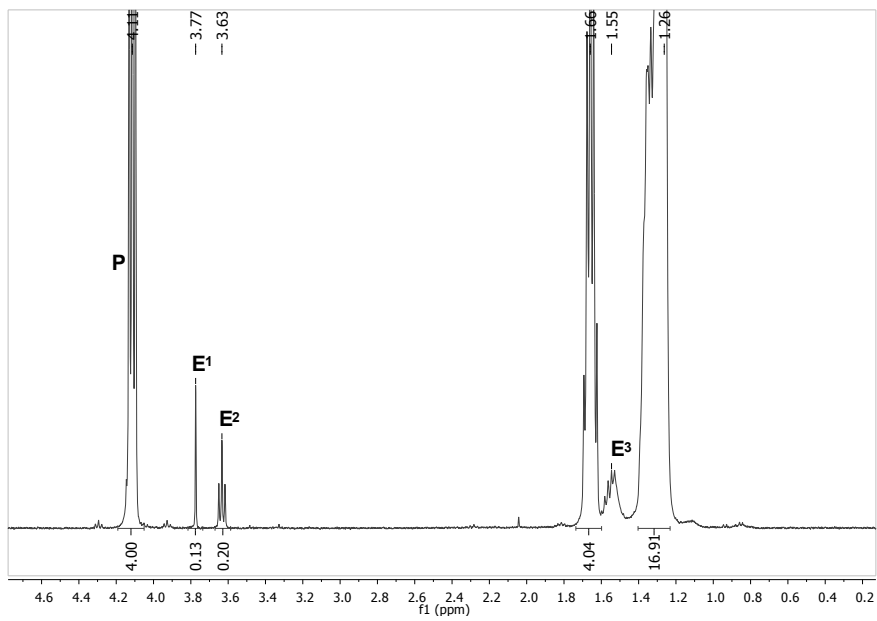


Figure S3. Molecular weight estimation for polycarbonates by ^1H NMR spectroscopy.

3. Hydrolytic Degradation Studies

Pellet Preparation

Pellets of 35-65 mg were prepared by melting the polymer in a DSC crucible aluminium lid, cooled to room temperature and vacuum dried for 24 h prior to the degradation studies. The pellets were exposed to 5 mL of different media at 40 °C, each in an 8 mL glass vial equipped with a magnetic stirring bar.

Polyacetals

The following media were used for longer-term experiments: conc. aq. HCl, 3 M aq. HCl, 20 wt% aq. NaOH. After the degradation experiments, the pellets were removed from the media, washed with water and acetone and dried for 24 h at 40°C.

Table S1. Hydrolytic degradation experiments of polyacetals in aqueous media.

<i>polymer pellet</i>	<i>medium</i>	<i>initial weight (mg)</i>	<i>pellet weight after degradation experiment (mg)</i>	<i>pellet weight after degradation experiment (%)</i>	<i>weight loss after degradation experiment (%)</i>
PA-18	20 wt% aq. NaOH	35.0	34.8	99.4	0.6
PA-19		39.3	39.3	100.0	0.0
PA-23		37.8	37.8	100.0	0.0
PA-18	3M aq. HCl	51.6	51.2	99.2	0.8
PA-19		50.1	49.8	99.4	0.6
PA-23		55.4	55.0	99.3	0.7
PA-18	conc. aq. HCl	43.2	41.0	94.9	5.1
PA-19		42.6	40.9	96.0	4.0
PA-23		47.2	46.1	97.7	2.3

Polycarbonates

The pellets from polycarbonate were exposed to 10 M NaOH in MeOH in short-term experiments. Longer-term experiments were performed in conc. aq. HCl, 2 wt% aq. NaOH and 20 wt% aq. NaOH. After the degradation experiments, the pellets were removed from the media, washed with water and acetone and dried for 24 h at 40 °C. For the short-term experiments the pellets were exposed for 1 h to MeOH before exposing to the methanolic NaOH solution again.

Table S2. Hydrolytic degradation experiments of long-chain polycarbonates in aqueous media.

<i>polymer pellet</i>	<i>medium</i>	<i>initial weight (mg)</i>	<i>pellet weight after degradation experiment (mg)</i>	<i>pellet weight after degradation experiment (%)</i>	<i>weight loss after degradation experiment (%)</i>
PC-18	20 wt% aq. NaOH	38.8	37.9	97.7	2.3
PC-19		49.1	48.5	98.8	1.2
PC-23		43.8	43.4	99.1	0.9
PC-18	2 wt% aq NaOH	35.9	35.4	98.6	1.4
PC-19		50.0	49.7	99.4	0.6
PC-23		47.9	47.7	99.6	0.4
PC-18	conc. aq. HCl	28.3	27.6	97.5	2.5
PC-19		64.0	63.0	98.4	1.6
PC-23		55.6	55.3	99.5	0.5

4. Synthesis of Long-Spaced Polyacetals and Polycarbonates

Monomer Synthesis

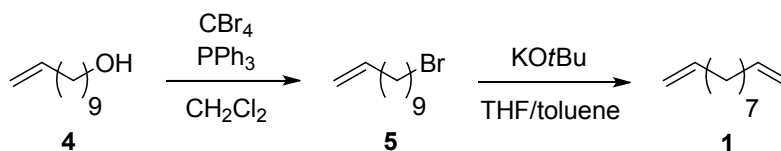


Figure S4. Synthesis of monomer 1.^[3]

Synthesis of 11-Bromo-1-undecene (5)^[3]

10-Undecenol (**4**; 71.0 g, 417 mmol) was dissolved in 350 mL of CH₂Cl₂ in a 1000 mL three-necked round bottom flask equipped with a condenser. After addition of tetrabromomethane (146 g, 440 mmol), the reaction mixture was cooled to 0 °C and triphenylphosphine (115 g, 440 mmol) was added in portions over a period of 30 minutes. The mixture was warmed to room temperature and refluxed over night. After cooling to room temperature, 300 mL of pentane was added. Triphenylphosphine oxide precipitated as a colorless solid. The suspension was filtered and the residue was washed with pentane (3 × 100 mL). The filtrate was evaporated under reduced pressure to yield a yellow oil. Compound **5** was obtained as a colorless oil by distillation under reduced pressure (bp = 105 °C at 9 mbar, 85.0 g, 365 mmol, 88 %).

¹H NMR (CDCl₃, 25 °C, 400 MHz): δ (ppm) = 5.81 (m, 1H, vinyl-CH), 4.96 (m, 2H, vinyl-CH₂), 3.41 (t, ³J = 6.9 Hz, 2H, CH₂Br), 2.02 (q, ³J = 6.8 Hz, 2H, CH₂-CH=CH₂), 1.85 (qui, ³J = 7.0 Hz, 2H, CH₂CH₂Br), 1.47-1.26 (m, 10H, CH₂). ¹³C NMR (CDCl₃, 25 °C, 101 MHz): δ (ppm) = 139.3 (CH₂=CH), 114.3 (CH₂=CH), 34.1, 33.9, 33.0, 29.5, 29.2, 29.0, 28.9, 28.3 (all CH₂). Elemental analysis calculated for C₁₁H₂₁Br: 56.66 C, 9.08 H; found: 56.51 C, 9.41 H.

Synthesis of Undeca-1,10-diene (1)^[3]

11-Bromo-1-undecene (**5**; 10.7 g, 45.7 mmol) was dissolved in 100 mL of a 2:1 mixture of dry THF and toluene in a 250 mL round bottom flask under inert gas atmosphere. Potassium *tert*-butoxide (10.25 g, 91.34 mmol) was added over a period of two hours at room temperature. The reaction mixture became turbid. Stirring was continued at room temperature over night. After addition of 50 mL of water, 50 mL of 1 M aq. HCl solution and 200 mL of CH₂Cl₂, the organic layer was separated and washed with 50 mL of saturated aq. NaHCO₃ solution and 50 mL of water, followed by drying with MgSO₄. The solvents were evaporated under reduced pressure to yield a yellow oil.

Compound **1** was obtained as a colorless oil by distillation under reduced pressure (bp = 75 °C at 15 mbar, 6.32 g, 41.5 mmol, 71 %).

¹H NMR (CDCl₃, 25 °C, 400 MHz): δ (ppm) = 5.81 (m, 2H, vinyl-CH), 4.96 (m, 4H, vinyl-CH₂), 2.04 (m, 4H, CH₂CH=CH₂), 1.38 (m, 4H, CH₂CH₂CH=CH₂), 1.29 (m, 6H, CH₂). ¹³C NMR (CDCl₃, 25 °C, 101 MHz): δ (ppm) = 139.4 (CH₂=CH), 114.3 (CH₂=CH), 34.0, 29.5, 29.2, 29.1 (all CH₂).

Synthesis of Bis(undec-10-en-1-yloxy)methane (**2**)

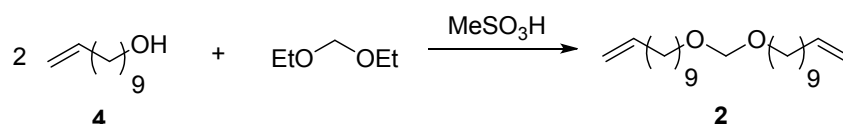


Figure S5. Preparation of monomer **2**

In a 50 mL Schlenk tube equipped with a stirring bar, 10-undecenol (**4**; 5.43 g, 31.9 mmol), diethoxymethane (1.66 g, 15.9 mmol) and methanesulfonic acid (150 mg, 1.54 mmol) were added under inert gas atmosphere. The reaction mixture was heated to 80 °C for 12 hours at atmosphere pressure. Then a dynamic vacuum of 100 mbar was applied for 5 hours at 80 °C to remove the byproduct ethanol from the reaction mixture. The mixture was cooled to room temperature and directly loaded on a silica column using pentane/ethyl acetate = 10/1 as the eluent. Compound **2** could be obtained as a colorless oil (4.07 g, 11.5 mmol, 72 %).

¹H NMR (CDCl₃, 25 °C, 400 MHz): δ (ppm) = 5.81 (m, 2H, vinyl-CH), 4.95 (m, 4H, vinyl-CH₂), 4.66 (s, 2H, OCH₂O), 3.97 (t, ³J = 6.7 Hz, 4H, CH₂OCH₂OCH₂), 2.04 (m, 4H, CH₂CH=CH₂), 1.58 (m, 4H, CH₂CH₂OCH₂OCH₂CH₂), 1.41-1.23 (m, 24H, CH₂). ¹³C NMR (CDCl₃, 25 °C, 101 MHz): δ (ppm) = 139.4 (CH₂=CH), 114.3 (CH₂=CH), 95.4 (OCH₂O), 68.0 (CH₂OCH₂OCH₂), 34.0, 29.9, 29.7, 29.6, 29.3, 29.1, 26.4 (all CH₂). Elemental analysis calculated for C₂₃H₄₄O₂: 78.35 C, 12.58 H; found: 78.38 C, 13.20 H.

Synthesis of Di(undec-10-en-1-yl) carbonate^[4]

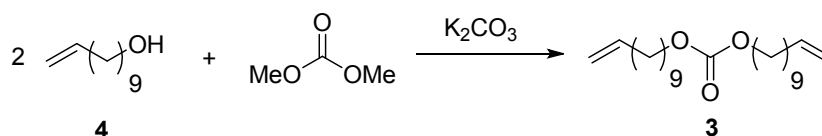


Figure S6. Preparation of monomer **3**

In a 50 mL Schlenk tube equipped with a stirring bar, 10-undecenol (**4**; 8.09 g, 47.5 mmol), dimethyl carbonate (2.14 g, 23.8 mmol) and potassium carbonate (164 mg; 1.18 mmol) were added under inert gas atmosphere. The reaction mixture was heated to 100 °C for 2 hours at atmosphere pressure. Then a dynamic vacuum of 100 mbar was applied for 5 hours at 100 °C to remove the byproduct methanol from the reaction mixture. The reaction mixture was cooled to room temperature and directly loaded on a silica column using pentane/ethyl acetate = 10/1 as the eluent. Compound **3** could be obtained as a colorless oil (5.81 g, 15.85 mmol, 67 %).

¹H NMR (CDCl₃, 25 °C, 400 MHz): δ (ppm) = 5.81 (m, 2H, vinyl-CH), 4.96 (m, 4H, vinyl-CH₂), 4.12 (t, ³J = 6.7 Hz, 4H, CH₂OC(O)OCH₂), 2.04 (m, 4H, CH₂CH=CH₂), 1.66 (m, 4H, CH₂CH₂OC(O)OCH₂CH₂), 1.41-1.23 (m, 24H, CH₂). ¹³C NMR (CDCl₃, 25 °C, 101 MHz): δ (ppm) = 155.6 (C=O), 139.4 (CH₂=CH), 114.3 (CH₂=CH), 68.2 (CH₂OC(O)OCH₂), 34.0, 29.6, 29.5, 29.4, 29.2, 29.1, 28.8, 25.9 (all CH₂). Elemental analysis calculated for C₂₃H₄₂O₃: 75.36 C, 11.55 H; found: 75.58 C, 12.09 H.

Polymerization Procedure to Generate Unsaturated Long-Spaced Polyacetals

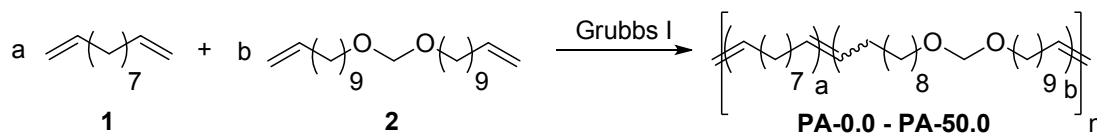


Figure S7. Preparation of the unsaturated polyacetals **PA-0.0 – PA-50.0**.

A mixture (altogether ca. 250 mg) of the appropriate amounts of the monomers **1** and **2** was weighed in a 25 mL Schlenk tube equipped with a stirr bar under an inert gas atmosphere. 0.5 mol-% of Grubbs 1st generation catalyst was added at room temperature and the mixture was moderately stirred applying a reduced pressure of 150 mbar (dynamic vacuum). Over a period of 2 hours, the viscosity increased significantly and the pressure was reduced stepwise to 10 mbar while the reaction temperature was raised to 65 °C. Polymerization was continued for two days at 65 °C and a pressure of 0.1 mbar. The mixture was cooled to room temperature and the catalyst was quenched by addition of 1 mL of ethyl vinyl ether and 5 mL of chloroform. The mixture was stirred for 30 min at room temperature and the polymer was dissolved.

For **PA-50.0**, **PA-21.3**, **PA-9.8**, **PA-4.9**, **PA-1.5** and **PA-0.0** the polymers were precipitated in 150 mL of ice-cold methanol. The unsaturated polymers were isolated by filtration in virtually quantitative yield as colorless or grayish solids.

For **PA-39.1H** and **PA-29.9H**, solvents were evaporated under reduced pressure to yield the unsaturated polymers as highly viscous, brownish materials in virtually quantitative yield.

^1H NMR (CDCl_3 , 25 °C, 400 MHz): δ (ppm) = 5.38 *trans* and 5.34 *cis* (m, $\text{CH}=\text{CH}$), 4.66 (s, 2H, OCH_2O), 3.97 (t, $^3J = 6.7$ Hz, 4H, $\text{CH}_2\text{OCH}_2\text{OCH}_2$), 1.98 (m, $\text{CH}_2\text{CH}=\text{CHCH}_2$), 1.58 (m, 4H, $\text{CH}_2\text{CH}_2\text{OCH}_2\text{OCH}_2\text{CH}_2$), 1.39-1.21 (br, CH_2). ^{13}C NMR (CDCl_3 , 25 °C, 101 MHz): δ (ppm) = 130.5 (*trans* $\text{CH}=\text{CH}$), 130.1 (*cis* $\text{CH}=\text{CH}$), 95.4 (OCH_2O), 68.0 ($\text{CH}_2\text{OCH}_2\text{OCH}_2$), 34.6, 32.8, 29.9, 29.8, 29.7, 29.5, 29.4, 29.3, 28.8, 27.4, 26.1, 25.2 (all CH_2).

Polymerization Procedure to Generate Unsaturated Long-Spaced Polycarbonates

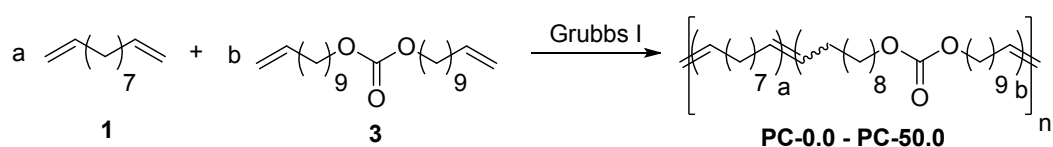


Figure S8. Preparation of the unsaturated polycarbonates **PC-0.0 – PC-50.0**.

A mixture (altogether ca. 250 mg) of the appropriate amounts of the monomers **1** and **3** was weighed in a 25 mL Schlenk tube under argon atmosphere. 0.5 mol-% of Grubbs 1st generation catalyst was added and the mixture was kept at a reduced pressure of 150 mbar (dynamic vacuum) at room temperature with moderate stirring. Over a period of 2 hours, viscosity increased significantly and the pressure was reduced stepwise to 10 mbar while the reaction temperature was raised to 65 °C. Polymerization was continued for two days at 65 °C and a pressure of 0.1 mbar. The mixture was cooled to room temperature and the catalyst was quenched by addition of 1 mL of ethyl vinyl ether and 5 mL of chloroform. The mixture was stirred for 30 min at room temperature. The polymer was dissolved and then precipitated in 150 mL of ice-cold methanol. The unsaturated polymer was isolated by filtration in virtually quantitative yield as a colorless solid.

^1H NMR (CDCl_3 , 25 °C, 400 MHz): δ (ppm) = 5.38 *trans* and 5.34 *cis* (m, $\text{CH}=\text{CH}$), 4.12 (t, $^3J = 6.7$ Hz, 4H, $\text{CH}_2\text{OC}(\text{O})\text{OCH}_2$), 1.98 (m, $\text{CH}_2\text{CH}=\text{CHCH}_2$), 1.66 (m, 4H, $\text{CH}_2\text{CH}_2\text{OC}(\text{O})\text{OCH}_2\text{CH}_2$), 1.39-1.21 (br, CH_2). ^{13}C NMR (CDCl_3 , 25 °C, 101 MHz): δ (ppm) = 155.6 ($\text{C}=\text{O}$), 130.5 (*trans* $\text{CH}=\text{CH}$), 130.1 (*cis* $\text{CH}=\text{CH}$), 68.2 ($\text{CH}_2\text{OC}(\text{O})\text{OCH}_2$), 34.6, 32.8, 29.9, 29.8, 29.7, 29.5, 29.4, 29.3, 28.8, 27.4, 26.1, 25.2 (all CH_2).

Hydrogenation Procedure to Generate Saturated Polyacetals and Polycarbonates

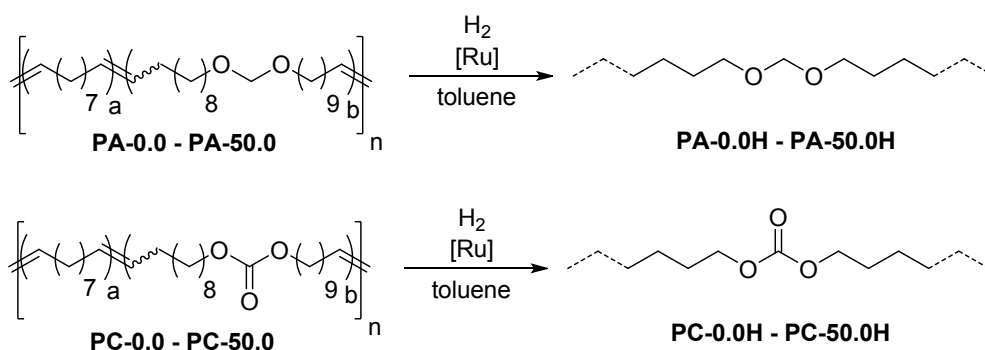


Figure S9. Hydrogenation to generate saturated polyacetals and polycarbonates

Preparation of the hydrogenation catalyst [(PCy₃)₂Cl₂Ru=CHOEt]: 1.0 mL of ethyl vinyl ether (0.75 g, 10.4 mmol) was added to Grubbs 1st generation catalyst (124 mg, 0.15 mmol) in a Schlenk tube under an argon atmosphere, and the mixture was stirred at room temperature for an hour. Excessive ethyl vinyl ether was evaporated under reduced pressure and the residue was dried in vacuum for 4 hours. Again, 1.0 mL of ethyl vinyl ether (0.75 g, 10.4 mmol) was added and the mixture was stirred for an hour at room temperature. The solvent was evaporated and the residue was dried in vacuum. The ruthenium catalyst was obtained as an orange solid in quantitative yield and used for the hydrogenations without further purification. Full conversion to the Fischer carbene was monitored by ¹H NMR spectroscopy, illustrated by the shifting of the alkylidene proton singlet (Ru=CHOEt) from 19.99 ppm to 14.56 ppm (CDCl₃, 25 °C, 400 MHz) and the absence of aromatic proton signals.

For hydrogenation, 200 mg of the unsaturated polymer was dissolved in 7 mL of toluene at 50 °C and 2 mg of ruthenium catalyst was added. Hydrogenation was conducted at 110 °C with a H₂ pressure of 40 bar in a pressure reactor equipped with a magnetic stir bar for 2 days. For the preparation of **PA-0.0H** (or **PC-0.0H**), *o*-xylene and a hydrogenation temperature of 140 °C was applied. The reactor was cooled to room temperature, vented, and the reaction mixture was dissolved in 30 mL of boiling toluene. The hot solution was added to 150 mL of ice-cold methanol and the polymer precipitated. The saturated polymer could be isolated by filtration as a lightly grey solid in quantitative yield.

Polyacetals: ¹H NMR (C₂D₂Cl₄, 130 °C, 400 MHz): δ (ppm) = 4.60 (s, OCH₂O), 3.49 (t, ³J = 6.6 Hz, CH₂OCH₂OCH₂), 1.56 (m, CH₂CH₂OCH₂OCH₂CH₂), 1.40 – 1.20 (br, CH₂). ¹³C NMR (C₂D₂Cl₄, 130 °C, 100 MHz): δ (ppm) = 95.0 (OCH₂O), 67.7 (CH₂OCH₂OCH₂), 33.7, 29.6, 29.5, 29.4, 29.3, 29.0, 28.8, 26.1 (all CH₂).

Polycarbonates: ¹H NMR (C₂D₂Cl₄, 130 °C, 400 MHz): δ (ppm) = 4.09 (t, ³J = 6.7 Hz, CH₂OC(O)OCH₂), 1.65 (qui, ³J = 7.0 Hz, CH₂CH₂OC(O)OCH₂CH₂), 1.39 – 1.24 (m, CH₂). ¹³C NMR (C₂D₂Cl₄, 130 °C, 100 MHz): δ (ppm) = 155.2 (CO), 68.0 (CH₂OC(O)OCH₂), 33.7, 29.3, 29.1, 29.0, 28.8, 28.6, 25.6 (all CH₂).

5. DSC of Polyacetals and Polycarbonates

DSC Traces of Polyacetals and Polycarbonates from Diol Polycondensation

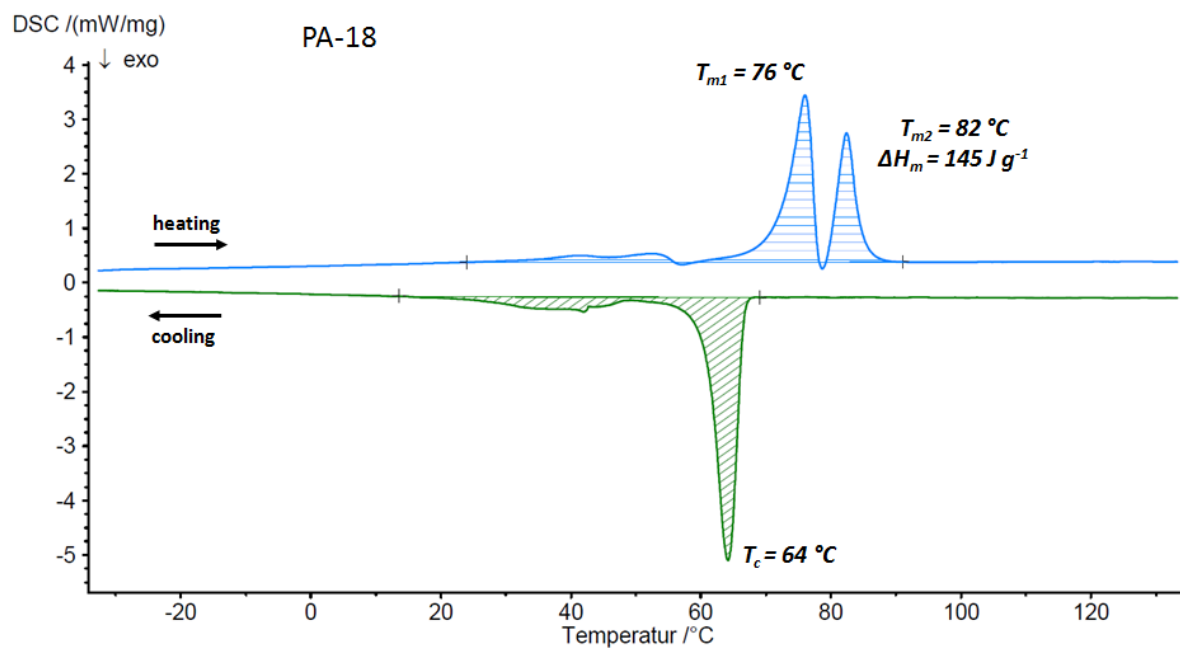


Figure S10. DSC trace of PA-18.

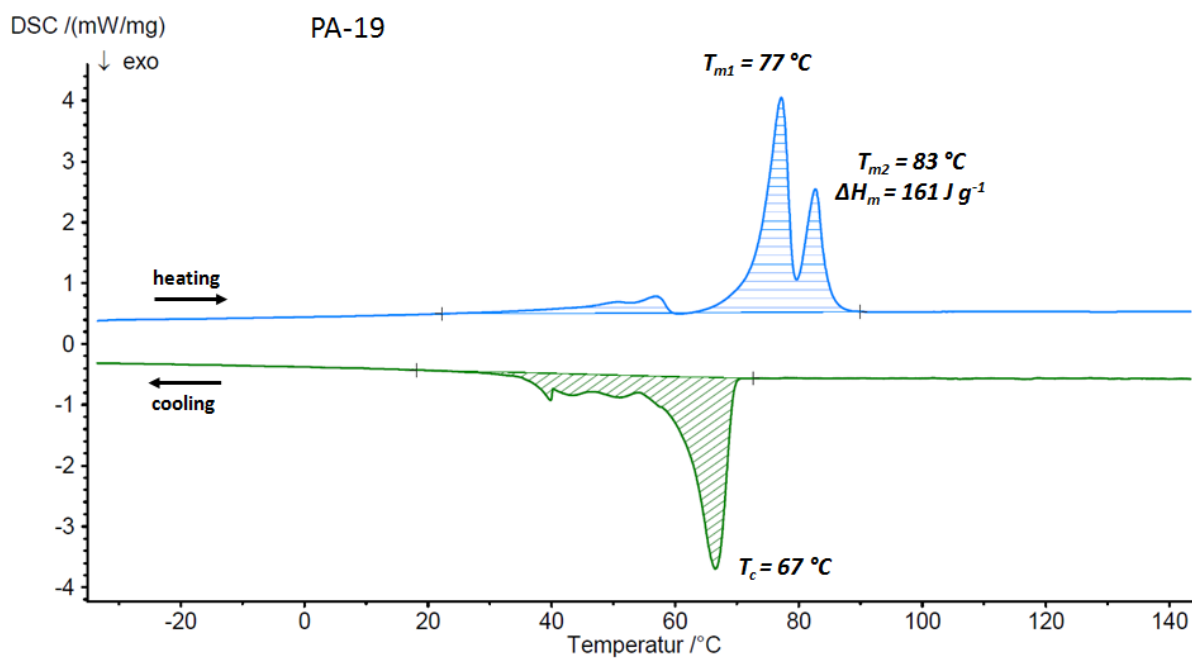


Figure S11. DSC trace of PA-19.

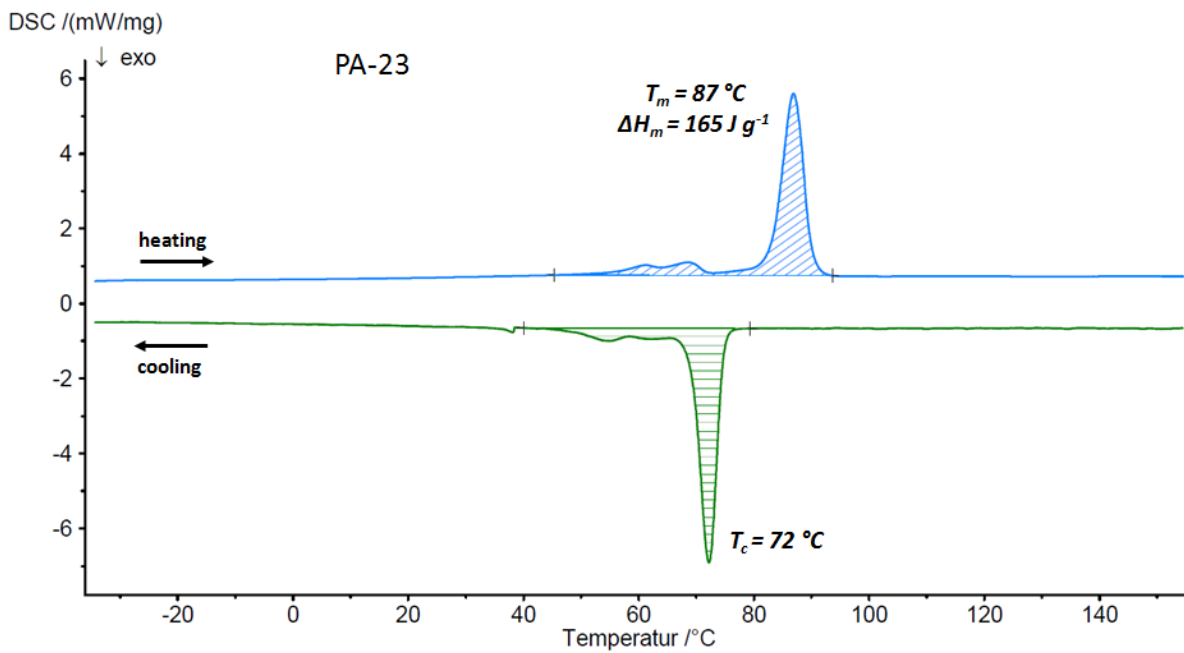


Figure S12. DSC trace of PA-23.

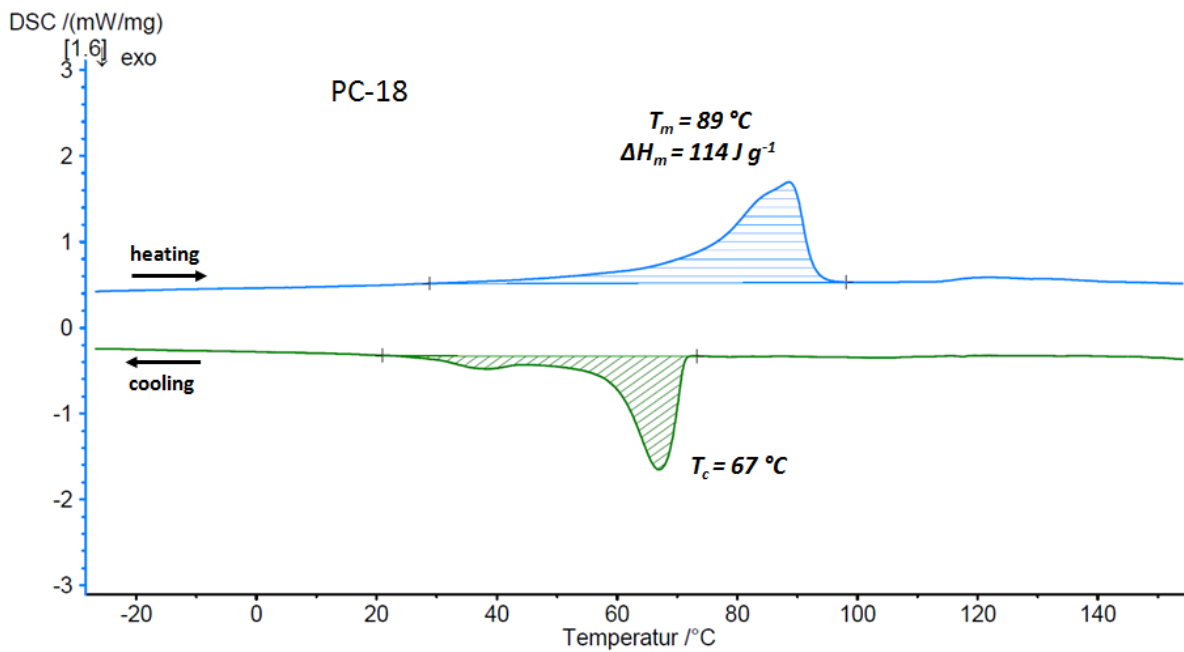


Figure S13. DSC trace of PC-18.

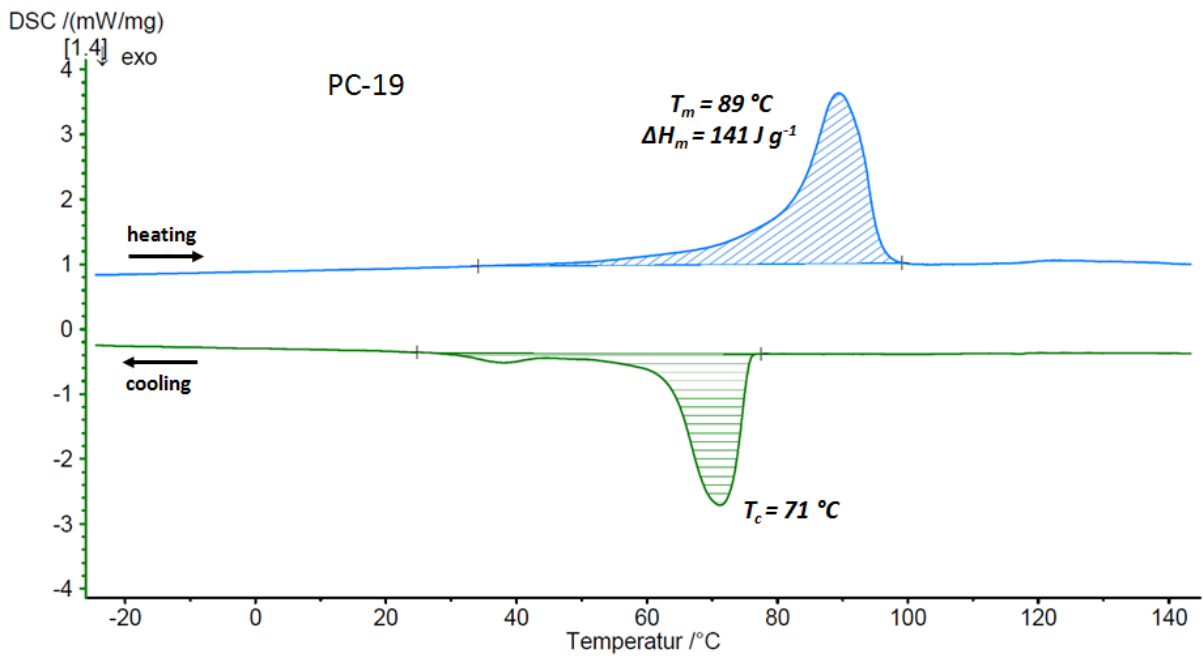


Figure S14. DSC trace of PC-19.

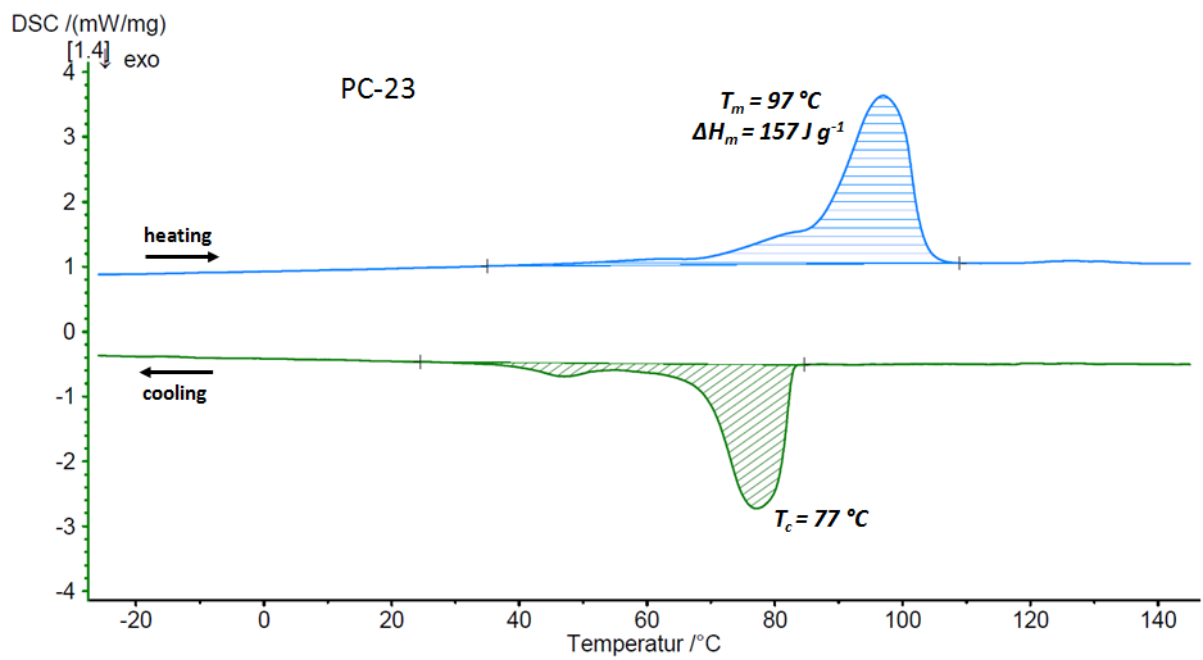


Figure S15. DSC trace of PC-23.

DSC Traces of Polyacetals from ADMET Copolymerization/Hydrogenation

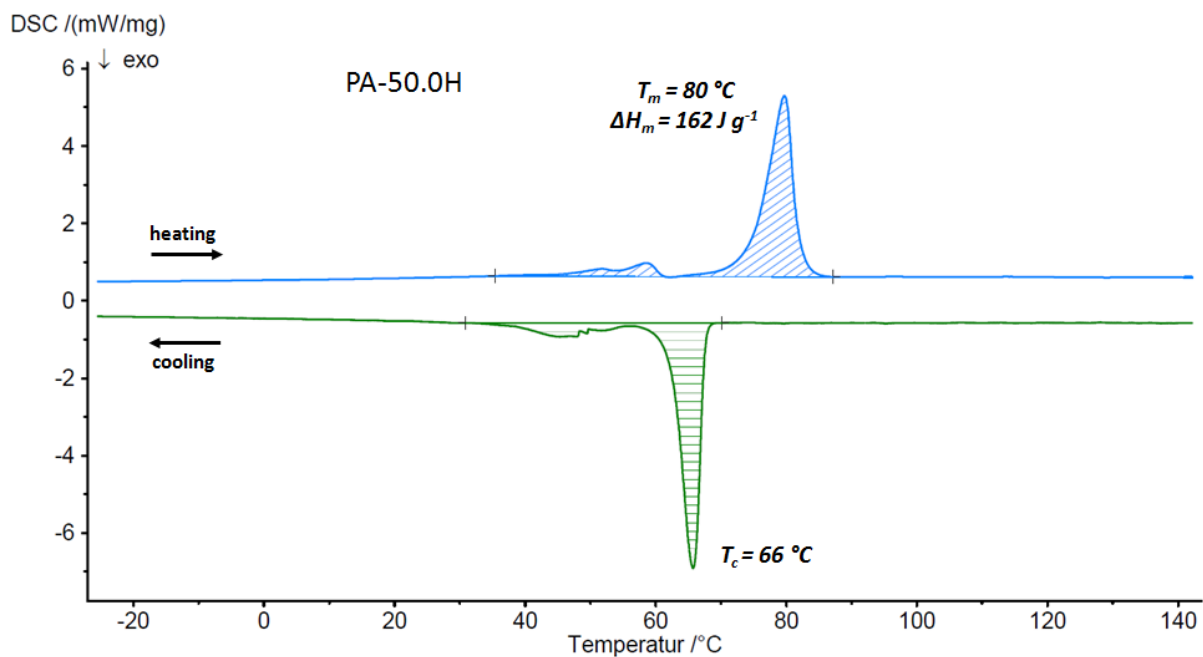


Figure S16. DSC trace of PA-50.0H.

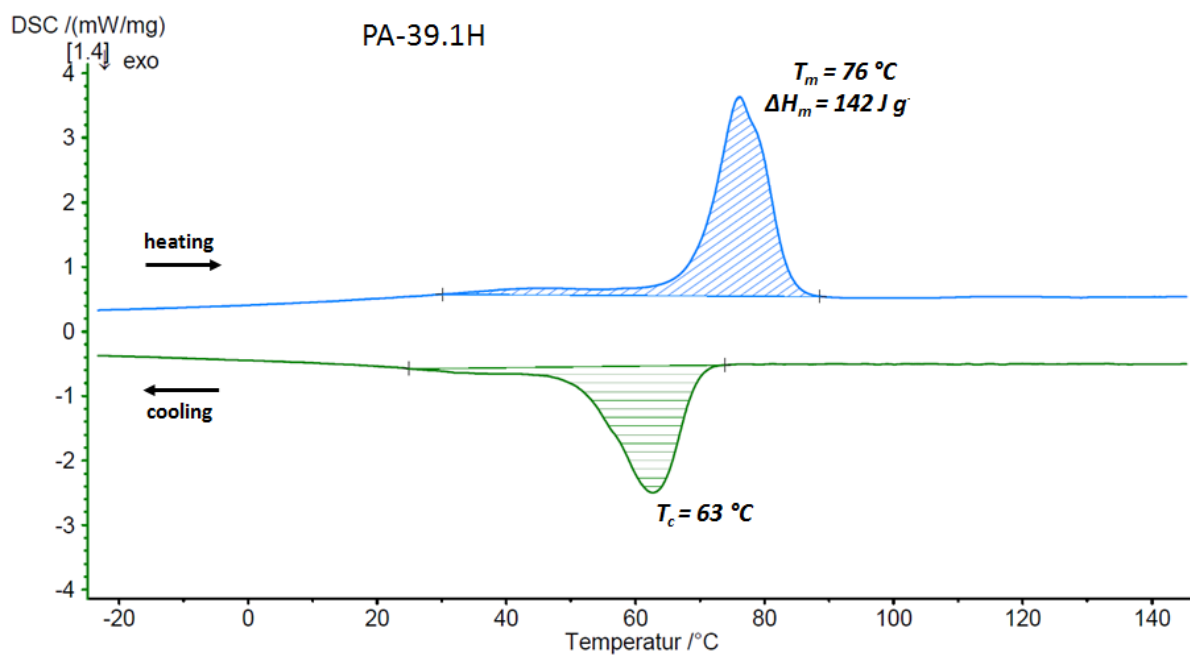


Figure S17. DSC trace of PA-39.1H.

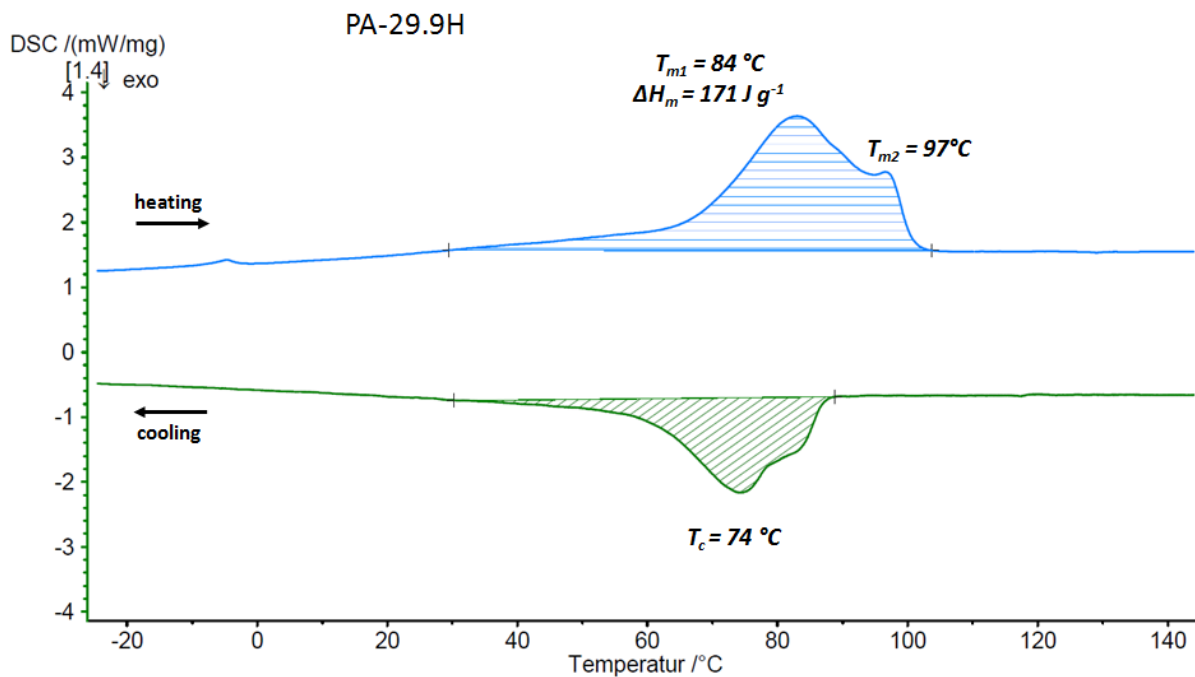


Figure S18. DSC trace of PA-29.9H.

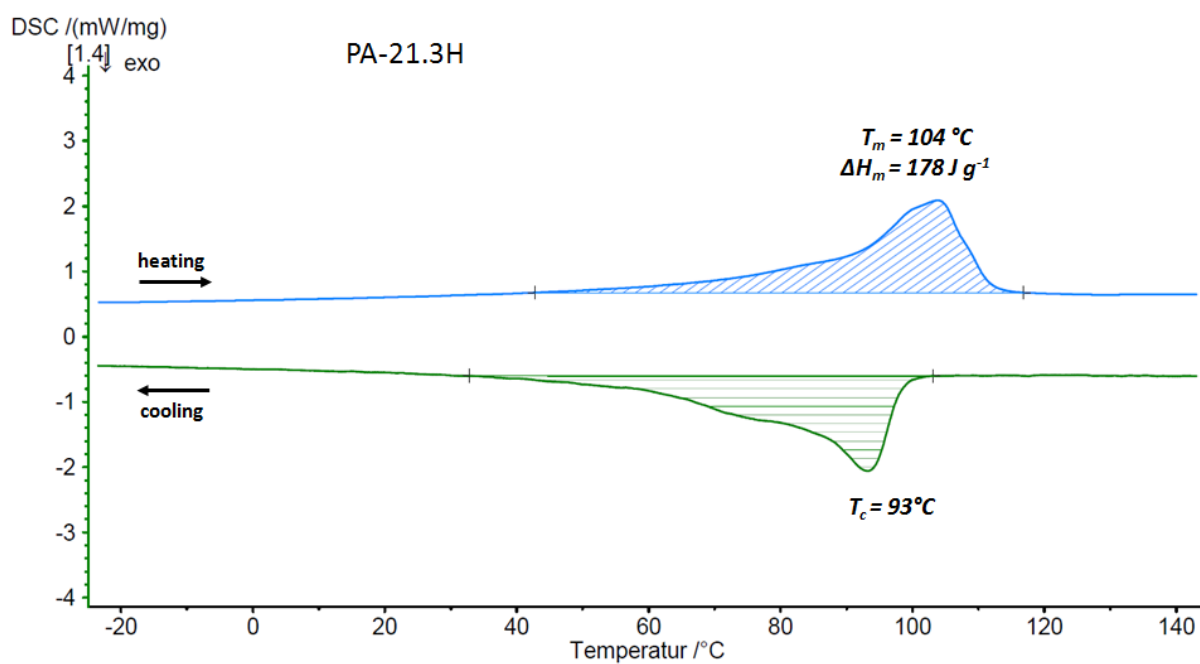


Figure S19. DSC trace of PA-21.3H.

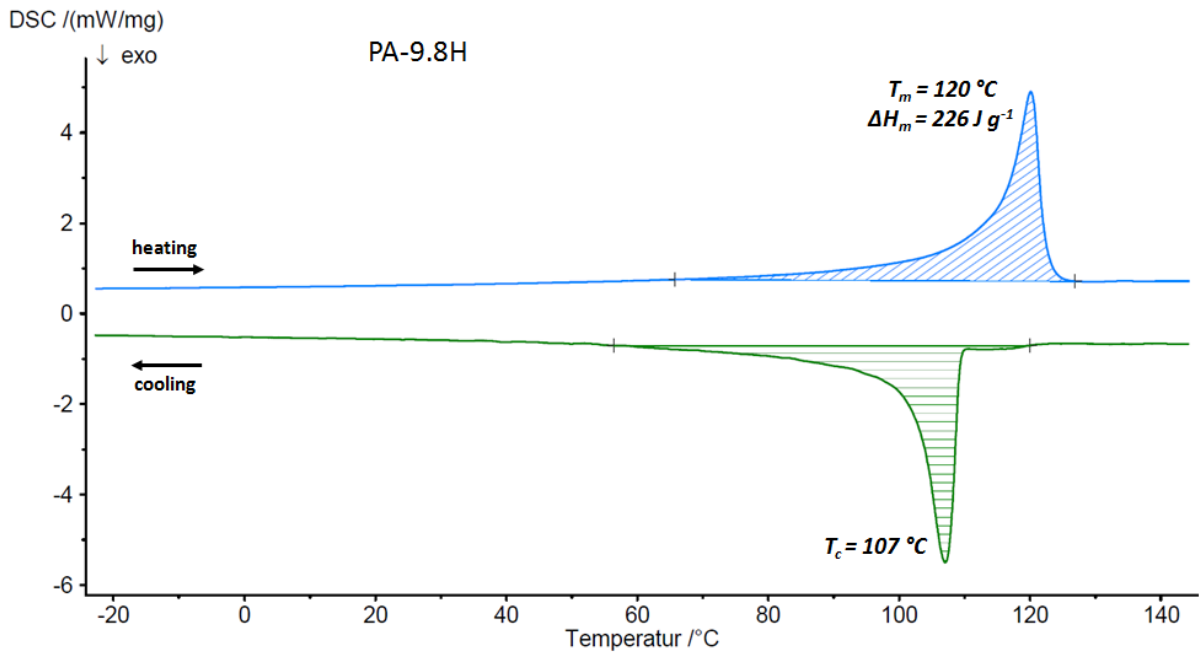


Figure S20. DSC trace of PA-9.8H.

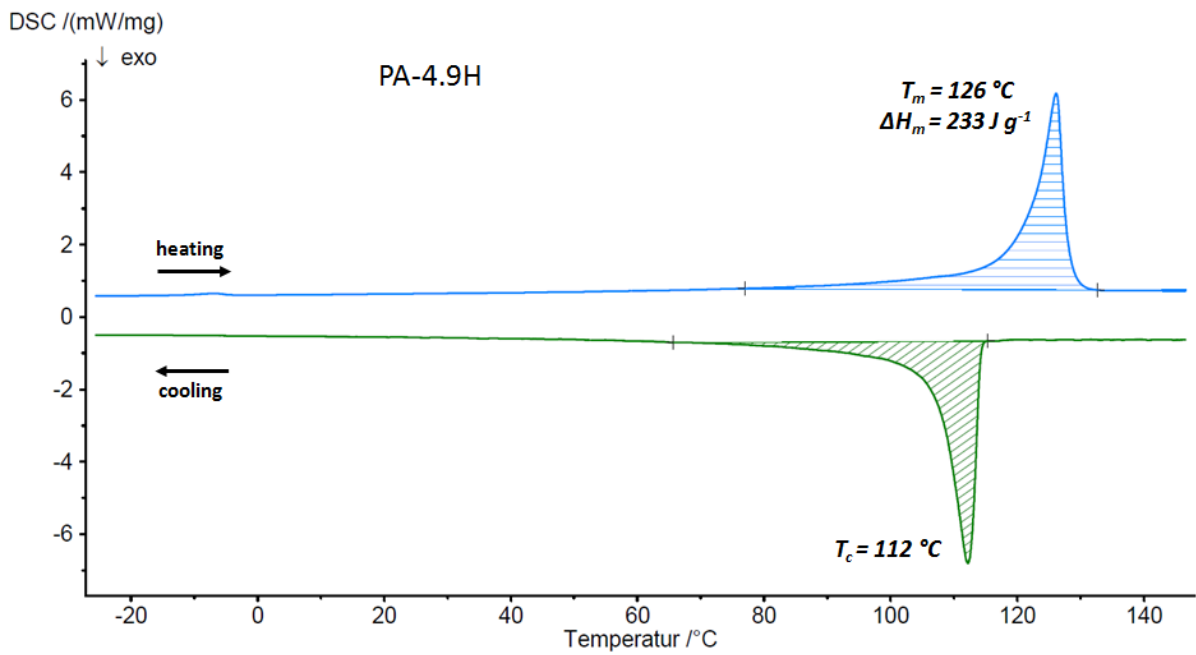


Figure S21. DSC trace of PA-4.9H.

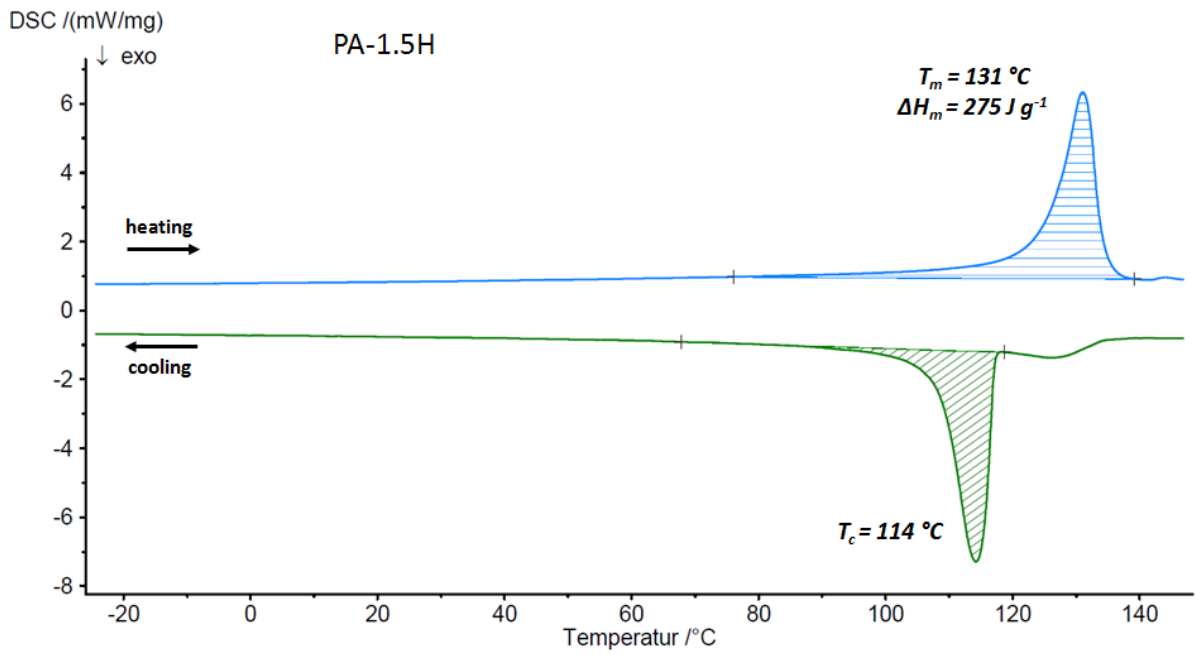


Figure S22. DSC trace of PA-1.5H.

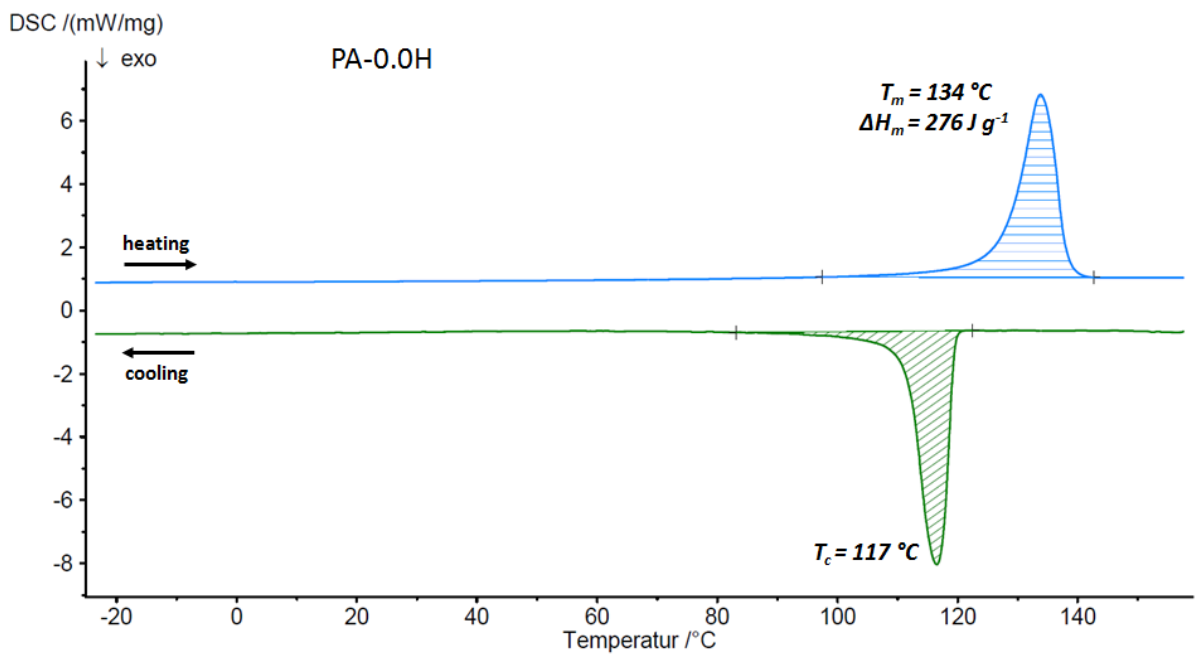


Figure S23. DSC trace of PA-0.0H.

DSC Curves of Polycarbonates from ADMET Copolymerization

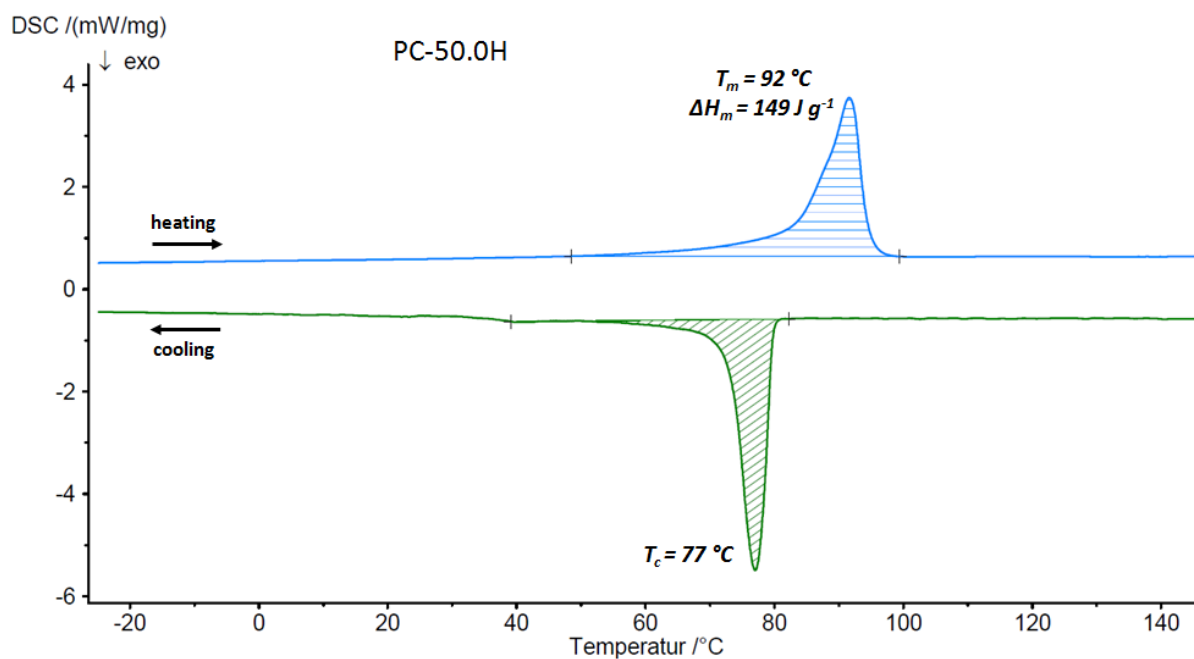


Figure S24. DSC trace of PC-50.0H.

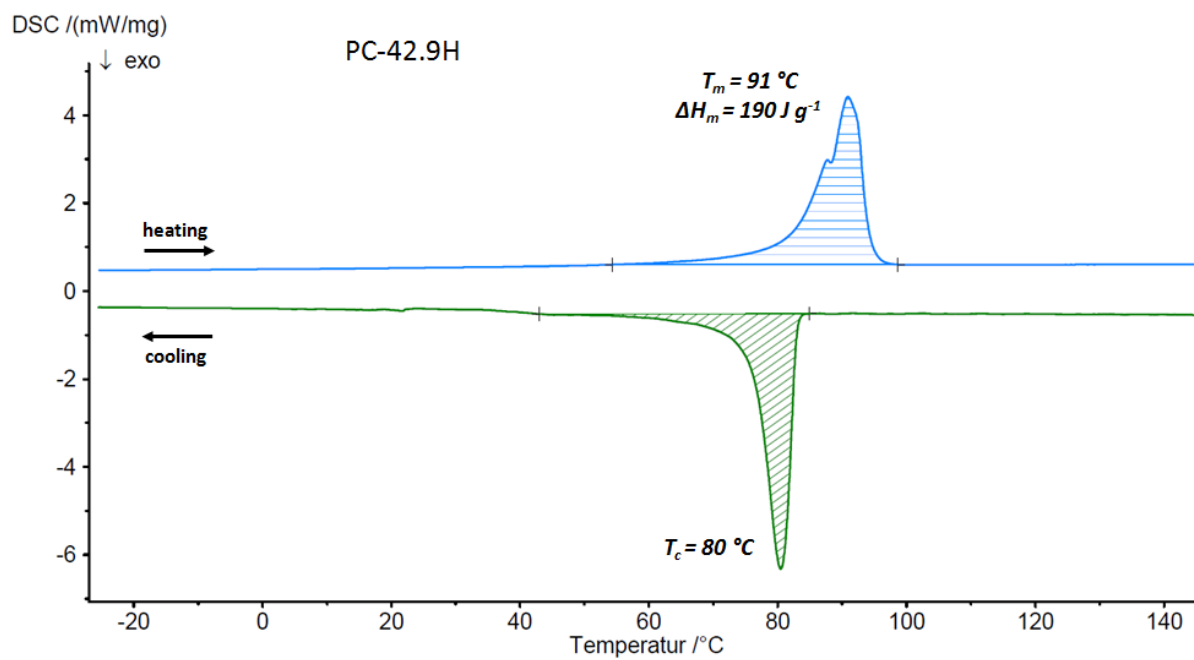


Figure S25. DSC trace of PC-42.9H.

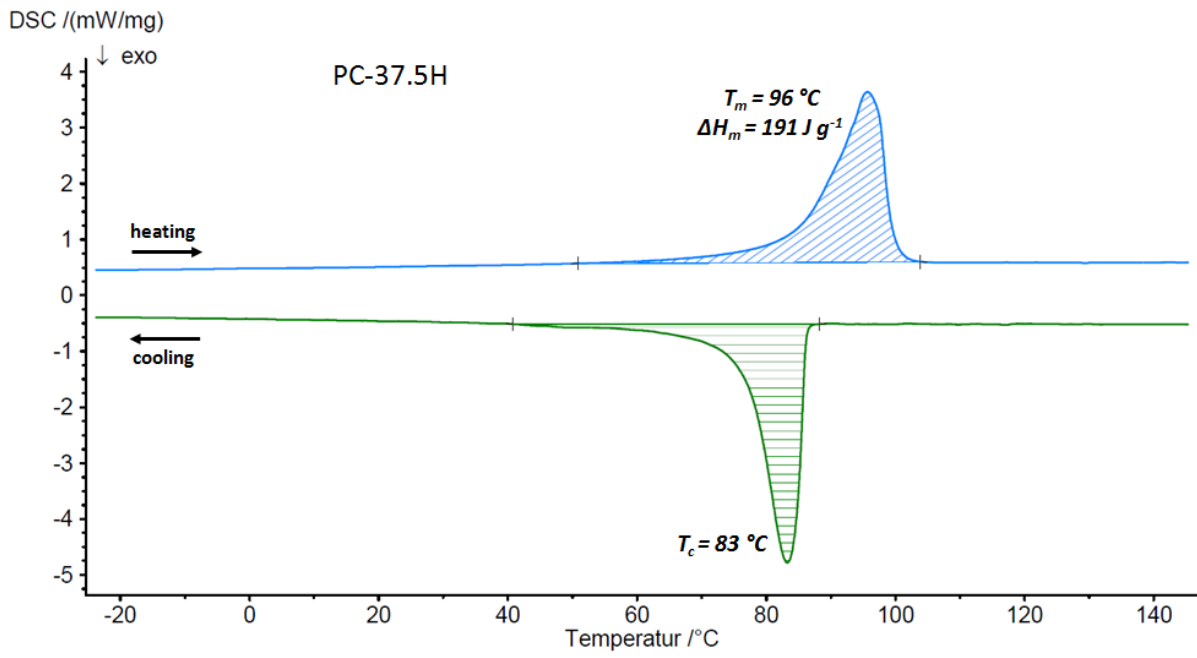


Figure S26. DSC trace of PC-37.5H.

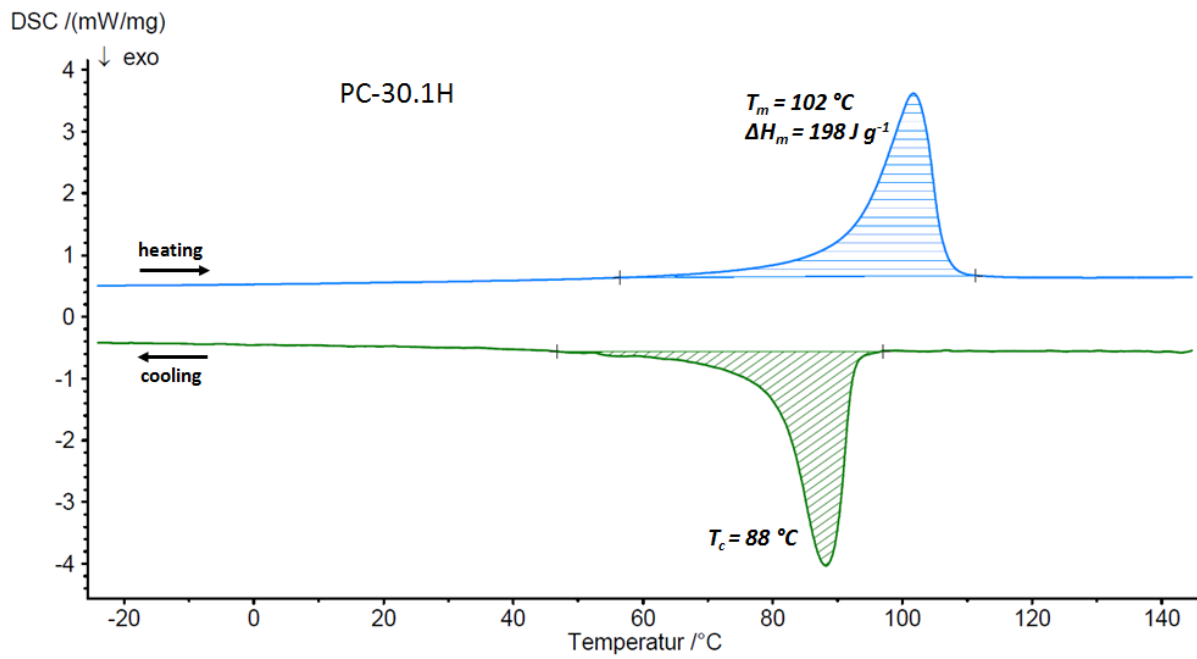


Figure S27. DSC trace of PC-30.1H.

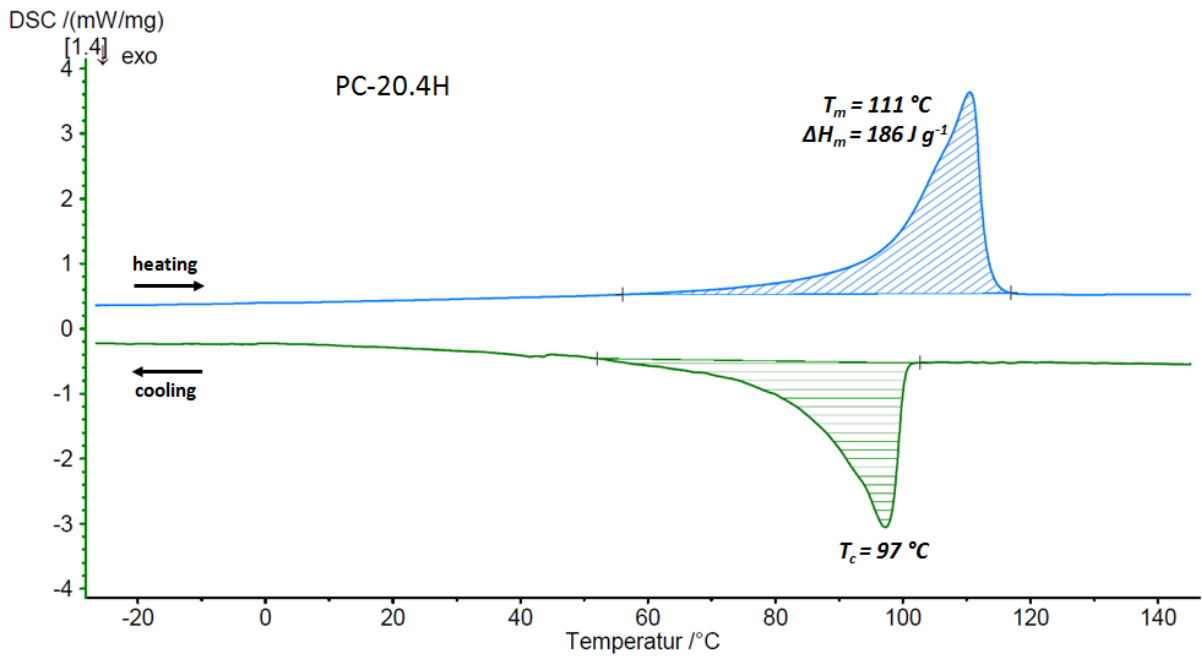


Figure S28. DSC trace of PC-20.4H.

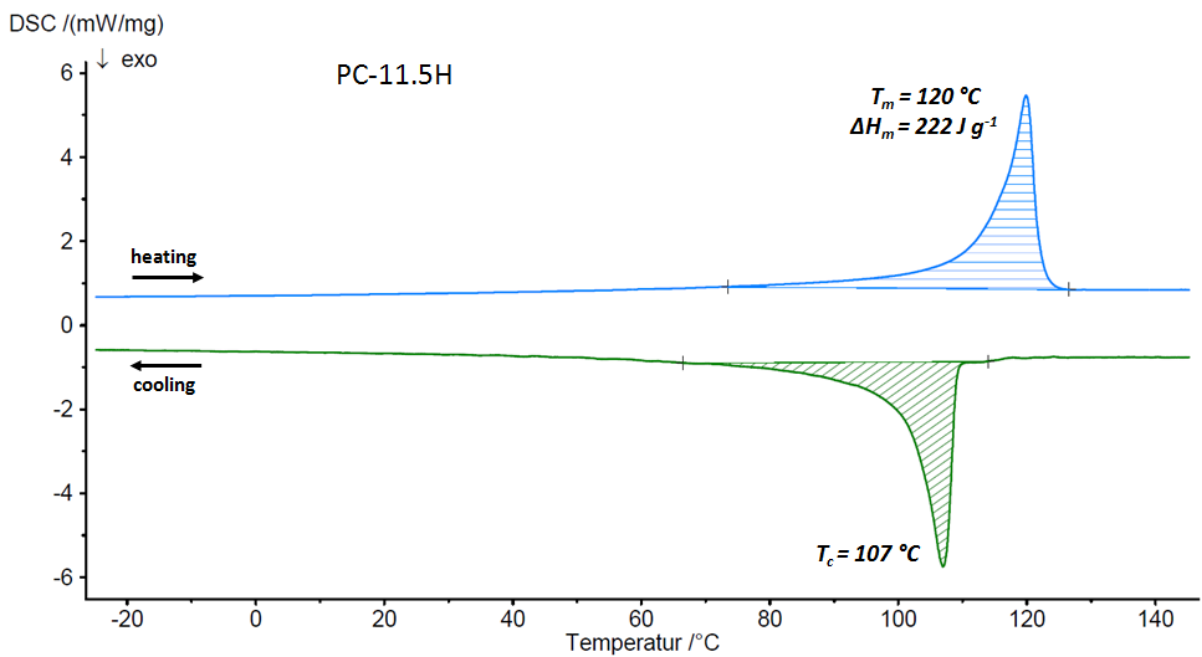


Figure S29. DSC trace of PC-11.5H.

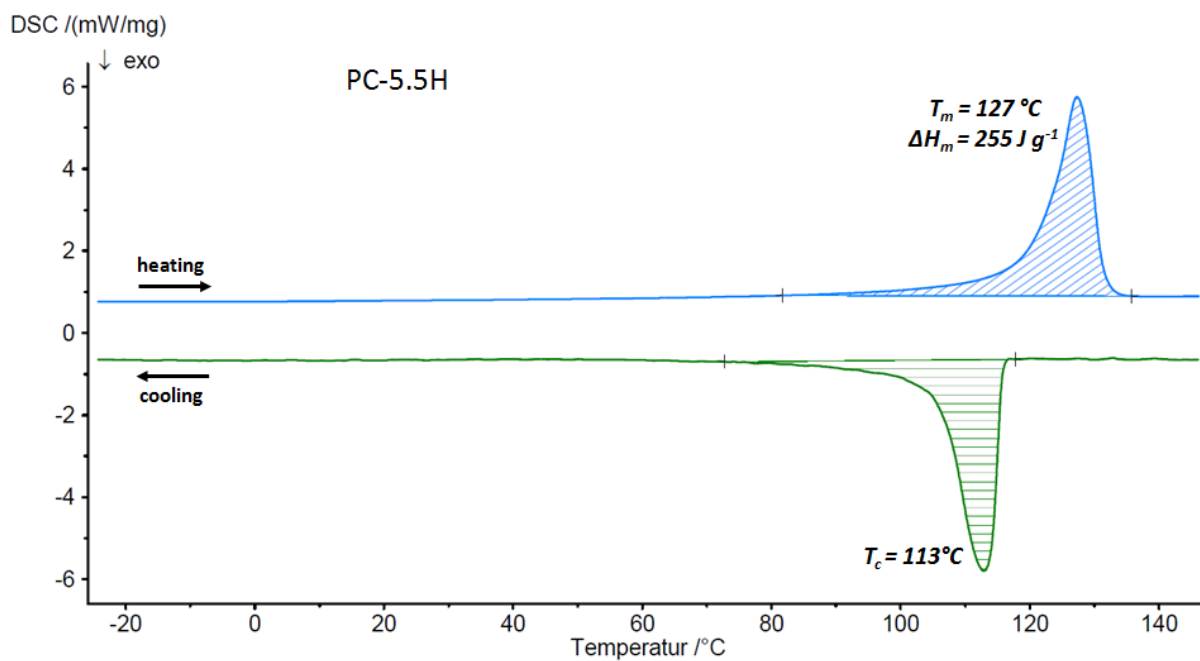


Figure S30. DSC trace of PC-5.5H.

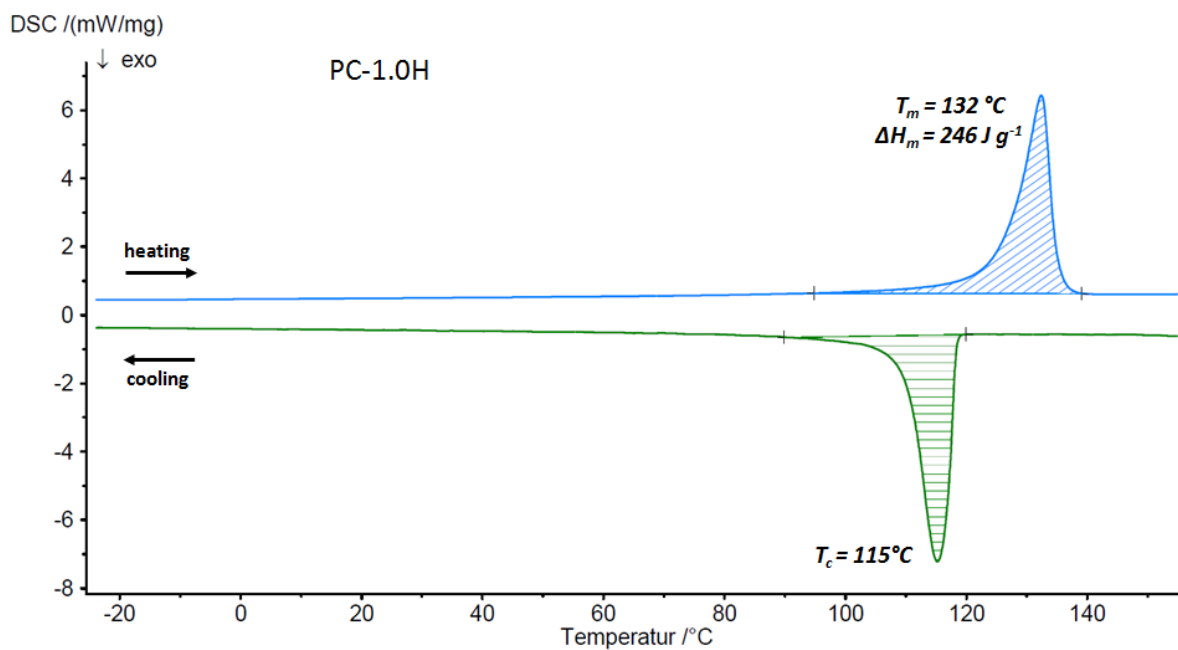


Figure S31. DSC trace of PC-1.0H.

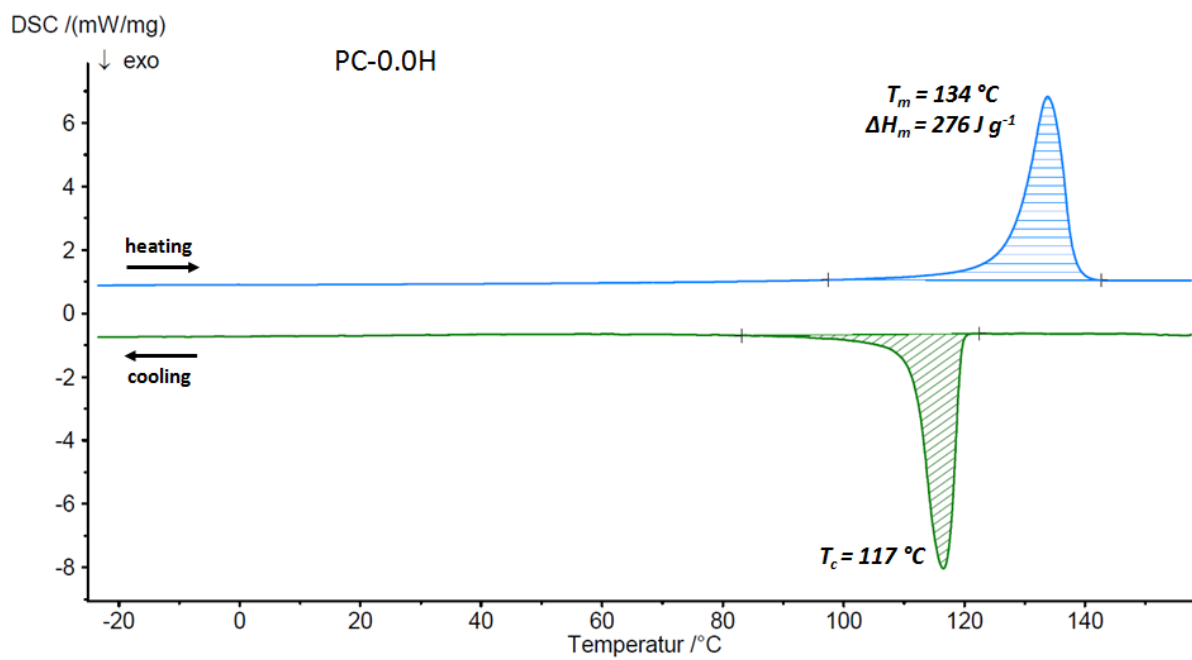


Figure S32. DSC trace of PC-0.0H.

6. WAXD Diagrams of Polycarbonates

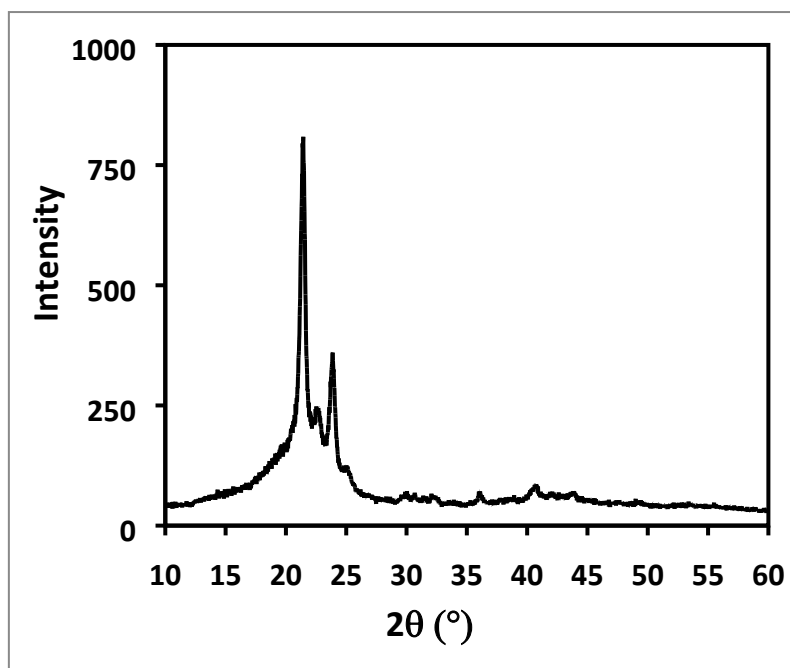


Figure S33. WAXD diagram of PC-18.

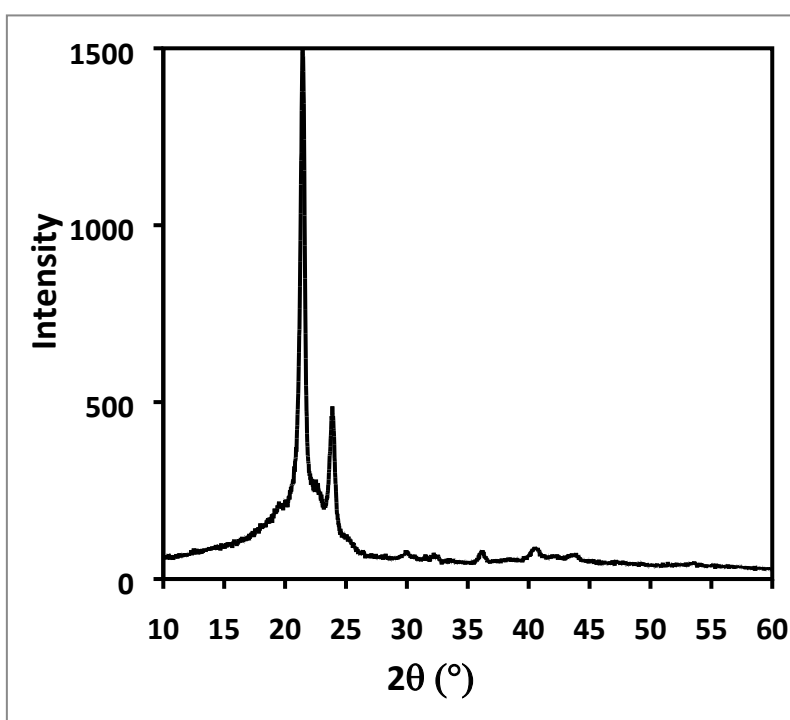


Figure S34. WAXD diagram of PC-23.

7. IR Spectra of Polyacetals and Polycarbonates



Figure S35. IR spectra of long-spaced polycarbonates **PC-50.0H** – **PC-0.0H**.

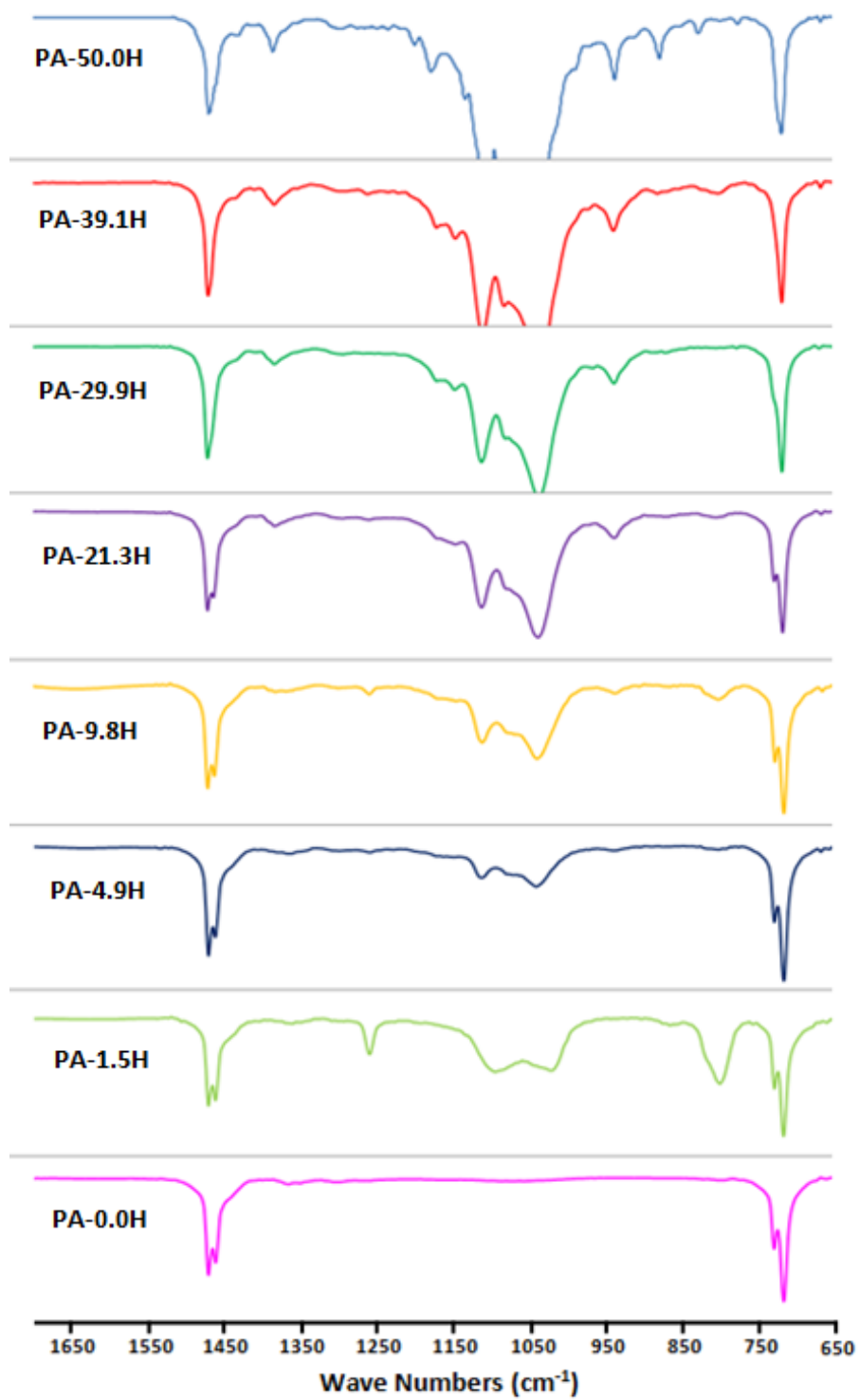


Figure S36. IR spectra of long-spaced polyacetals PA-50.0H – PA-0.0H.

8. Melting Points of Long-Spaced Polyacetals, Polycarbonates and Polyesters vs. Mole Fraction of Defect Units

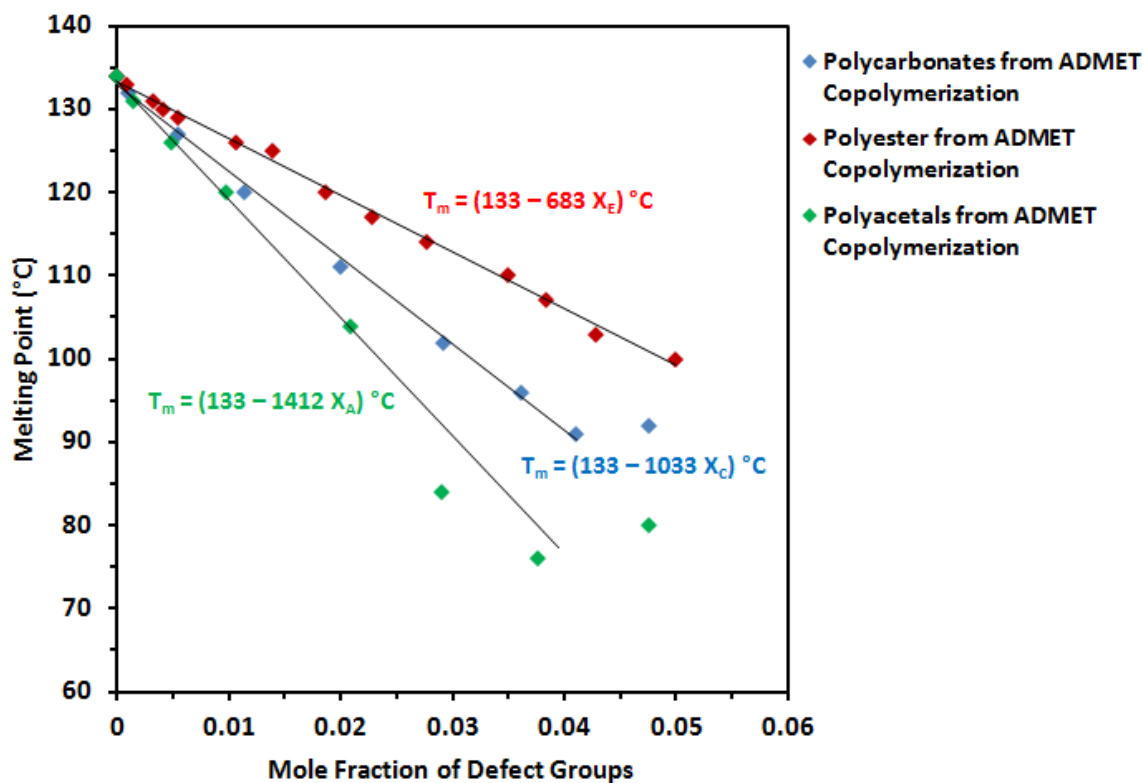


Figure S37. Peak melting points of long-spaced polyacetals (green), polycarbonates (blue) and polyesters (red) versus the mole fraction of defect groups and their linear regressions.

Table S3. Content of acetal groups in long-spaced polyacetals

<i>compound</i>	T_m (°C)	<i>acetals per 1000 methylene units</i>	<i>mole fraction of acetals</i>
PA-50.0H	80	50	0.04762
PA-39.1H	76	39.1	0.03763
PA-29.9H	84-97	29.9	0.02903
PA-21.3H	104	21.3	0.02086
PA-9.8H	120	9.8	0.0097
PA-4.9H	126	4.9	0.00488
PA-1.5H	131	1.5	0.0015
PA-0.0H	134	0	0

Table S4. Content of carbonate groups in long-spaced polycarbonates

<i>compound</i>	T_m (°C)	<i>carbonates per 1000 methylene units</i>	<i>mole fraction of carbonates</i>
PC-50.0H	92	50	0.04762
PC-42.9H	91	42.9	0.04113
PC-37.5H	96	37.5	0.03614
PC-30.1H	102	30.1	0.02922
PC-20.4H	111	20.4	0.01999
PC-11.5H	120	11.5	0.01137
PC-5.5H	127	5.5	0.00547
PC-1.0H	132	1	0.00099
PC-0.0H	134	0	0

Table S5. Content of ester groups in long-spaced polyesters^[4]

<i>compound</i>	T_m (°C)	<i>esters per 1000 methylene units</i>	<i>mole fraction of esters</i>
PE-52.6H	100	52.6	0.04997
PE-44.8H	103	44.8	0.04288
PE-40.1H	107	40	0.03846
PE-36.2H	110	36.2	0.03494
PE-28.6H	114	28.6	0.0278
PE-23.3H	117	23.3	0.02277
PE-19.1H	120	19.1	0.01874
PE-14.1H	125	14.1	0.0139
PE-10.7H	126	10.7	0.01059
PE-5.5H	129	5.5	0.00547
PE-4.2H	130	4.2	0.00418
PE-3.2H	131	3.2	0.00319
PE-0.9H	133	0.9	0.0009
PE-0.0H	134	0	0

9. References

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- [3] P. Ortmann and S. Mecking, *Macromolecules*, 2013, **46**, 7213 – 7218.
- [4] H. Mutlu, J. Ruiz, S. C. Solleder and M. A. R. Meier, *Green Chem.*, 2012, **14**, 1728 – 1735.