

Supporting Information

Long-Spaced Polyamides: Elucidating the Gap between Polyethylene Crystallinity and Hydrogen Bonding

*Patrick Ortmann, Tobias A. Lemke and Stefan Mecking**

Chair of Chemical Materials Science, Department of Chemistry, University of Konstanz, Universitätsstrasse 10,
D-78457 Konstanz, Germany.

*Corresponding author:
stefan.mecking@uni-konstanz.de

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1. General Methods and Materials

THF and toluene were distilled from sodium, triethylamine was distilled from KOH and stored under inert gas conditions. DMSO (extra dry) was purchased from Acros. All other solvents were used in technical grade as received.

Tetrabromomethane, 10-undecenoic acid, sodium azide, triethylamine, Grubbs 1st generation catalyst (benzylidene-bis(tricyclohexylphosphine)-dichlororuthenium), Hoveyda-Grubbs 1st generation catalyst (dichloro(*o*-isopropoxyphenylmethylene)(tricyclohexylphosphine)ruthenium), Hoveyda-Grubbs 2nd generation catalyst ([1,3-bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene]-dichloro(*o*-isopropoxyphenylmethylene)-ruthenium) and ethyl vinyl ether were supplied by Sigma Aldrich. LiAlH₄ was purchased from Merck. Triphenylphosphine, potassium *tert*-butoxide, thionyl chloride, and Wilkinson's catalyst (chlorotris(triphenylphosphine)rhodium) were supplied by Acros. 10-Undecenol was purchased from ACME Synthetic Chemicals (Mumbai, India). Hydrogen (5.0) was supplied from Air Liquide. All deuterated solvents for nuclear magnetic resonance (NMR) spectroscopy were supplied by Eurisotop.

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 recorded in the second heating cycles.

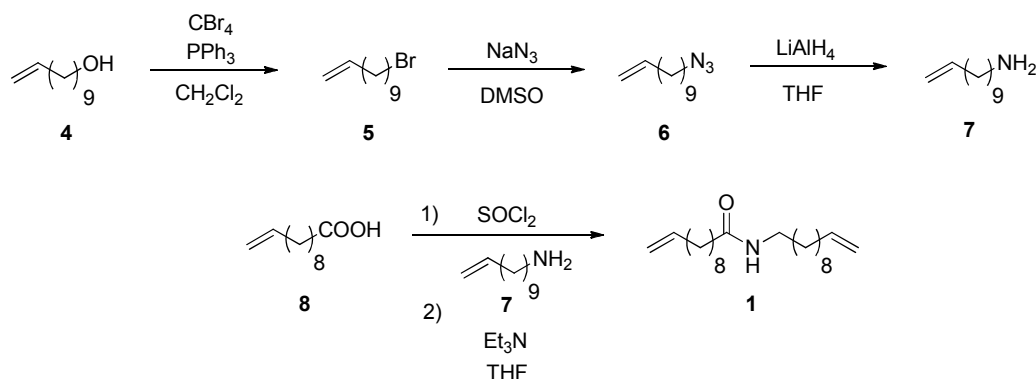
Gel permeation chromatography (GPC) measurements were carried out on a Polymer Laboratories PL-GPC 50 with two PLgel 5 µm MIXED-C columns in THF at 40 °C against polystyrene standards with refractive index detection.

Infrared (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. Monomer Synthesis

2.1 Synthesis of the Amide Functionalized Diene Monomer (1)^[1]



Scheme S1. Synthesis of the amide monomer **1**.

Synthesis of 11-bromoundec-1-ene (**5**)^[2,3]

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 over a period of 30 minutes. The mixture was warmed to room temperature and refluxed over night. The reaction mixture was cooled to room temperature and 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 (m, 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 11-Azidoundec-1-ene (**6**)^[1]

11-Bromoundec-1-ene **5** (11.61 g, 49.80 mmol) was dissolved in 80 mL of dry DMSO in a 250 mL Schlenk flask under inert gas atmosphere and sodium azide (6.47 g, 99.60 mmol) was added. The reaction mixture was stirred at room temperature for 30 minutes and then heated to 60 °C for 2 hours. The mixture was cooled to room temperature and 200 mL of CH₂Cl₂ and 200 mL of water were added. The organic phase was separated, washed with water (3 × 100 mL) and dried with MgSO₄. The solvents were evaporated in vacuum to yield compound **6** as lightly yellow oil, which was used in the following reaction step without further purification (9.19 g, 47.06 mmol, 94 %).

^1H NMR (CDCl_3 , 25 °C, 400 MHz): δ (ppm) = 5.81 (m, 1H, vinyl-CH), 4.95 (m, 2H, vinyl-CH₂), 3.25 (t, 3J = 7.0 Hz, 2H, CH₂N₃), 2.04 (m, 2H, CH₂CH=CH₂), 1.60 (m, 2H, CH₂CH₂N₃), 1.41-1.23 (m, 12H, CH₂). ^{13}C NMR (CDCl_3 , 25 °C, 101 MHz): δ (ppm) = 139.3 (CH₂=CH), 114.3 (CH₂=CH), 51.7 (CH₂N₃), 33.9, 29.6, 29.5, 29.3, 29.2, 29.1, 29.0, 26.9 (all CH₂). Elemental analysis calculated for C₁₁H₂₁N₃: 67.65 C, 10.84 H, 21.52 N; found: 67.40 C, 11.15 H, 21.44 N.

Synthesis of Undec-10-en-1-amine (7)^[1]

In a 1000 mL three necked round bottom flask equipped with a condenser, 300 mL of dry THF were cooled to 0 °C in an ice/water bath. LiAlH₄ (3.57 g, 94.12 mmol) was added slowly to give a grey suspension, which was stirred for 5 minutes. 11-Azidoundec-1-ene **6** (9.19 g, 47.06 mmol) was dissolved in 80 mL of dry THF and slowly added to the LiAlH₄ suspension over a period of 1 hour, stirred for further 30 minutes at 0 °C and then refluxed for additional 2 hours. (*Caution: decelerated gas evolution might occur.*) The mixture was cooled to 0 °C and then water was added dropwise until hydrogen gas evolution ceased. After further addition of 30 mL of water and 10 mL of a 20 % aq. NaOH solution, the suspension was filtered over a Büchner funnel. The residue was extracted with THF (3 x 50 mL). The filtrates were combined and the solvents were evaporated in vacuum to a volume of about 100 mL. 200 mL of CH₂Cl₂ and 200 mL of water were added, the organic phase was separated and dried with MgSO₄. The solvents were evaporated in vacuum to yield compound **7** as a lightly yellow oil, which solidified over the following days. The product was used in the following reaction step without further purification (7.22 g, 42.63 mmol, 91 %).

^1H NMR (CDCl_3 , 25 °C, 400 MHz): δ (ppm) = 5.81 (m, 1H, vinyl-CH), 4.95 (m, 2H, vinyl-CH₂), 2.68 (t, 3J = 7.0 Hz, 2H, CH₂NH₂), 2.04 (m, 2H, CH₂CH=CH₂), 1.48-1.23 (m, 16H, NH₂ and CH₂). ^{13}C NMR (CDCl_3 , 25 °C, 101 MHz): δ (ppm) = 139.4 (CH₂=CH), 114.3 (CH₂=CH), 42.4 (CH₂NH₂), 34.0, 29.7, 29.6, 29.3, 29.1, 27.1 (all CH₂).

Synthesis of *N*-(Undec-10-en-1-yl)undec-10-enamide (**1**)^[1]

Undec-10-enoic acid **8** (4.58 g, 24.87 mmol) was placed in a 200 mL Schlenk tube equipped with a condenser and thionyl chloride (2.71 mL, 4.44 g, 37.31 mmol) was added under inert gas atmosphere. The mixture was stirred at room temperature for 3 hours until the gas evolution ceased and then refluxed for another 2 hours. The reaction mixture was cooled to room temperature and excessive thionyl chloride was distilled off in vacuum to yield the acid chloride as a reddish oil, which was used in the amidation reaction without further purification.

Undec-10-en-1-amine **7** (4.21 g, 24.87 mmol) and triethylamine (3.45 mL, 2.52 g, 24.87 mmol) were dissolved in 100 mL of dry THF in a 250 mL round bottom flask under inert gas atmosphere. The acid chloride was added dropwise over a period of 1 hour and the reaction mixture was stirred at room temperature over night. 150 mL of CH₂Cl₂ and 100 mL of water were added. The organic phase was separated and washed with water (2 x 50 mL), dried with MgSO₄ and the solvents were evaporated in vacuum. The crude product was purified by column chromatography using pentane/ethyl acetate = 2/1 as the eluent to yield compound **1** as a colorless solid (6.74 g, 20.09 mmol, 81 %).

^1H NMR (CDCl_3 , 25 °C, 400 MHz): δ (ppm) = 5.80 (m, 2H, vinyl-CH), 5.38 (br, 1H, NH), 4.95 (m, 4H, vinyl-CH₂), 3.23 (m, 2H, CONHCH₂), 2.14 (t, 3J = 7.5 Hz, 2H, CH₂CONH), 2.03 (m, 2H, CH₂CH=CH₂), 1.61 (m, 2H,

$\text{CH}_2\text{CH}_2\text{CONH}$), 1.48 (m, 2H, $\text{CONHCH}_2\text{CH}_2$), 1.48-1.23 (m, 22H, CH_2). ^{13}C NMR (CDCl_3 , 25 °C, 101 MHz): δ (ppm) = 173.2 (CO), 139.3 ($\text{CH}_2=\text{CH}$), 114.3 ($\text{CH}_2=\text{CH}$), 39.6, 37.1, 33.9, 29.9, 29.6, 29.5, 29.4, 29.2, 29.1, 29.0, 27.1, 26.0 (all CH_2). Elemental analysis calculated for $\text{C}_{22}\text{H}_{41}\text{NO}$: 78.74 C, 12.32 H, 4.17 N; found: 78.69 C, 12.49 H, 4.30 N.

2.2 Synthesis of Undeca-1,10-diene (**2**)^[3,4]

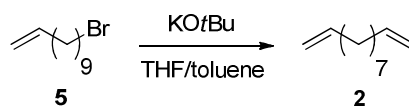


Figure S2. Synthesis of monomer **2**.

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 CH_2Cl_2 , the organic layer was separated and washed with 50 mL of saturated aq. NaHCO_3 solution and 50 mL of water, followed by drying with MgSO_4 . The solvents were evaporated under reduced pressure to yield a yellow oil. Compound **2** 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 (CDCl_3 , 25 °C, 400 MHz): δ (ppm) = 5.81 (m, 2H, vinyl- CH), 4.96 (m, 4H, vinyl- CH_2), 2.04 (m, 4H, $\text{CH}_2\text{CH}=\text{CH}_2$), 1.38 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$), 1.29 (m, 6H, CH_2). ^{13}C NMR (CDCl_3 , 25 °C, 101 MHz): δ (ppm) = 139.4 ($\text{CH}_2=\text{CH}$), 114.3 ($\text{CH}_2=\text{CH}$), 34.0, 29.5, 29.2, 29.1 (all CH_2).

2.3 Synthesis of the Ester Functionalized Diene Monomer (**3**)^[1,3,5,6]

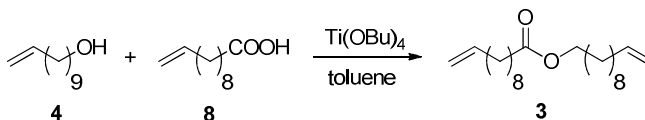


Figure S3. Synthesis of monomer **3**.

10-Undecenol **4** (16.93 g, 99.42 mmol) and undec-10-enoic acid **8** (18.32 g, 99.42 mmol) were dissolved in 100 mL of dry toluene under an argon atmosphere in a 250 mL round bottom flask equipped with a Dean-Stark apparatus. After addition of $\text{Ti}(\text{OBu})_4$ (677 mg, 1.99 mmol) the reaction mixture was refluxed for two days and then cooled to room temperature. After addition of 100 mL of water, 10 mL of acetic acid and 100 mL of toluene, the organic layer was separated and washed with saturated aqueous NaHCO_3 solution (20 mL) and water (20 mL). The organic layer was dried with MgSO_4 and evaporated. After column chromatography using

pentane/diethyl ether = 4/1 as the eluent, compound **3** was isolated as a colorless oil (24.39 g, 72.48 mmol, 73 %).

^1H NMR (CDCl_3 , 25 °C, 400 MHz): δ (ppm) = 5.81 (m, 2H, vinyl-CH), 4.96 (m, 4H, vinyl-CH₂), 4.05 (t, 3J = 6.7 Hz, 2H, COOCH₂), 2.28 (t, 3J = 7.5 Hz, 2H, CH₂COO), 2.03 (m, 4H, CH₂CH=CH₂), 1.61 (m, 4H, CH₂CH₂COOCH₂CH₂), 1.41-1.23 (m, 22H, CH₂). ^{13}C NMR (CDCl_3 , 25 °C, 101 MHz): δ (ppm) = 174.2 (C=O), 139.4 (CH₂=CH), 114.3 (CH₂=CH), 64.5 (COOCH₂), 34.6, 34.0, 33.9, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 29.0, 28.8, 26.1, 25.2 (all CH₂). Elemental analysis calculated for C₂₂H₄₄O₂: 78.51 C, 11.98 H; found: 78.61 C, 12.05 H.

3. Polymer Synthesis

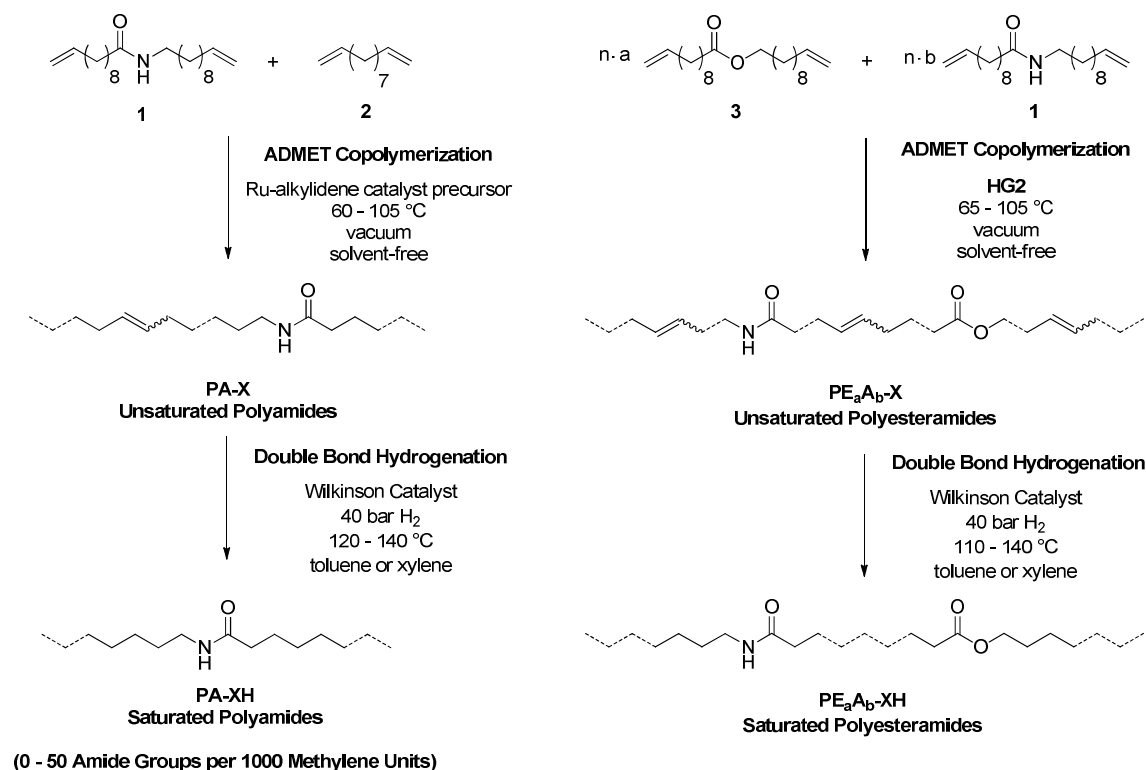


Figure S4. Left: ADMET copolymerization to generate unsaturated polyamides and hydrogenation to saturated polyamides. Right: ADMET copolymerization to synthesize unsaturated polyesteramides and hydrogenation to saturated polyesteramides.

3.1 Preparation of Unsaturated Polyamides

General polymerization procedure: A mixture (ca. 250 mg) of the appropriate amounts of the amide functionalized diene **1** and the purely aliphatic diene **2** was weighed in a 25 mL Schlenk tube equipped with a stirring bar under nitrogen atmosphere. The mixture was heated to 60 °C to yield a homogeneously molten monomer solution. 0.5 mol% of the corresponding ruthenium alkylidene catalyst precursor was added, and the mixture was kept at a reduced pressure of 150 mbar (dynamic vacuum) and stirred moderately. For polyamides with moderate to high amide contents, the reaction temperature was adapted according to the melting points of the resulting unsaturated polyamides as displayed in Table 3 (in the main text) to prevent the reaction mixture from solidifying. After 10 minutes, the pressure was reduced stepwise to 0.1 mbar. Polymerization was continued for 24 hours. The mixture was cooled to room temperature. 10 mL of chloroform and 1 mL of ethyl vinyl ether were added, the polymer was dissolved under moderate heating and the solution was stirred for 30 minutes. The polymer was precipitated in 150 mL of ice-cold methanol to yield the unsaturated polyamide in virtually quantitative yield as a colorless solid.

¹H NMR (CDCl₃, 25 °C, 400 MHz): δ (ppm) = 5.54 (br, CONH), 5.38 (m, *trans* CH=CH), 5.34 (m, *cis* CH=CH), 3.22 (m, CONHCH₂), 2.14 (t, ³J = 7.6 Hz, CH₂CONH), 2.00 (m, *cis* CH₂CH=CHCH₂), 1.96 (m, *trans* CH₂CH=CHCH₂), 1.61 (m, CH₂CH₂CONH), 1.48 (m, CONHCH₂CH₂), 1.34-1.24 (br, CH₂). ¹³C NMR (CDCl₃, 25 °C, 101 MHz): δ (ppm) = 173.2 (CONH), 130.5 (*trans* CH=CH), 130.1 (*cis* CH=CH), 39.7 (CONHCH₂), 37.1 (CH₂CONH), 32.8 (*trans* CH₂CH=CHCH₂), 27.4 (*cis* CH₂CH=CHCH₂), 29.9, 29.8, 29.7, 29.6, 29.5, 29.3, 29.2, 27.1, 26.0 (all CH₂).

3.2 Preparation of Unsaturated Polyesteramides

General polymerization procedure: A mixture (ca. 250 mg) of the appropriate amounts of the amide functionalized diene **1** and the ester functionalized diene **3** was weighed in a 25 mL Schlenk tube equipped with a stirring bar under nitrogen atmosphere. The mixture was heated to 65 °C to yield a homogeneously molten monomer solution. 0.5 mol% of Hoveyda-Grubbs 2nd generation catalyst was added and the mixture was kept at a reduced pressure of 150 mbar (dynamic vacuum) and stirred moderately. For polyesteramides with moderate to high amide contents, the reaction temperature was adapted according to the melting points of the resulting unsaturated polyesteramides as displayed in Table 5 (in the main text) to prevent the reaction mixture from solidifying. After 10 minutes, the pressure was reduced stepwise to reach 0.1 mbar. Polymerization was continued for 24 hours and then cooled to room temperature. 10 mL of chloroform and 1 mL of ethyl vinyl ether were added, the polymer was dissolved under moderate heating and the solution was stirred for 30 minutes. The polymer was precipitated in 150 mL of ice-cold methanol to yield the unsaturated polyesteramide in virtually quantitative yield as a colorless solid.

¹H NMR (CDCl₃, 25 °C, 400 MHz): δ (ppm) = 5.60 (br, CONH), 5.37 (m, *trans* CH=CH), 5.34 (m, *cis* CH=CH), 4.05 (t, ³J = 6.7 Hz, COOCH₂), 3.22 (m, CONHCH₂), 2.28 (t, ³J = 7.5 Hz, CH₂COO), 2.14 (t, ³J = 7.6 Hz, CH₂CONH), 1.99 (m, *cis* CH₂CH=CHCH₂), 1.96 (m, *trans* CH₂CH=CHCH₂), 1.65-1.57 (m, CH₂CH₂COOCH₂CH₂ and CH₂CH₂CONH), 1.48 (m, CONHCH₂CH₂), 1.35-1.23 (m, CH₂). ¹³C NMR (CDCl₃, 25 °C, 101 MHz): δ (ppm) = 174.1 (COO), 173.2 (CONH), 130.5 (*trans* CH=CH), 130.1 (*cis* CH=CH), 64.6 (COOCH₂), 39.7 (CONHCH₂), 37.1 (CH₂CONH), 34.6 (CH₂COO), 32.8 (*trans* CH₂CH=CHCH₂), 27.4 (*cis* CH₂CH=CHCH₂), 32.7, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 28.8, 27.1, 26.1, 26.0, 25.2 (all CH₂).

3.3 Preparation of Saturated Polyamides and Polyesteramides

General hydrogenation procedure: 150 mg of the unsaturated polyamide or polyesteramide was dissolved in 8 mL of hot toluene (for **PA-0.0** xylene was used; for polymers with amide contents >30 amide groups per 1000 methylene units phase-separated systems were obtained). After addition of 2 mg of Wilkinson's catalyst, the reaction mixture was transferred into a stainless steel pressure reactor equipped with a magnetic stirring bar. The reactor was closed and pressurized with 40 bar of hydrogen gas and heated to 130 °C for 24 hours. Then, the reactor was cooled to room temperature, vented and the precipitated polymer was dissolved in 40 mL of boiling toluene (for **PA-0.0H** xylene was used, for polymers with amide contents >30 amide groups per 1000 methylene units, tetrachloroethane was used). The polymer was precipitated in 250 mL of ice-cold methanol and isolated by filtration to obtain the hydrogenated compound as grayish solids in virtually quantitative yield.

Polyamides: ^1H NMR ($\text{C}_2\text{D}_2\text{Cl}_4$, 130 $^\circ\text{C}$, 400 MHz): δ (ppm) = 5.22 (s, CONH), 3.18 (m, CONHCH₂), 2.10 (t, 3J = 7.3 Hz, CH₂CONH), 1.58 (m, CH₂CH₂CONH), 1.47 (m, CONHCH₂CH₂), 1.31-1.26 (br, CH₂). ^{13}C NMR ($\text{C}_2\text{D}_2\text{Cl}_4$, 130 $^\circ\text{C}$, 101 MHz): δ (ppm) = 173.0 (CONH), 30.3, 30.0, 29.9, 29.8, 29.7, 29.6, 27.4, 26.1 (all CH₂).

Polyesteramides: ^1H NMR ($\text{C}_2\text{D}_2\text{Cl}_4$, 130 $^\circ\text{C}$, 400 MHz): δ (ppm) = 5.23 (br, CONH), 4.03 (t, 3J = 6.7 Hz, COOCH₂), 3.19 (m, CONHCH₂), 2.25 (t, 3J = 7.4 Hz, CH₂COO), 2.10 (t, 3J = 7.3 Hz, CH₂CONH), 1.63-1.58 (m, CH₂CH₂COOCH₂CH₂ and CH₂CH₂CONH), 1.47 (m, CONHCH₂CH₂), 1.36-1.24 (m, CH₂). ^{13}C NMR ($\text{C}_2\text{D}_2\text{Cl}_4$, 130 $^\circ\text{C}$, 101 MHz): δ (ppm) = 173.2 (COO), 173.2 (CONH), 64.1 (COOCH₂), 34.2 (CONHCH₂), 29.6, 29.4, 29.3, 29.2, 29.1, 29.0, 28.9, 28.6, 26.7, 25.8, 25.4, 24.8 (all CH₂)

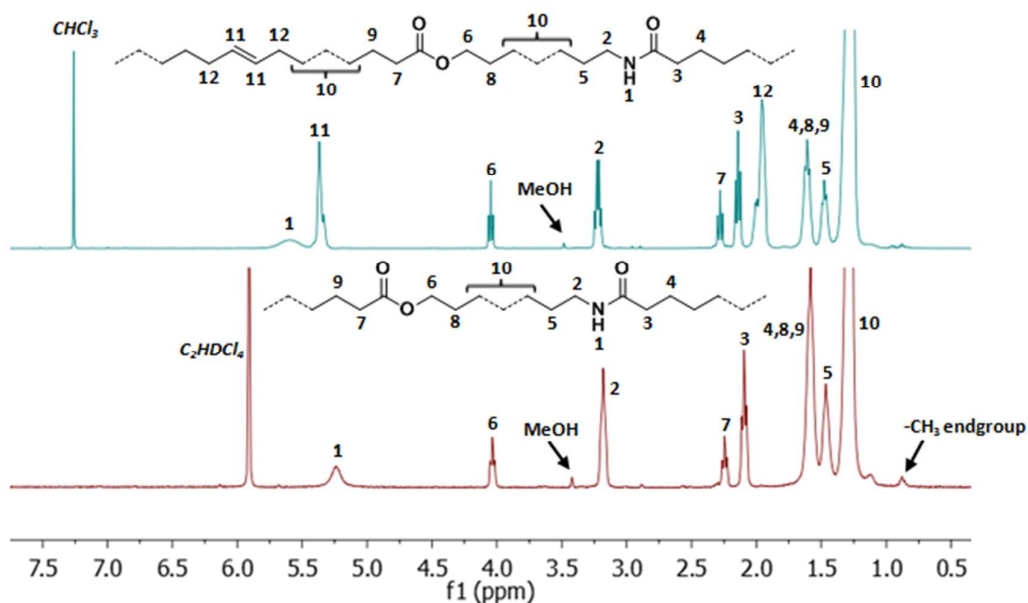


Figure S5. ^1H NMR spectra of the unsaturated polyesteramide **PE_{0.25}A_{0.75}-51.6** (top, CDCl_3 , 400 MHz, 25 $^\circ\text{C}$) and the corresponding saturated polyesteramide **PE_{0.25}A_{0.75}-51.6H** (bottom, $\text{C}_2\text{D}_2\text{Cl}_4$, 400 MHz, 130 $^\circ\text{C}$).

4. DSC Traces and IR Spectra of Saturated Polyamides

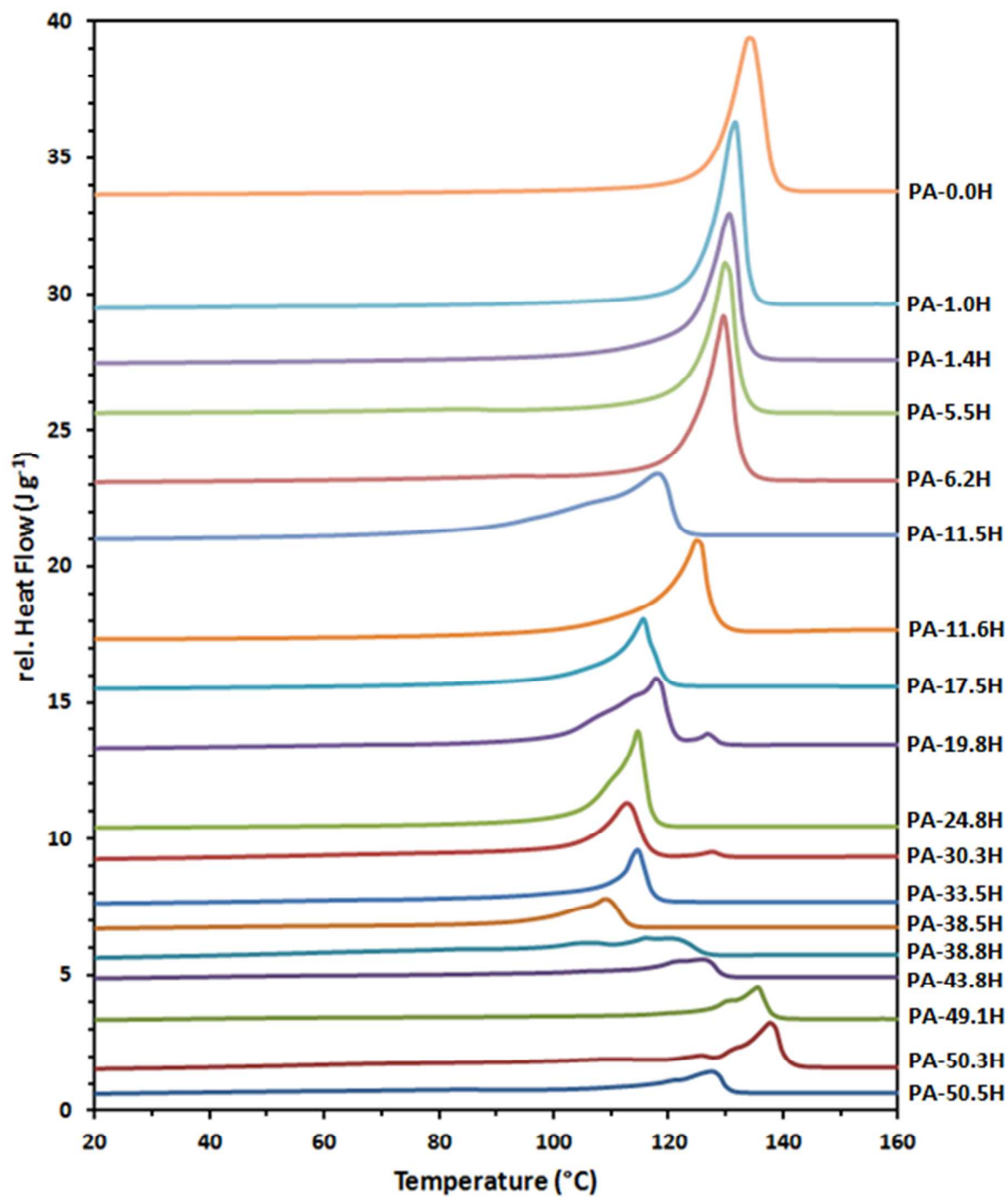


Figure S6. DSC heating traces of saturated polyamides. Second heating cycles shown, heating rate $10^{\circ}\text{C min}^{-1}$.

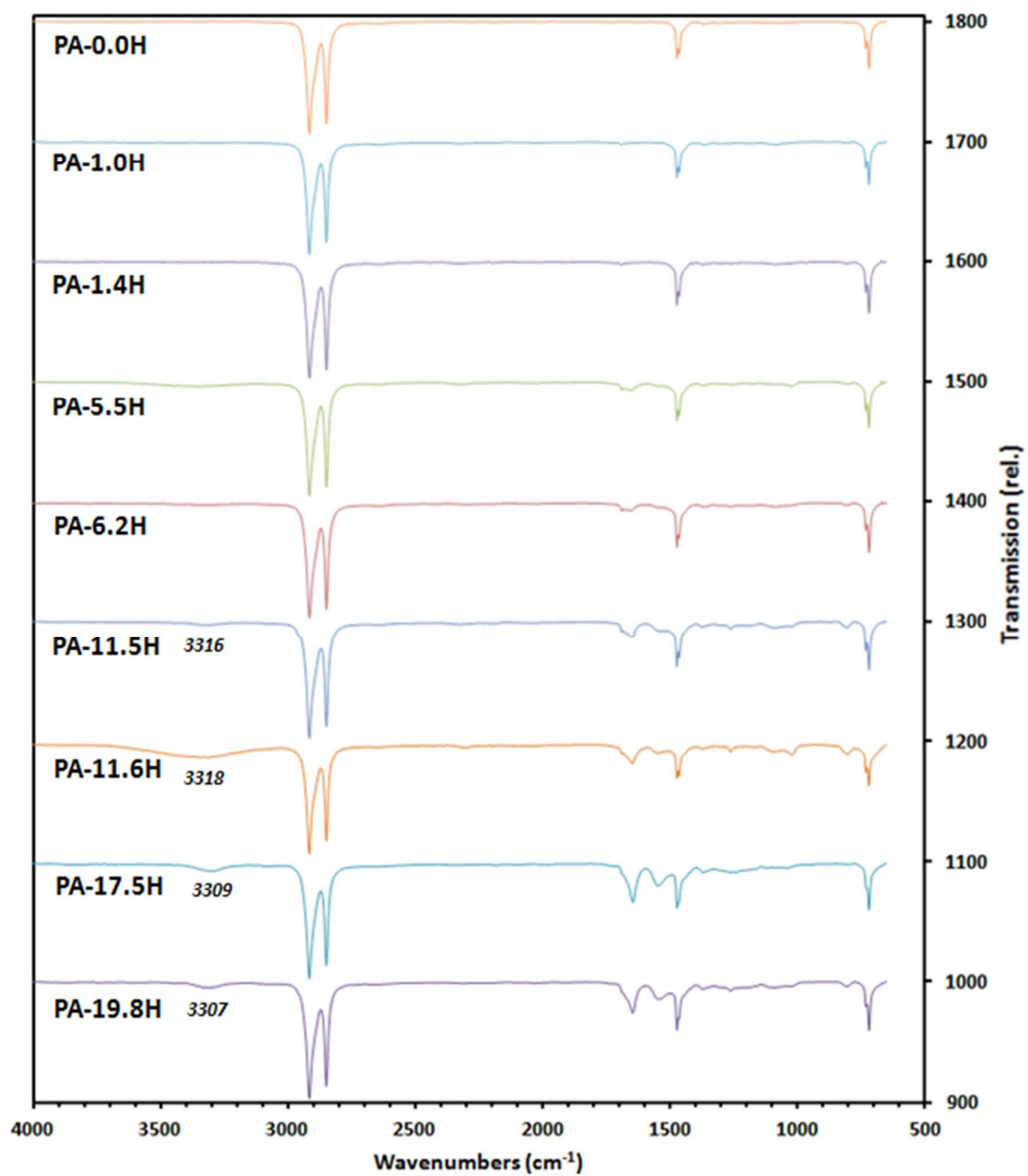


Figure S7. IR spectra of saturated polyamides PA-0.0H to PA-19.8H.

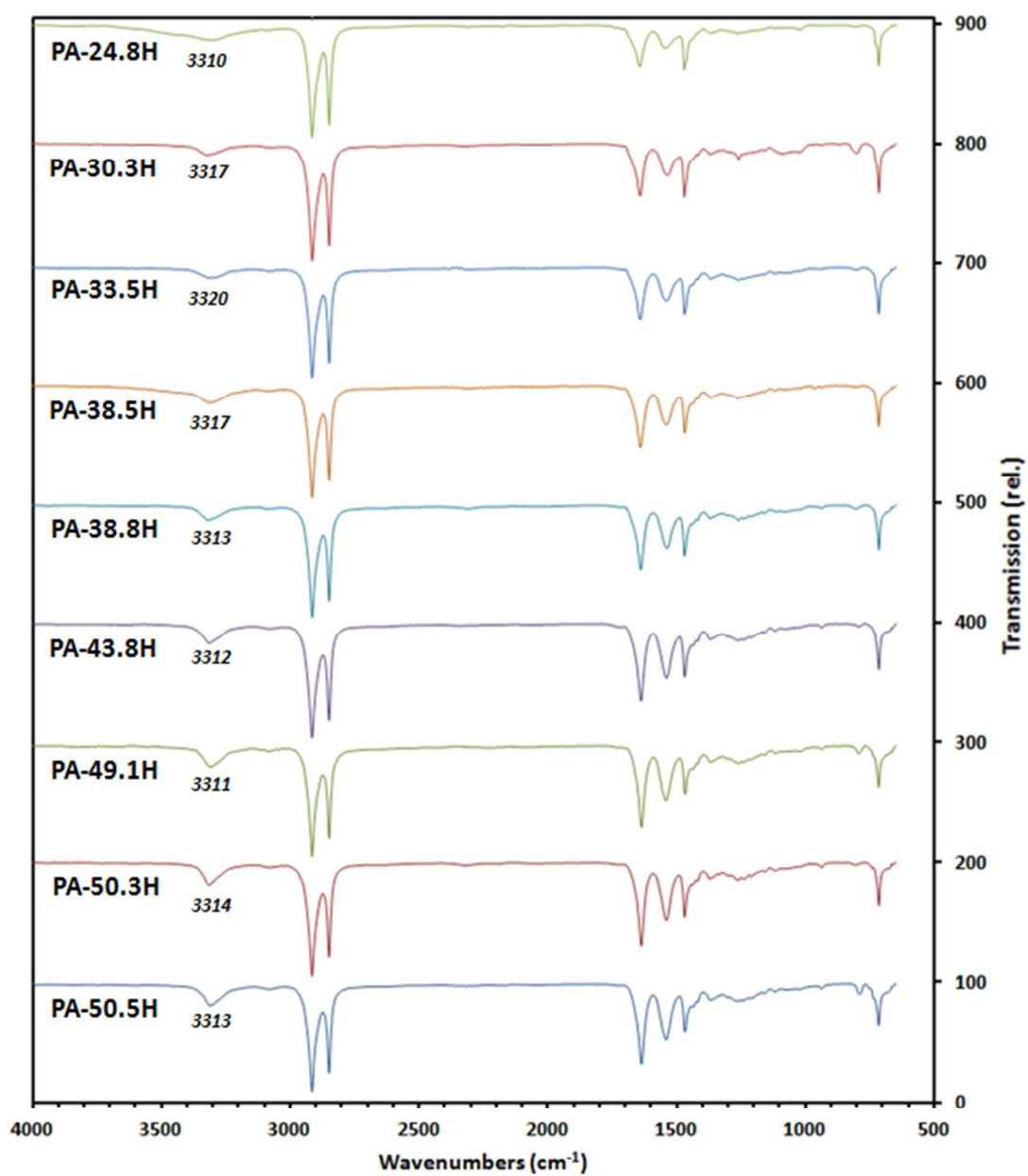


Figure S8. IR spectra of saturated polyamides PA-24.8H to PA-50.5H.

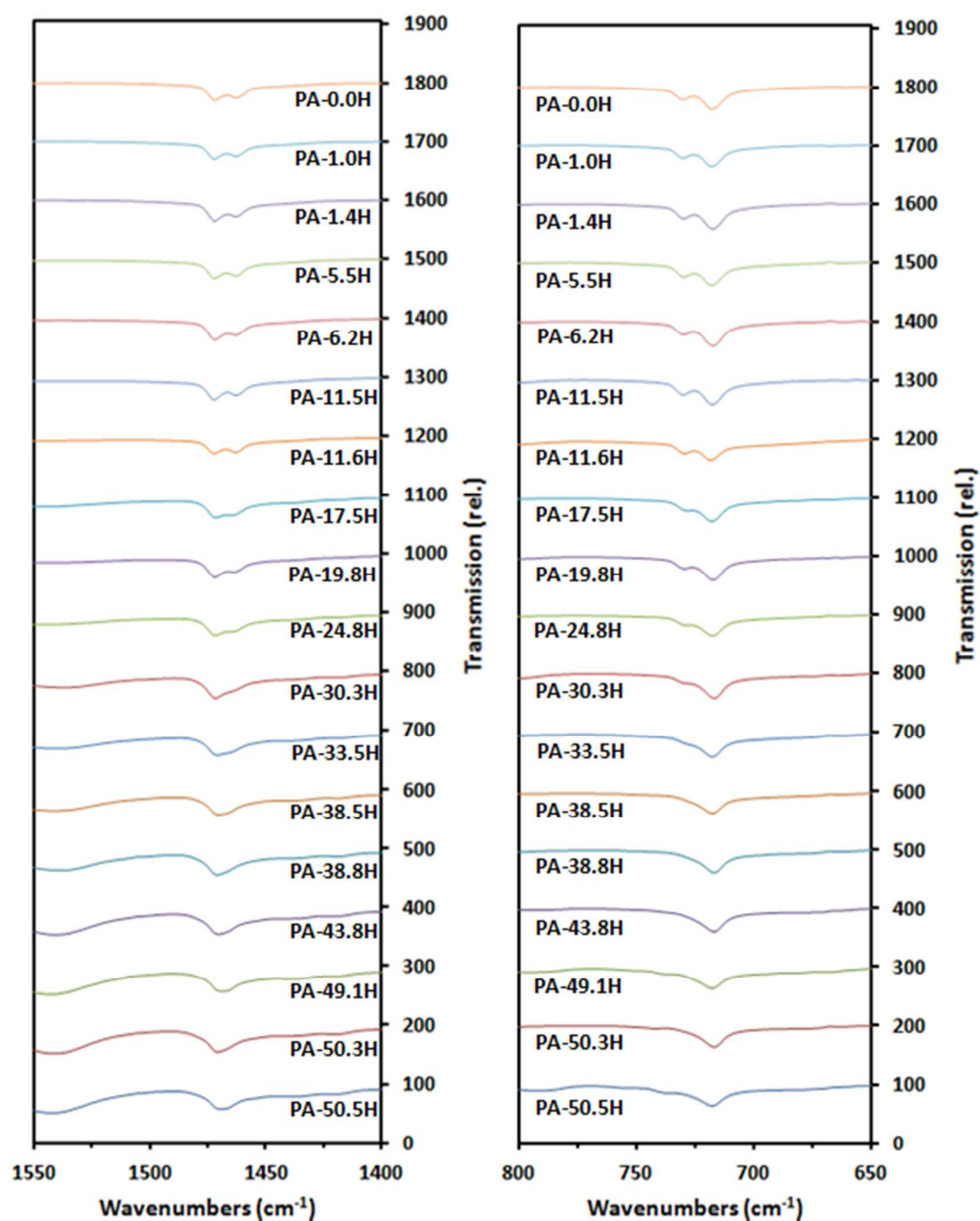


Figure S9. IR spectra of saturated polyamides, selected regions for the CH₂ scissoring (1460-1475 cm⁻¹) and the CH₂ rocking vibrations (715-735 cm⁻¹).

5. DSC Traces and IR spectra of Saturated Polyesteramides

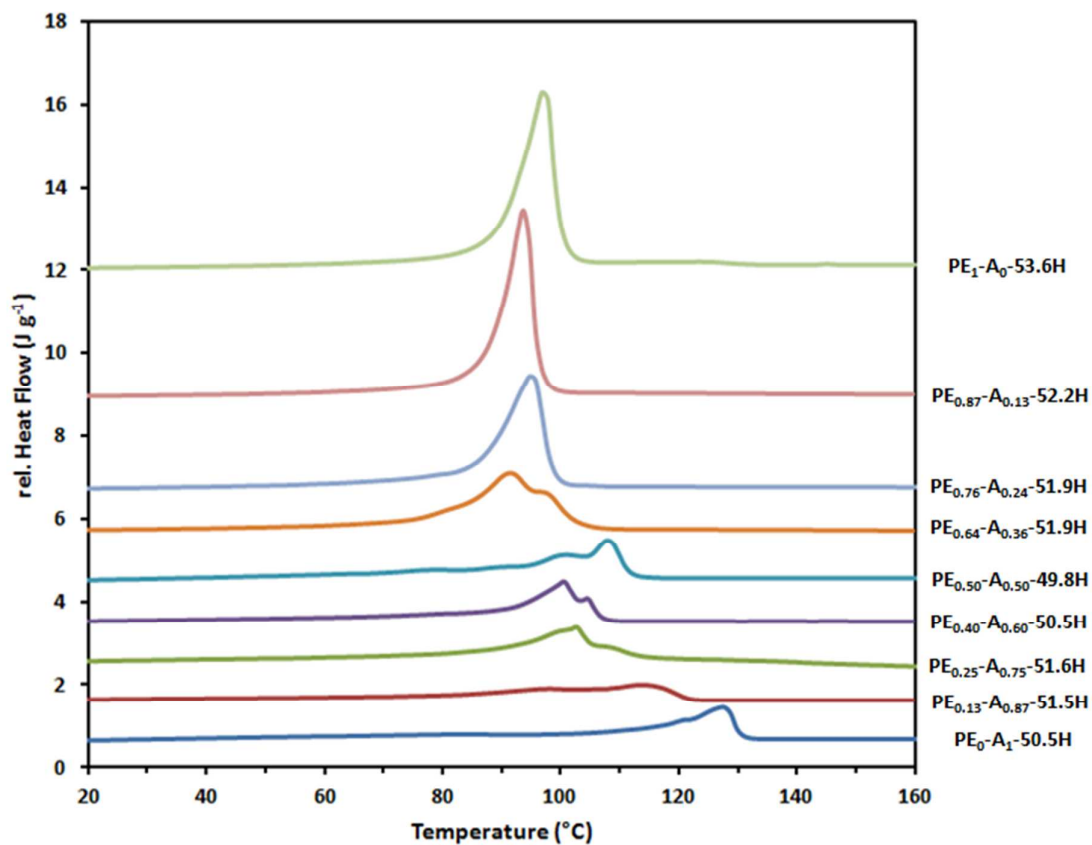


Figure S10. DSC heating traces of saturated polyesteramides. Second heating cycles shown, heating rate $10\text{ }^{\circ}\text{C min}^{-1}$.

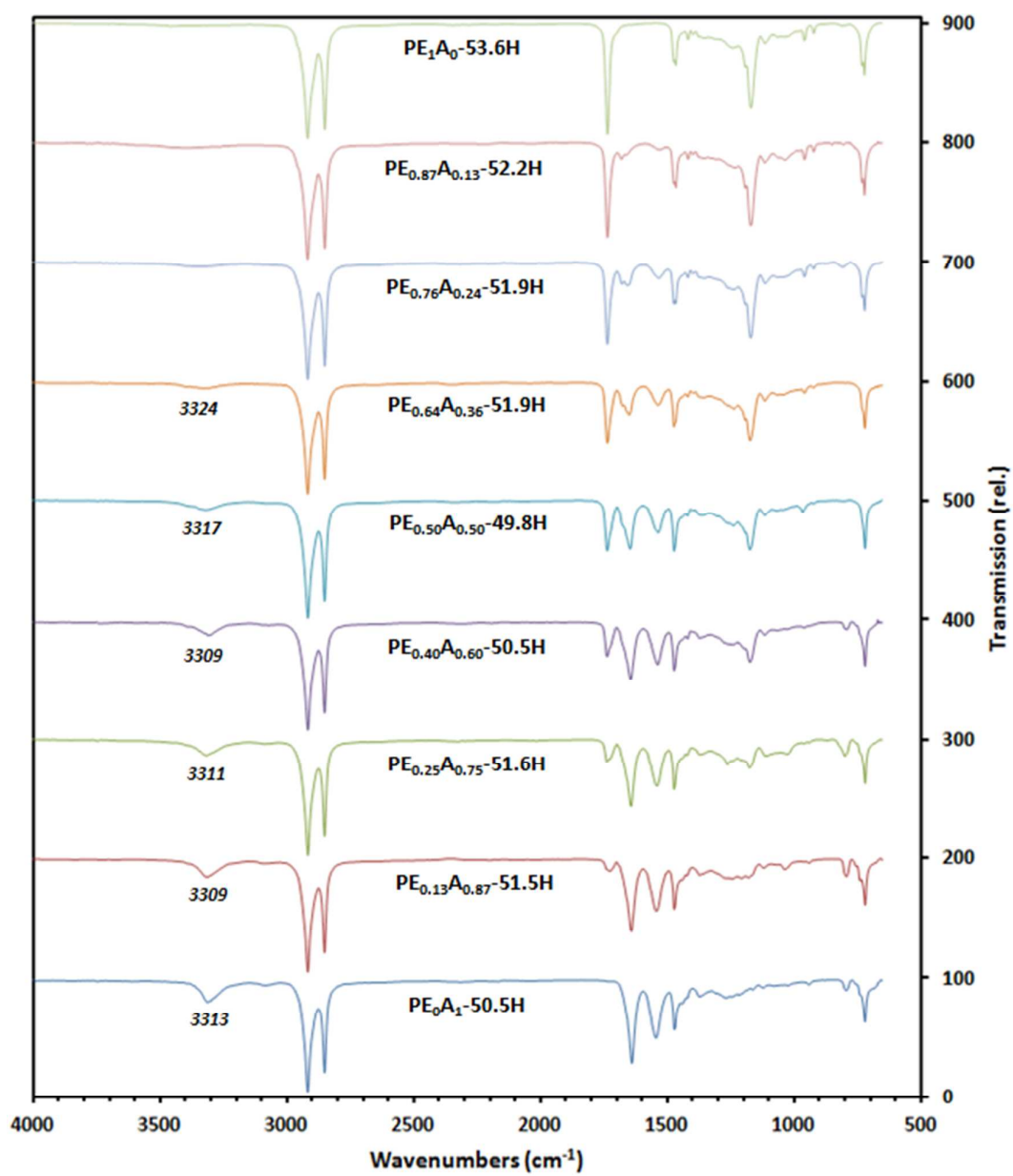


Figure S11. IR spectra of saturated polyesteramides.

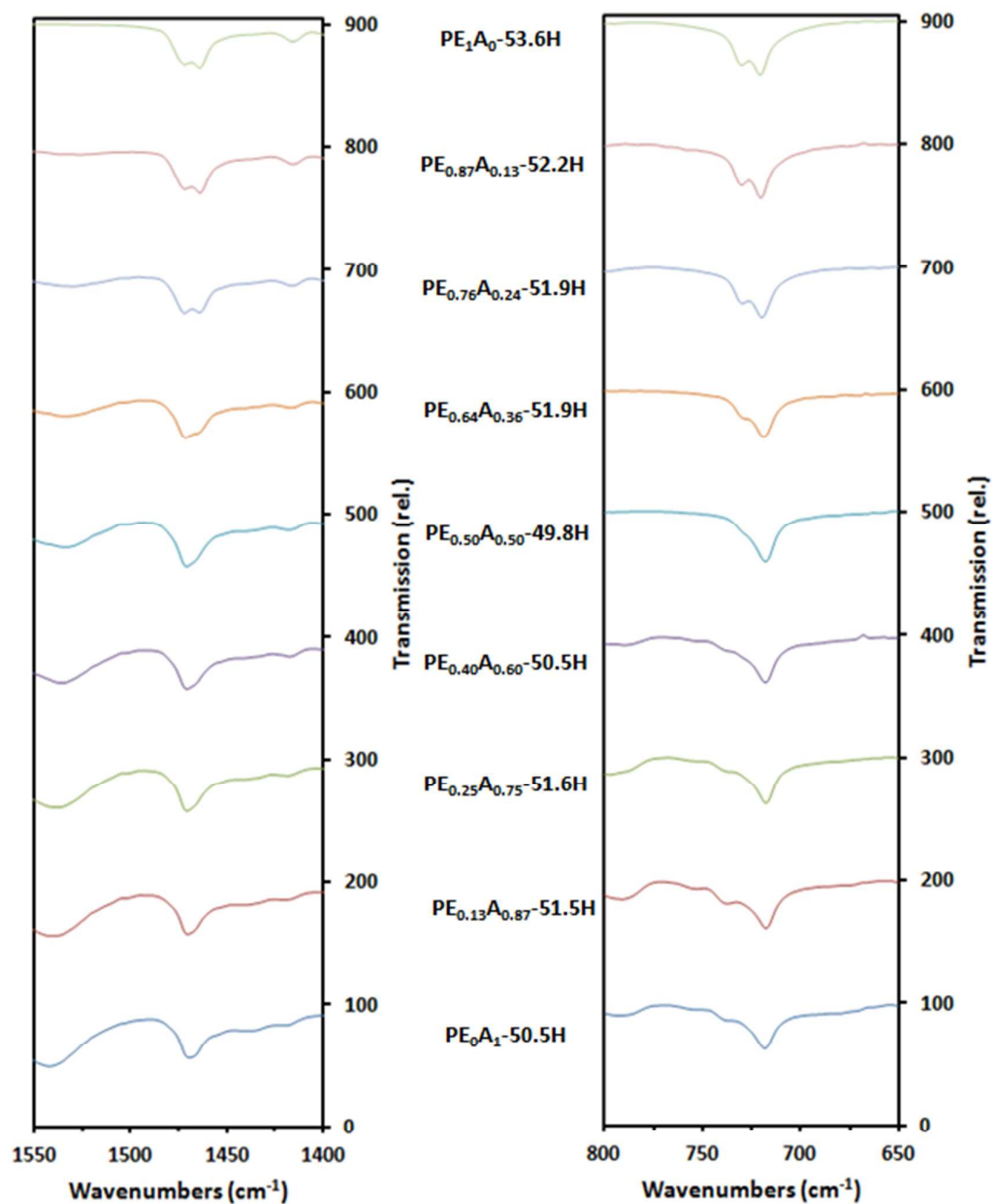


Figure S12. IR spectra of saturated polyesteramides, selected regions for the CH₂ scissoring (1460-1475 cm⁻¹) and the CH₂ rocking vibrations (715-735 cm⁻¹).

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