Electronic Supplementary Material (ESI) for Polymer Chemistry.

Synthesis and properties of poly(norbornene)s with lateral aramid groups

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Experimental section

Materials

All commercially available reagents and solvents of analytical grade were purchased from Sigma Aldrich, Acros, Honeywell or Fluorochem and were used without further purification, unless otherwise specified. Solvents of technical grade were purified by distillation, if necessary. Deuterated solvents such as Methanol-d_4, DMSO-d_6, $CDCl_3$ were purchased from Cambridge Isotope Laboratories. Dry NMP over molecular sieves (4 Å) was purchased from Acros. For manual or automated column chromatography silica gel (technical grade, pore size 60 Å, 230 - 400 mesh, 40-63 µm particle size) was used.

Standard analysis techniques

Standard ^{1}H and ^{13}C nuclear magnetic resonance spectra were recorded either on a Bruker Avance III 300 spectrometer at 300 MHz (^{1}H) and 75 MHz (^{13}C) or a Bruker DPX 400 spectrometer at 400 MHz (^{1}H) and 100 MHz (^{13}C). All NMR signals were referenced internally to residual solvent signals. Electron spray ionization (ESI) mass spectra were recorded on a Bruker-Ion Trap MS esquire HCT mass spectrometer. High-resolution mass spectrometry (HRMS) was recorded on a Bruker FTMS 4.7 T BioAPEX II ESI-MS. RP-HPLC analysis was performed on a HP 1090 Liquid Chromatograph (Hewlett Packard) using a PerfectSil column (MZ Analysentechnik, Mainz, Germany, 250 x 4.0 mm; 120 ODS - 2.5 µm). Samples were dissolved in ACN and eluted with an ACN/ water gradient buffered with 0.1% TFA starting from 10% acetonitrile rising to 100% over a period of 40 min. UV signals were detected at 254 nm. Analytical thin layer chromatography was performed on TLC plates from Merck (Kieselgel F-254 pre-coated aluminum sheets) and visualized under UV-light at 254 nm or stained with ninhydrin, $KMnO_4$ or a Silica gel/iodo mixture. Automated column chromatography was realized with a Biotage Isolera One system. Relative molecular weights and molecular weight distributions were measured by gel permeation chromatography (GPC) equipped with a Viscotek GPCmax VE2001 GPC Solvent/Sample Module, Viscotek UV-Detector 2600, Viscotek VE3580 RI-Detector, and two Viscotek T6000 M columns (7.8 x 300 mm, 103 - 107 g mol^{-1} each). All measurements

were carried out at room temperature using THF as the eluent with a flow rate of 1 mL min^{-1}. The system was calibrated with Malvern PolyCAL™UCS-PS polystyrene standards in a range from 10^3 to 3 x 10^6 g mol^{-1}. GPC in chloroform was carried out with an instrument consisting of a Duratec vacuum degasser, a KNAUER Smartline Pump 1050 and a set of two MZ-Gel SDplus linear columns (300 x 8 mm, 5 µm particle size). Signal detection occurred by use of an Applied Biosystems 759A UV detector (set to 254 nm wavelength) and a Knauer Smartline 2300 RI-detector (refractive index). Calibration was done using polystyrene standards as for gel permeation chromatography in THF.

Thermogravimetric analysis (TGA)

Thermal stability experiments have been performed on a Pyris 1 TGA (Perkin Elmer) using the following temperature program: 5 min equilibration at 25°C, temperature ramp from 25°C to 120°C at a rate of 20 K min^{-1}, 10 min isothermic condition to remove residual solvents and subsequent temperature ramp from 120°C to 600°C at a rate of 20 K min^{-1}. All experiments were performed under nitrogen flow.

Differential scanning calorimetry (DSC)

DSC measurements were conducted at a Mettler Toledo STAR system operating at heating and cooling rates of 10°C min^{-1} in the range of -80 to 300°C under nitrogen atmosphere with samples being encapsulated in standard aluminum DSC pans. Data is reported from the second heating cycle in this manuscript unless otherwise indicated.

Compression molding of polymer films

The as prepared polymers were compression-molded into thin films in a Carver® model 3851-0. The materials were placed between Kapton® sheets held apart by thin Aluminum spacers and compressed at a temperature of T_g+50°C for 3 min with 1333 psi then the pressure was increased to 4000 psi for 15 min. Films of a thickness 0.12 ± 0.01 mm were obtained.

Dynamic mechanical analysis (DMA)

Temperature dependent DMA measurements were conducted on a TA Instruments DMA Q800 in strain mode, performing a temperature sweep. The 0.12 ± 0.01 mm thick polymer films were cut into rectangular strips with a width of 5.3 mm and a length of around 12 - 15 mm. The measurement distance was 9 ± 1 mm. Samples were first equilibrated for 2 min at -20°C, before the storage modulus E' was measured upon variation of temperature from -20 to 200°C (heating rate of 5 K min^{-1}). A strain amplitude of 15 µm at a frequency of 1 Hz was applied. Stress-strain measurements were performed on the same instrument using the strain mode and dog-bone shaped samples. Samples were measured at 25°C applying a strain ramp from 0 - 500% at a rate of 5% min^{-1}.

Dynamic light scattering (DLS)

DLS data was collected at constant temperature (22°C) on a commercial goniometer instrument (3D LS Spectrometer, LS Instruments AG, Switzerland). The primary beam was formed by a linearly polarized laser beam (Cobolt 05-01 diode pumped solid state laser, λ = 660 nm, P_{max} = 500mW) and the scattered light was collected by single-mode optical fibers equipped with integrated collimation optics at angles: 30°, 90° and 120°. The incoming laser beam passed through a Glan-Thompson polarizer with an extinction ratio of 10^{-6}, and another Glan-Thompson polarizer, with an extinction ratio of 10^{-8}, was mounted in front of the collection optics. Concentrations and solvents are indicated in the respective experiments.

Cross-polarized light microscopy (POM)

Birefringent behaviour was investigated using an Olympus BX51 micro-scope equipped with a Mettler Toledo PP82HT heating stage, an Olympus DP72 digital acquisition system and two polarizing filters to enable cross-polarized imaging. Polymers were placed as precipitated onto glass slides and heated to temperature indicated in the individual experiment description.

Powder X-ray Diffraction (XRD)

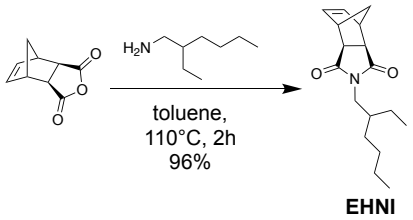
XRD on precipitated polymers and annealed samples (as indicated) was per-formed at a STADIP diffractometer (STOE, Transmission Diffractometer) equipped with a curved

germanium mono-chromator (111), Mythen1K detector (Dectris) at a wave-length λ = 1.540598 Å (Cu Kα1 radiation).

Annealing of polymer samples Polymer samples were annealed using a Mettler Toledo STAR System DSC. In either hexane or methanol precipitated polymers were placed in a standard DSC aluminum pan and heated under nitrogen atmosphere from 25°C to 15°C above their respective T_g (heating rate 10 K min^{-1}) and kept subsequently under isothermic conditions for 60 min. After, they have been cooled to 25°C under their respective T_g very slowly (cooling-rate 1 K min^{-1}). Finally, cooling to room temperature proceeded with a cooling rate of 10 K min^{-1}.

Synthesis of monomers.

***N*-(2-ethylhexyl)-*exo*-norbornene-5,6-dicarboximide (EHNI)**



5-Norbornene-2,3-dicarboxylic acid anhydride (500 g, 3.05 mol) was heated to 180°C for 2 h and recrystallized from acetone several times to obtain the pure *exo*-carbic anhydride (101,9 g, 20% yield).12 (Purity of *exo* form was monitored by NMR until 95% was reached.) To a round bottom flask connected to a Claisen condenser containing *exo*-carbic anhydride (32.83 g, 200 mmol), toluene (200 mL) was added until complete dissolution of the solid. Then 2-ethylhexylamine (26.88 g, 208 mmol) was added and the reaction mixture was heated at 110°C. After 2 h of stirring at 110°C the solution was heated to 150°C to remove toluene by distillation. The crude product was then purified by column silica gel chromatography (10% ethyl acetate in hexane) to afford the monomer as yellow oil with 96% yield. ^{1}H NMR (300 MHz,$CDCl_3$) δ (ppm) 0.78 - 0.92 (m, 6 H) 1.14 - 1.36 (m, 9 H) 1.49 (dt, J=9.81, 1.38 Hz, 1 H) 1.68 (spt, J=6.25 Hz, 1 H) 2.52 - 2.74 (m, 2 H) 3.19 - 3.28 (m, 2 H) 3.34 (d, J=7.15 Hz, 2 H) 6.13 - 6.37 (m, 2 H); ^{13}C NMR (75 MHz, CHLOROFORM-d) δ (ppm) 10.2, 13.9, 22.9, 23.8, 28.3, 30.4, 37.6, 42.4, 42.7, 45.1 (2C), 47.7 (2C), 137.7 (2C),

178.3 (2C); HR-MS (ESI^+): m/z calculated for $[C_{17}H_{25}NO_2Na]^+$: 298.17775, mass found: 298.17765.

Methyl 4-amino-2-hydroxybenzoate (1)

4-aminosalicylic acid (10.0 g, 0.065 mol) was dissolved in methanol (150 mL) and concentrated sulfuric acid (12 mL) and heated to reflux for 14 h. Methanol was reduced and the residue dissolved in saturated $NaHCO_3$ (slightly basic pH) and extracted three times with ethyl acetate. The combined organic layers were washed with brine, dried over magnesium sulfate and evaporated under reduced pressure. After column chromatography (20% ethyl acetate in hexane) the product was obtained as a beige solid (8.8 g, 0.053 mol) in 80.5% yield. ^{1}H NMR (400 MHz, DMSO-d6) δ (ppm) 3.78 (s, 3 H) 6.00 (d, J=2.20 Hz, 1 H) 6.12 (dd, J=8.74, 2.14 Hz, 3 H) 7.45 (d, J=8.68 Hz, 1 H) 10.76 (s, 1 H); ^{13}C NMR (101 MHz, DMSO-d_6) δ ppm 51.5, 98.6, 99.6, 106.6, 131.0, 156.0, 162.9, 169.9; HR-MS (ESI^+): m/z calculated for $[C_8H_{10}NO_3]^+$: 190.04746, mass found: 190.04763.

Methyl 4-amino-2-((2-ethylhexyl)oxy)benzoate (2)

All solids were dried under Schlenk conditions for 14 h prior to use. Then methyl 4-amino-2-hydroxybenzoate 1 (10.0 g, 0.060 mol), 18-crown-6 (3.16 g, 0.263 mol) and potassium carbonate (30.4 g, 0.263 mol) were suspended in freshly distilled acetone. Ethylhexyl bromide (50.8 g, 0.263 mol) was added and the reaction was heated to reflux and stirred for 24 h under inert atmosphere. Then acetone was reduced, the residue dissolved in water and extracted three times with DCM. The combined organic layers were washed with brine and dried over anhydrous magnesium sulfate. The solvent was evaporated and the residue purified with automated column chromatography (ethyl acetate gradient from 0% to 20% in hexane) to yield the product as a yellow viscous oil in 90.5% yield. ^{1}H NMR (400 MHz, DMSO-d6) δ ppm 1.59 - 1.72 (m, 1 H) 3.65 (s, 3 H) 3.77 (d, J=5.50 Hz, 2 H) 5.84 (br. s., 2 H) 6.12 (dd, J=8.56, 1.96 Hz, 1 H) 6.20 (d, J=1.96 Hz, 1 H) 7.48 (d, J=8.56 Hz, 1 H); ^{13}C NMR (101 MHz, DMSO-d6) δ ppm 10.9, 13.9, 22.5, 23.2, 28.4, 29.9, 38.7, 50.6, 69.7,

97.1, 105.4, 105.6, 133.4, 154.5, 160.9, 165.7; HR-MS (ESI^+): m/z calculated for $[C_{16}H_{25}NO_3Na]^+$: 302.17267, mass found: 302.17210.

4-Amino-2-((2-ethylhexyl)oxy)benzoic acid (3)

Methyl 4-amino-2-((2-ethylhexyl)oxy)benzoate 2 (12.6 g, 0.045 mol) and potassium hydroxide (3.8 g, 0.067 mol) were dissolved in a 1:1 (v/v) mixture of ethanol and water (50 mL) and heated to reflux at 90°C. After the reaction was complete (followed with HPLC, 4 h) the reaction was allowed to cool to room temperature. Ethanol was removed and the aqueous residue was acidified to pH 3 with concentrated HCl and extracted three times with ethyl acetate. The combined organic layers were washed with brine and dried over anhydrous magnesium sulfate. The solvent was evaporated and the residue purified with automated column chromatography (30% ethyl acetate in hexane) to yield the product as a white solid in 88.2% yield. ^{1}H NMR (300 MHz, DMSO-d_6) δ ppm 0.80 - 0.94 (m, 6 H) 1.21 - 1.54 (m, 8 H) 1.61 - 1.77 (m, 1 H) 3.82 (d, J=5.50 Hz, 2 H) 5.84 (s, 2 H) 6.13 (dd, J=8.48, 1.97 Hz, 1 H) 6.21 (d, J=1.93 Hz, 1 H) 7.50 (d, J=8.53 Hz, 1 H) 11.31 (s, 1 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 11.0, 14.0, 22.9, 23.9, 28.9, 30.5, 39.2, 72.1, 97.4, 107.3, 108.28, 135.5, 152.7, 159.6, 165.7; HR-MS (ESI^+): m/z calculated for $[C_{15}H_{24}NO_3]^+$: 266.17507, mass found: 266.17445.

N-(3-(2-ethylhexyloxy)-4-carboxyphenyl)-exo-norbornene-5,6-dicarboximide (4)

exo-carbic anhydride (3.85 g, 0.0235 mol) and compound **3** (6.48 g, 0.0244 mol) were placed in a round bottom flask and dissolved with 50 mL toluene. The flask was connected to a Claisen condenser and the reaction mixture was heated at 110°C for 4 h. After, the reaction was heated to 150°C to remove toluene by distillation. The crude product was then purified by automated column chromatography (5% methanol in dichloromethane) to afford the product as a beige solid in 81.3% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm

0.82 - 0.93 (m, 6 H) 1.21 - 1.51 (m, 10 H) 1.68 (quin, J=5.99 Hz, 1 H) 2.86 (s, 2 H) 3.15 - 3.25 (m, 2 H) 3.88 (d, J=5.50 Hz, 2 H) 6.37 (t, J=1.77 Hz, 2 H) 6.88 (dd, J=8.13, 1.77 Hz, 1 H) 7.03 (d, J=1.71 Hz, 1 H) 7.68 (d, J=8.19 Hz, 1 H) 12.72 (br. s., 1 H); ^{13}C NMR (101 MHz, DMSO-d_6) δ ppm 11.0, 13.9, 22.5, 23.2, 28.4, 29.8, 38.7, 42.9, 45.0 (2C), 47.7 (2C), 70.8, 112.2, 118.6, 121.8, 130.7, 135.9, 137.9 (2C), 157.8, 167.0, 176.5 (2C); HR-MS (ESI$^+$): m/z calculated for $[C_{24}H_{29}NO_5Na]^+$: 434.19379, mass found: 434.19496.

_N_-(4-((4-carboxy-3-(2-ethylhexyloxy)phenyl)carbamoyl)-3-(2-ethylhexyloxy)phenyl)-_exo_-norbornene-5,6-dicarboximide (5)

Well dried compound 4 (7.54 g, 0.0183 mol) was dissolved in 15 mL dry NMP in a Schlenk flask. Thionyl chloride (2.62 g, 0.022 mol) was added dropwise under stirring and allowed to react for 14 h. After excess thionyl chloride was removed with Schlenk vacuum. In 15 mL dry NMP dissolved 4-amino-2-((2-ethylhexyl)oxy)benzoic acid 3 was added to the reaction afterwards at 0°C. The reaction was allowed to warm to room temperature and stirred for 5 h. After the solution was precipitated in ice cold water and filtered. The crude residue was resolved in a minimum amount of ethyl acetate and purified by automated column chromatography (30% ethyl acetate in hexane) to afford the product in 68.9% yield as a beige solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm 0.75 - 0.91 (m, 12 H) 1.16 - 1.54 (m, 18 H) 1.66 - 1.76 (m, 2 H) 2.87 (s, 2 H) 3.23 (s, 2 H) 3.87 (d, J=5.62 Hz, 2 H) 3.90 - 3.98 (m, 2 H) 6.38 (t, J=1.65 Hz, 2 H) 6.95 (dd, J=8.01, 1.65 Hz, 1 H) 7.10 (d, J=1.59 Hz, 1 H) 7.30 - 7.38 (d, 1 H) 7.53 (s, 1 H) 7.63 (d, J=8.07 Hz, 1 H) 7.68 (d, J=8.44 Hz, 1 H) 10.36 (s, 1 H) 12.22 (br. s., 1 H); ^{13}C NMR (101 MHz, DMSO-d_6) δ ppm 10.9, 11.0, 13.8, 13.9, 22.4, 22.5, 23.3, 23.3, 28.4, 28.5, 29.8, 30, 38.6, 38.8, 43, 45 (2C), 47.8 (2C), 70.4, 71, 103.6, 110.4, 111.9, 115.5, 119.2, 125.8, 129.5, 132.2, 135.3, 137.9 (2C), 143.6, 156.3, 158.9, 164.7, 166.7, 176.7 (2C); HR-MS (ESI$^+$): m/z calculated for $[C_{39}H_{50}N_2O_7Na]^+$: 681.35102, mass found: 681.35116.

_N_-(4-((4-((4-carboxy-3-(2-ethylhexyloxy)phenyl)carbamoyl)-3-(2-ethylhexyloxy)phenyl)carbamoyl)-3-(2-ethylhexyloxy)phenyl)-_exo_-norbornene-5,6-dicarboximide (monoEtHexROD)

Well dried compound 5 (8 g, 0.0121 mol) was dissolved in 20 mL dry NMP in a Schlenk flask. Thionyl chloride (2.17 g, 0.0182 mol) was added dropwise under stirring and allowed to react for 14 h. Excess thionyl chloride was removed with Schlenk vacuum. Afterwards dry methyl 4-amino-2-((2-ethylhexyl)oxy)benzoic acid **2** dissolved in 5 mL dry NMP was added dropwise to the reaction at 0°C. The reaction was allowed to warm at room temperature and stirred for 5 h. Then the solution was precipitated in ice-cold water and filtered. The crude residue was resolved in a minimum amount of ethyl acetate and purified by automated column chromatography (30% ethyl acetate in hexane) to afford the product in 68.9% yield as a beige solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm 0.76 - 0.94 (m, 18 H) 1.18 - 1.55 (m, 26 H) 1.68 - 1.75 (m, 2 H) 1.80 - 1.84 (m, 1 H) 2.88 (s, 2 H) 3.24 (s, 2 H) 3.76 (s, 3 H) 3.89 (d, J=5.50 Hz, 2 H) 3.98 (dd, J=11.19, 5.56 Hz, 4 H) 6.39 (t, J=1.77 Hz, 2 H) 6.97 (dd, J=8.07, 1.71 Hz, 1 H) 7.12 (d, J=1.71 Hz, 1 H) 7.29 - 7.45 (m, 2 H) 7.54 (s, 1 H) 7.70 (d, J=8.56 Hz, 2 H) 7.66 (d, J=8.07 Hz, 2 H) 10.15 (s, 1 H) 10.41 (s, 1 H); ^{13}C NMR (101 MHz, DMSO-d_6) δ ppm 10.8, 10.8, 11, 13.8, 13.8, 13.9, 13.9, 22, 22.4, 22.5, 23.3, 23.3, 24.8, 26.3, 28.4, 28.4, 28.5, 29.8, 30, 30.9, 34.2, 38.6, 38.8, 45 (2C), 47.7 (2C), 51.4, 70.3, 70.8, 70.9, 103.2, 103.6, 110.4, 111.9, 114.1, 118.8, 119.2, 125.6, 129.6, 131, 132.2, 135.3, 137.9 (2C), 143.1, 144, 156.3, 156.8, 159.1, 164.1, 164.6, 165.6, 176.6 (2C); HR-MS (ESI$^+$): m/z calculated for $[C_{55}H_{74}N_3O_9]^+$: 920.54196, mass found: 920.54218.

Methyl 4-aminobenzoate (6)

To a solution of 4-aminobenzoic acid (30 g, 0.219 mol) in methanol (500 mL), H_2SO_4 (64.36 g, 0.656 mol) was added dropwise. The reaction mixture was stirred at 80°C for 24 h under argon atmosphere. After the reaction mixture was cooled to room temperature and neutralized with a saturated $NaHCO_3$ until no further gas evolution was observed. The solid was filtered and washed with methanol. The filtrate was concentrated under reduced pressure. The crude product was diluted with water and the aqueous layer was extracted three times with ethyl acetate. The combined organic layers were washed with

brine, dried over $MgSO_4$ and filtered. Solvent was removed under reduced pressure to afford the product as a white solid in 94% yield. The product was used for the next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 3.86 (s, 3 H) 4.07 (br. s., 2 H) 6.60 - 6.68 (m, 2 H) 7.82 - 7.89 (m, 2 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 51.56 (s, 1 C) 113.8 (2C), 119.71 (s, 1 C) 131.6 (2C), 150.8, 167.1; HR-MS (ESI^+): m/z calculated for $[C_8H_9NO_2Na]$+: 174.05255, mass found: 174.05227.

Methyl 4-((2,4-dimethoxybenzyl)amino)benzoate (7)

To a mixture of compound **6** (32.64 g, 0.216 mol) and 2,4-dimethoxybenzaldehyde (35.88 g, 0.216 mol) in dichloromethane, acetic acid (64.85 g, 1.080 mol) was added and the reaction mixture was stirred for 1 h at room temperature. The solution was cooled down to 0°C over an ice bath and $NaB(OAc)_3H$ (91.55 g, 0.432 mol) was added. The reaction was allowed to warm to room temperature and stirred for 14 h. The solution was neutralized with saturated $NaHCO_3$ until no further gas evolution was observed and extracted with dichloromethane three times. The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure to afford a yellow solid in 99% yield. The product was used for the next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 3.80 (s, 3 H) 3.84 (s, 3 H) 3.85 (s, 3 H) 4.31 (s, 2 H) 4.59 (br. s., 1 H) 6.44 (dd, J=8.25, 2.38 Hz, 1 H) 6.49 (d, J=2.32 Hz, 1 H) 6.56 - 6.64 (m, 2 H) 7.17 (d, J=8.19 Hz, 1 H) 7.80 - 7.88 (m, 2 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 42.6, 51.4, 55.3, 55.4, 98.7, 103.9, 111.7 (2C), 118.2, 118.7, 129.6, 131.4 (2C), 152, 158.4, 160.4, 167.3; HR-MS (ESI^+): m/z calculated for $[C_{17}H_{19}NO_4Na]^+$: 324.12063, mass found: 324.12040.

4-((2,4-dimethoxybenzyl)amino)benzoic acid (8)

Compound **7** (43 g, 0.144 mol) and KOH (24.2 g, 0.431 mol) were dissolved in a mixture of methanol/water (1:1, 800 mL). The solution was heated under reflux for 14 h. After methanol was removed under reduced pressure and the remaining aqueous layer was acidified to pH 4 with 3 N HCl. The precipitated solid was filtered, washed thoroughly with water and dried under reduced pressure to afford compound **8** as a yellow solid in 98% yield. The product was used for the next step without further purification. ^{1}H NMR (400

MHz, DMSO-d_6) δ (ppm) 3.73 (s, 3 H) 3.81 (s, 3 H) 4.18 (d, J=5.87 Hz, 2 H) 6.46 (dd, J=8.38, 2.38 Hz, 1 H) 6.52 - 6.59 (m, 3 H) 6.73 (t, J=5.81 Hz, 1 H) 7.11 (d, J=8.31 Hz, 1 H) 7.64 (d, J=8.80 Hz, 2 H) 11.95 (br. s., 1 H); ^{13}C NMR (101 MHz, DMSO- d_6) δ (ppm) 40.5, 55.2, 55.4, 98.4, 104.4, 111 (2C), 116.9, 118.6, 128.7, 131.1 (2C), 152.5, 157.9, 159.7, 167.5; HR-MS (ESI$^+$): m/z calculated for $[C^{16}H^{17}NO^4Na]^+$: 310.10498, mass found: 310.10515.

_N_-(4-carboxyphenyl)-_exo_-norbornene-5,6-dicarboximide (9)

To a round bottom flask connected to a reflux condenser containing exo-carbic anhydride (32.83 g, 0.200 mol), DMF (200 mL) was added until complete dissolution of the solid. Then 4-aminobenzoic acid (28.53 g, 0.208 mol) was added and the reaction mixture was heated at 130°C. After 4 h of stirring the reflux condenser was replaced by a Claisen condenser and DMF was removed by distillation. Then the crude product was poured into cold water (1 L) under stirring. The precipitate was filtrated, washed thoroughly with water and dried under reduced pressure to afford compound 9 as a white solid in 99% yield. The product was used for the next step without further purification. ^{1}H NMR (400 MHz, DMSO- d_6) δ (ppm) 1.36 - 1.55 (m, 2 H) 2.88 (s, 2 H) 3.22 (s, 2 H) 6.37 (s, 2 H) 7.42 (m, J=8.31 Hz, 2 H) 8.05 (m, J=8.31 Hz, 2 H) 13.13 (br. s., 1 H); ^{13}C NMR (101 MHz, DMSO-d_6) δ (ppm) 42.8, 45.1 (2C), 47.7 (2C), 126.9 (2C), 129.9 (2C), 130.5, 135.9, 137.8 (2C), 166.6, 176.5 (2C); HR-MS (ESI$^+$): m/z calculated for $[C_{16}H_{13}NO_4Na]^+$: 306.07368, mass found: 306.07401.

_N_-(4-((4-carboxyphenyl)(2,4-dimethoxybenzyl)carbamoyl)phenyl)-_exo_-norbornene-5,6-dicarboximide (10)

Compound **9** (8 g, 0.0282 mol) was dissolved in 280 mL of NMP, then $SOCl_2$ (3.7 g, 0.0311 mol) was added and the reaction mixture was stirred for 2 h. Then compound **8** (7.8 g, 0.0302 mol) was added to the solution and the reaction mixture was allowed to stirred for 48 h at room temperature. The reaction mixture was then poured into cold water under stirring. The precipitate was filtered off, washed thoroughly with water and dried under vacuum to give compound 10 as a white powder in 96% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 1.27 - 1.51 (m, 2 H) 2.74 - 2.88 (m, 2 H) 3.17 (s, 2 H) 3.64 (s, 3 H) 3.71 (s, 3 H)

5.02 (s, 2 H) 6.34 (t, J=1.77 Hz, 2 H) 6.41 - 6.51 (m, 2 H) 7.10 - 7.27 (m, 5 H) 7.44 (d, J=8.44 Hz, 2 H) 7.70 - 7.78 (m, 2 H) 12.94 (br. s., 1 H); ^{13}C NMR (101 MHz, DMSO- d_6) _ (ppm) 42.7, 45 (2C), 47.6 (2C), 47.7, 55.1, 55.3, 98.2, 104.6, 116.6, 126.4 (2C), 127.5 (2C), 128.4, 128.8 (2C), 129.7, 129.8 (2C), 133.1, 135.9, 137.8 (2C), 146.8, 157.9, 159.9, 166.6, 168.8, 176.5 (2C); HR-MS (ESI$^+$): m/z calculated for $[C_{32}H_{28}N_2O_7Na]^+$: 575.17887, mass found: 575.17848.

_N_-(4-((4-((4-carboxyphenyl)(2,4-dimethoxybenzyl)carbamoyl)phenyl)(2,4-dimethoxybenzyl)carbamoyl)phenyl)-_exo_-norbornene-5,6-dicarboximide (monDMBrod)

Compound **10** (8.47 g, 0.01533 mol) was dissolved in 160 mL of dry NMP for 20 min, then $SOCl_2$ (2.74 g, 0.023 mol) was added to the solution at room temperature. The mixture was stirred for 2 h. Compound **13** (5.08 g, 0.0169 mol) was added and the reaction mixture was allowed to stir for 48 h. The solution was then poured into cold water (9 times the volume of NMP) under stirring. The precipitate was filtered, dried under reduced pressure and purified by column chromatography THF/hexane (1:1) to afford a yellow solid in 60% yield. ^{1}H NMR (400 MHz, DMSO- d_6) δ (ppm) 1.39 - 1.48 (m, 2 H) 2.85 (s, 2 H) 3.19 (s, 2 H) 3.57 (s, 3 H) 3.60 (s, 3 H) 3.71 (s, 3 H) 3.70 (s, 3 H) 3.79 (s, 3 H) 4.91 (d, J=19.56 Hz, 4 H) 6.35 (t, J=1.77 Hz, 2 H) 6.37 - 6.47 (m, 4 H) 6.86 - 6.98 (m, 2 H) 6.98 - 7.16 (m, 8 H) 7.30 (d, J=8.19 Hz, 2 H) 7.68 (d, J=8.68 Hz, 2 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 43.1, 45.8 (2C), 47.8, 48 (2C), 48, 52.1, 55.1, 55.1, 55.3, 55.3, 98.3 (2C), 104.17, 104.21, 117.4, 117.5, 125.4 (2C), 127.1 (2C), 127.5 (2C), 127.6, 129.2 (2C), 129.5 (2C), 130 (2C), 130.6, 130.7, 133, 134.2, 135.8, 138 (2C), 144.6, 147.6, 158.3, 158.3, 160.4 (2C), 166.2, 169.2, 169.8, 176.7 (2C); HR-MS (ESI$^+$): m/z calculated for $[C_{49}H_{45}N_3O_{10}Na]^+$: 858.29972, mass found: 858.29951.

Polymerization and post-polymerization reactions

Polymerization polEHNI

A sealed Schlenk flask containing monomer **EHNI** (3 g, 10.9 mmol) and a stir bar was evacuated and charged with argon repeatedly for three consecutive times before

degassed DCM (10 mL) was added via syringe. The polymerization was initiated by quick addition of a solution of Grubbs' first-generation catalyst (49.4 mg, 0.06 mmol) in degassed dichloromethane (2 mL). Polymerization was quenched after 3 h with ethyl vinyl ether (2 mL) before the product was precipitated three times in methanol. The polymer was dried under Schlenk conditions to yield the respective polymers in 93% yield. GPC (THF): Mn: 61'300 $gmol^{-1}$, Đ: 1.1.

General procedure for polymerization of rod containing ROMP polymers polDMBrod-P10 - polDMBrod-P50 and polEtHexROD-P10 - polEtHexROD-P50

A sealed Schlenk flask containing respective monomers in the amounts calculated for 3 g (**polDMBrod**) and 1 g (**polEtHexROD**), respectively, of polymers of a molecular weight of 50'000 g mol^{-1} (amounts indicated in Table 4) was evacuated and charged with argon repeatedly (three times) before degassed DCM (VDCM) was added via syringe. The polymerization was initiated by quick addition of a solution of the appropriate amount of Grubbs' first-generation catalyst in degassed DCM (VG1). The reaction times at room temperature depended on the reactivity and rigidity of the monomers. Samples were monitored regarding the monomer conversion by GPC (THF) and the resulted times are indicated in Table 4. The polymerization was terminated with ethyl vinyl ether (2 mL) before the product was either precipitated three times in methanol or three times in hexane (for **polDMBrod-P35**, **polDMBrod-P50**, **polEtHexROD-P35** and **polEtHexROD-P50**). The polymers were dried under Schlenk conditions to afford the respective polymers in yields indicated in Table 4.

General procedure for DMB deprotection for polymers **polROD-P10** – **polROD-P50** DMB protected rod polymers (**polDMBrod-P10**, **-P25**, **-P35**, **-P50**) were placed in a round bottom flask and a mixture of DCM/TFA/TES (10/3/1, v/v/v, 14 mL per 200 mg of polymer) was added. The reaction was allowed to stir for 14h at room temperature. DCM was removed under reduced pressure and the polymer was then concentrated by removing TFA under Schlenk conditions. Subsequently the polymer was diluted in a minimum

amount of DCM and precipitated in either MeOH or hexane for **polDMBrod-P35** and **polDMBrod-P50** before filtrated and dried under reduced pressure to give the polymers **polROD-P10** – **polROD-P50**. GPC (THF) revealed tendency to aggregation with enhanced rod content (see Table 1).

Polymer	m(rod) [g]	m(EHNI) [g]	[a]V [mL]	m(G1) [mg]	[b]V(G1) [mL]	t_R [h]	Yield [%]
polDMBrod-P10	0.757	2.243	10	49.4	2	4.5	90
polDMBrod-P25	1.509	1.491	10	49.4	2	4.5	73
polDMBrod-P35	1.861	1.139	10	49.4	2	5	63
polDMBrod-P50	2.257	0.743	10	49.4	2	6	53
polEtHexROD-P10	0.271	0.73	5	16.8	1	4	85
polEtHexROD-P25	0.628	0.474	5	16.7	1	4	82
polEtHexROD-P35	0.63	0.356	5	16.6	1	6	56
polEtHexROD-P50	0.771	0.23	5	16.6	1	6	71

Table S 1. Amount of monomers and solvents used for polymerization of respective polymers. [a]Volume of DCM; [b]solution volume of G1 in DCM.

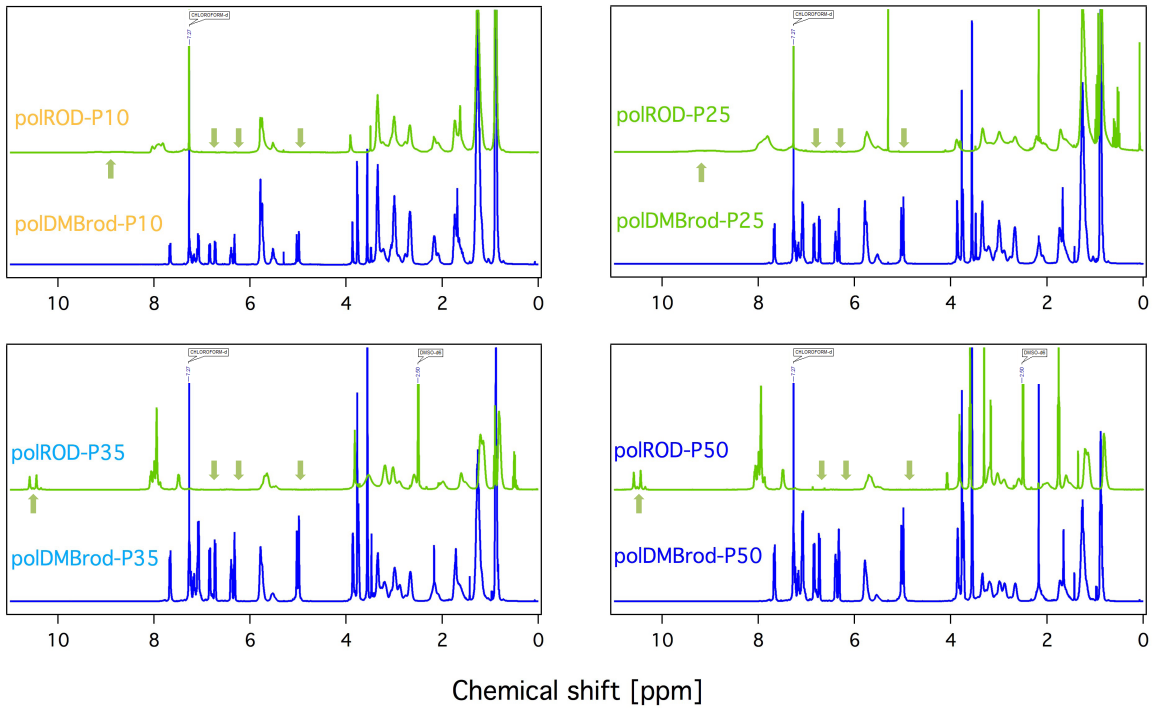


Figure S 1 ^{1}H NMR spectra (400 MHz, CHLOROFORM-*d*) for determination of DMB-deprotection.

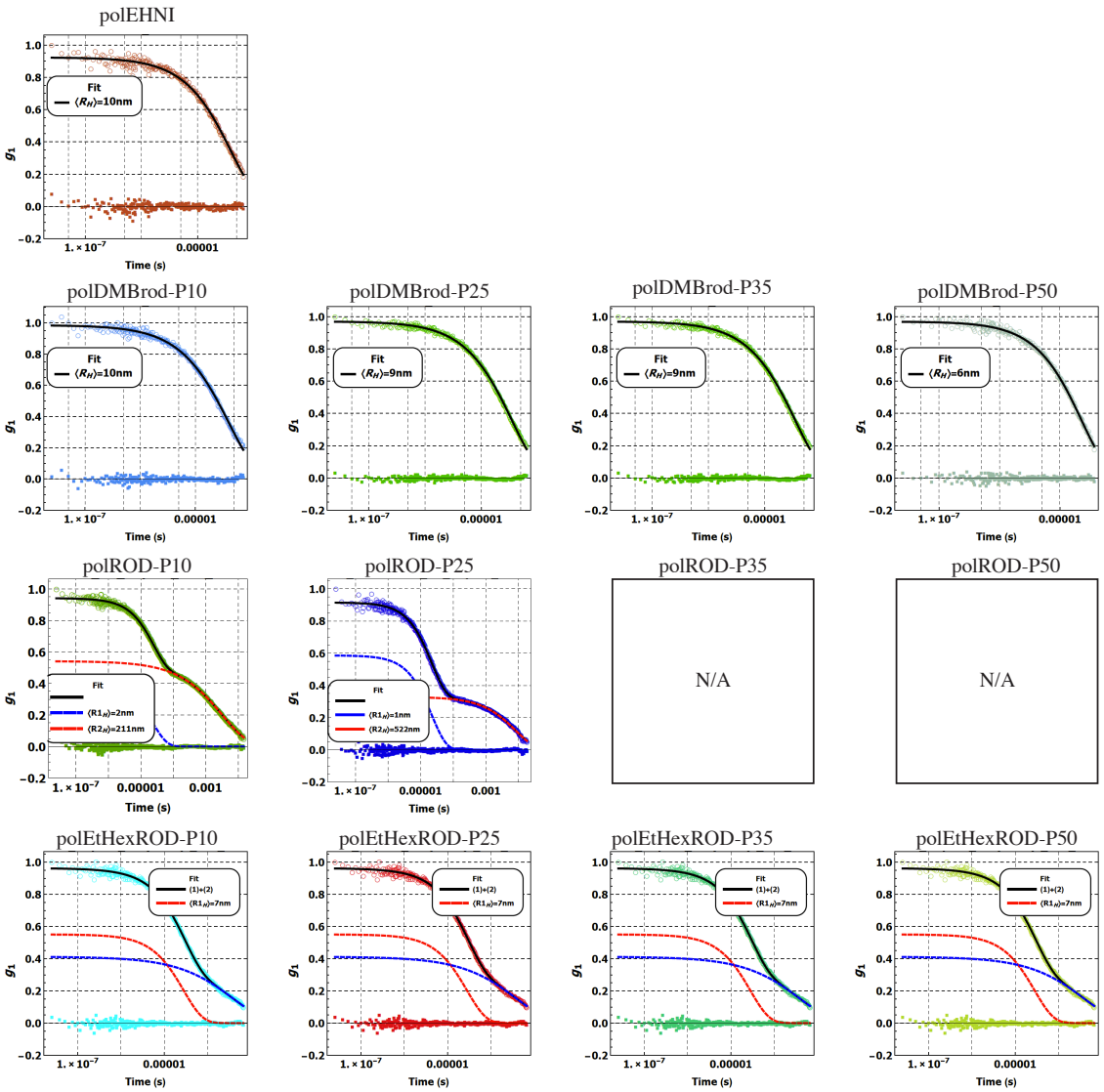


Figure S 2 Correlation functions and corresponding hydrodynamic radius calculated from DLS on polymer solutions of 0.5 mg mL^{-1} in THF. Note: Due to strong aggregation polROD-P35 and polROD-P50 were not possible to measure by means of DLS due to solubility problems.

Dynamic light scattering

Using 2 ml of a dilute suspensions, data were collected at constant room temperature (21 °C) on a commercial goniometer instrument (3D LS Spectrometer, LS Instruments AG, Switzerland). The primary beam was formed by a linearly polarized and collimated laser beam (Cobolt 05-01 diode pumped solid state laser, λ = 660 nm, P *max*. = 500 mW), and the scattered light was collected by single-mode optical fibers equipped with integrated collimation optics. The incoming laser beam passed through a Glan-Thompson polarizer with an extinction ratio of 10^{-6}, and another Glan-

Thompson polarizer, with an extinction ratio of 10^{-8}, was mounted in front of the collection optics. To construct the intensity auto-correlation function $g_2(t)$, the collected light was coupled into two APD detectors via laser-line filters (Perkin Elmer, Single Photon Counting Module), and their outputs were fed into a two-channel multiple-tau correlator. To improve the signal-to-noise ratio and to eliminate the impact of detector after-pulsing on $g_2(t)$ at early lag times below 1 µs, these two channels were cross-correlated. The field auto-correlation function was obtained via the Siegert relation:

$$g_1(t) = \sqrt{g_2(t) - 1}$$

The field auto-correlation functions were interpreted via the Nernst-Einstein equation describing translational self-diffusion, and were fitted against either a single stretched exponential function or the linear combination of two stretched exponential functions, where the first mode was used to interpret single particles and the second mode represented clusters / agglomerates.

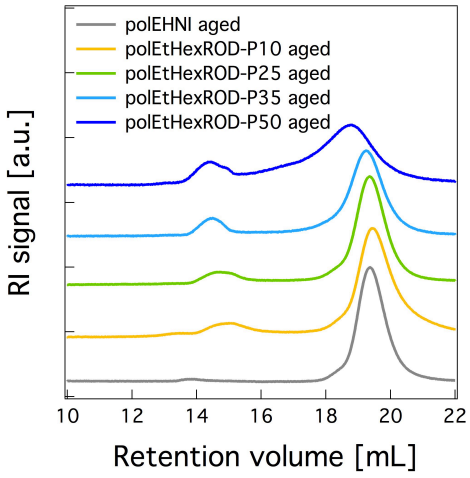


Figure S 3 GPC data (solvent THF, polystyrene standards) of aged (2 month) **polEtHexROD**.

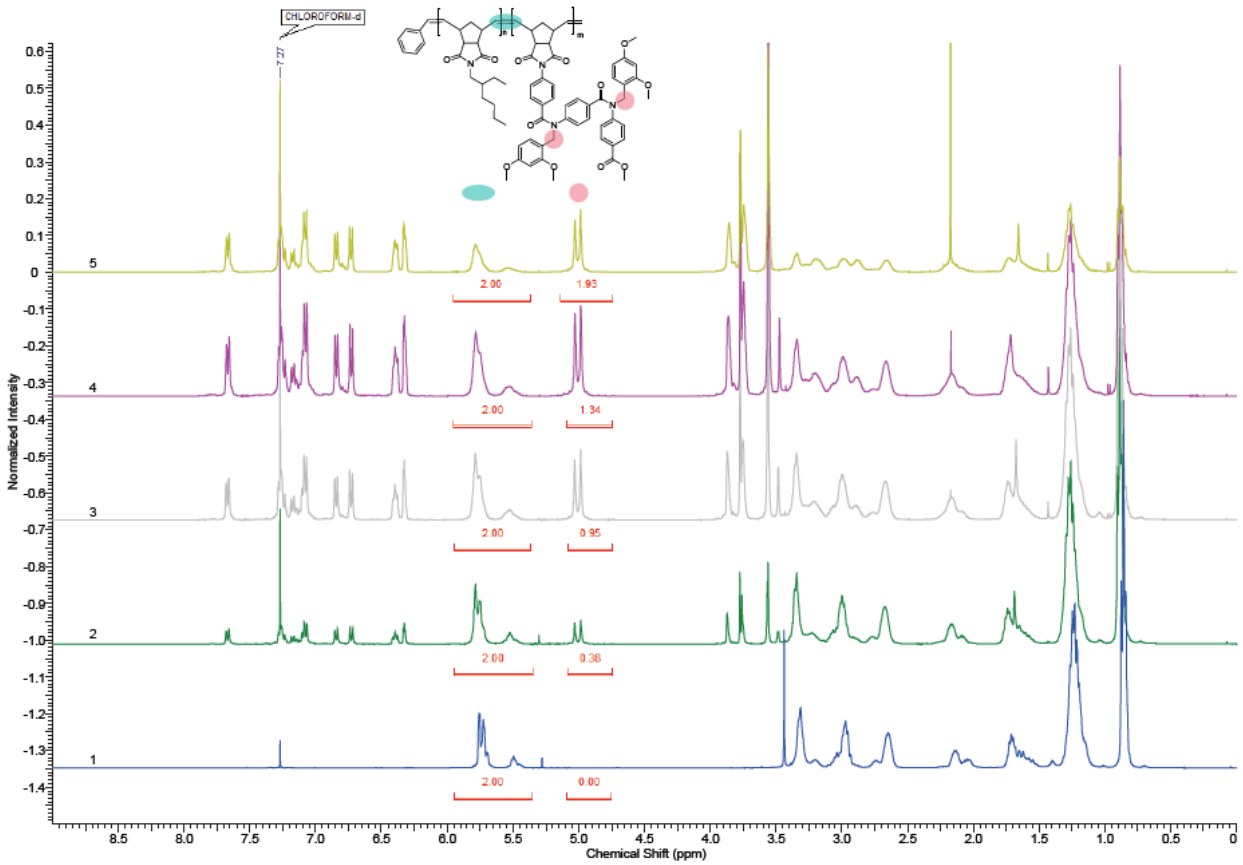


Figure S 4 Determination of practical rod content by ^{1}H NMR spectra (400 MHz, CHLOROFORM-*d*) comparison of **polDMBrod**.

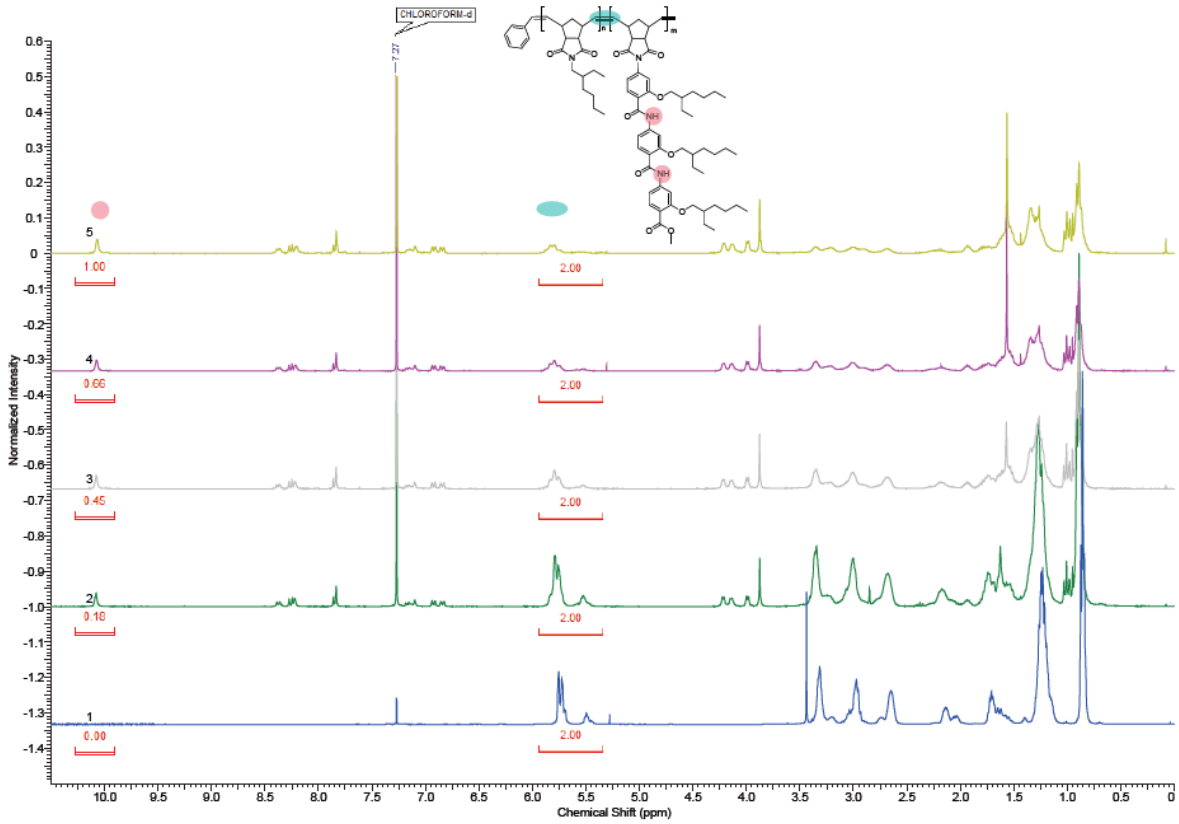


Figure S 5 Determination of practical rod content by $_1$H NMR spectra (400 MHz, CHLOROFORM-*d*) comparison of **polEtHexROD**

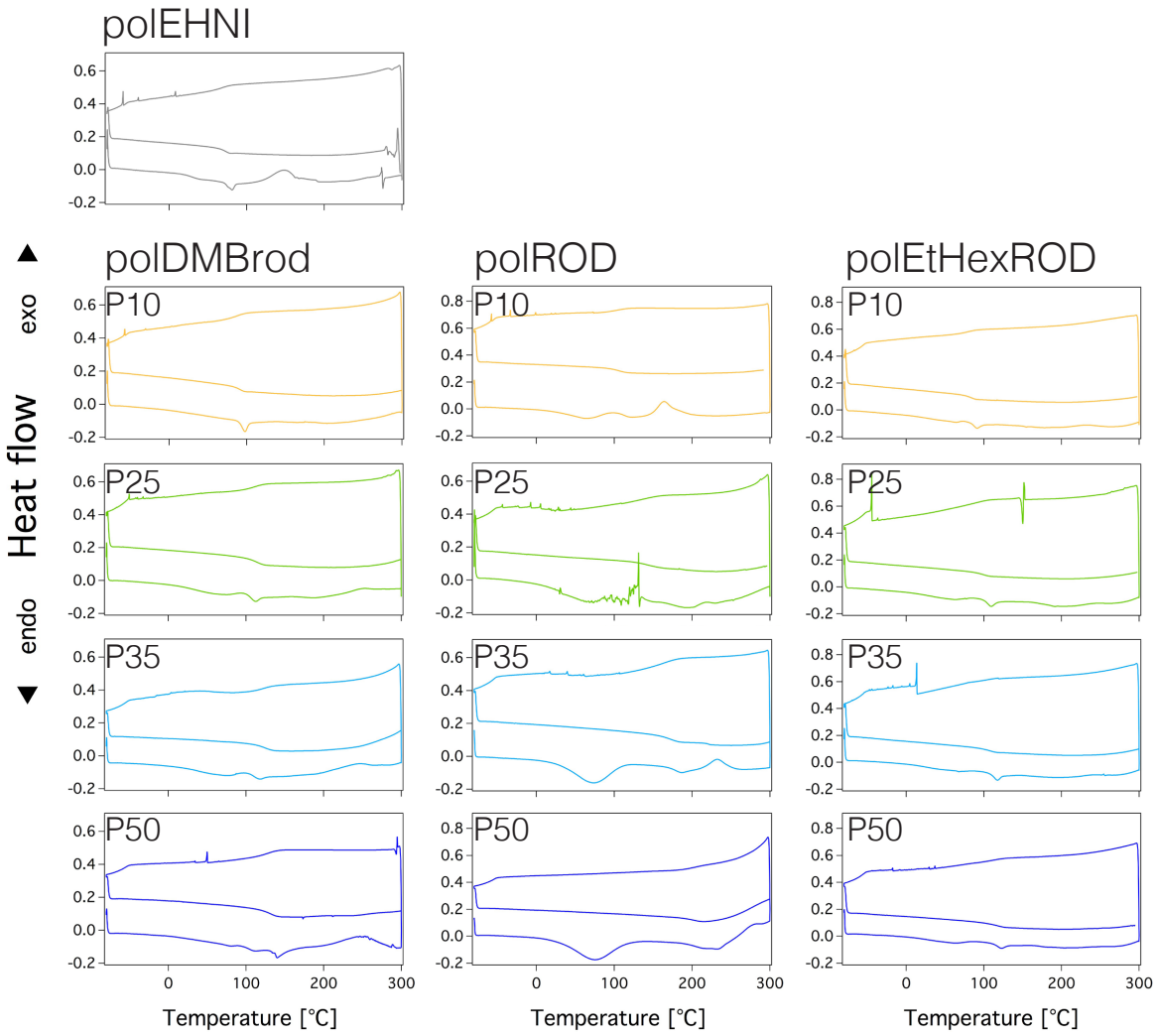


Figure S 6 DSC curvatures indicating first heating, cooling and second heating cycles for **polEHNI, polDMBrod, polROD** and **polEHNI** samples between -80 and 300◦C at heating rate of 10 K min-1.

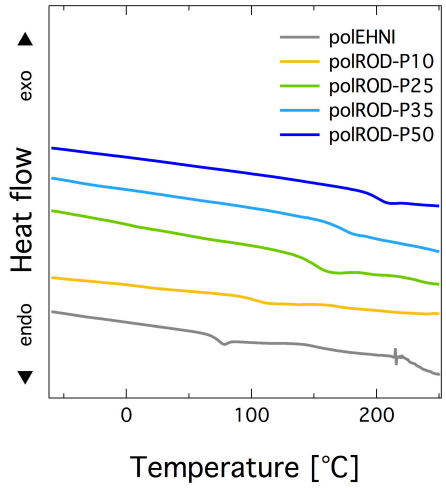


Figure S 7 DSC curvatures obtained from **polROD** and **polEHNI** samples annealed 15°C above their respective T_g for 1 h and subsequent slow cooling to room temperature. Second heating cycle reported.

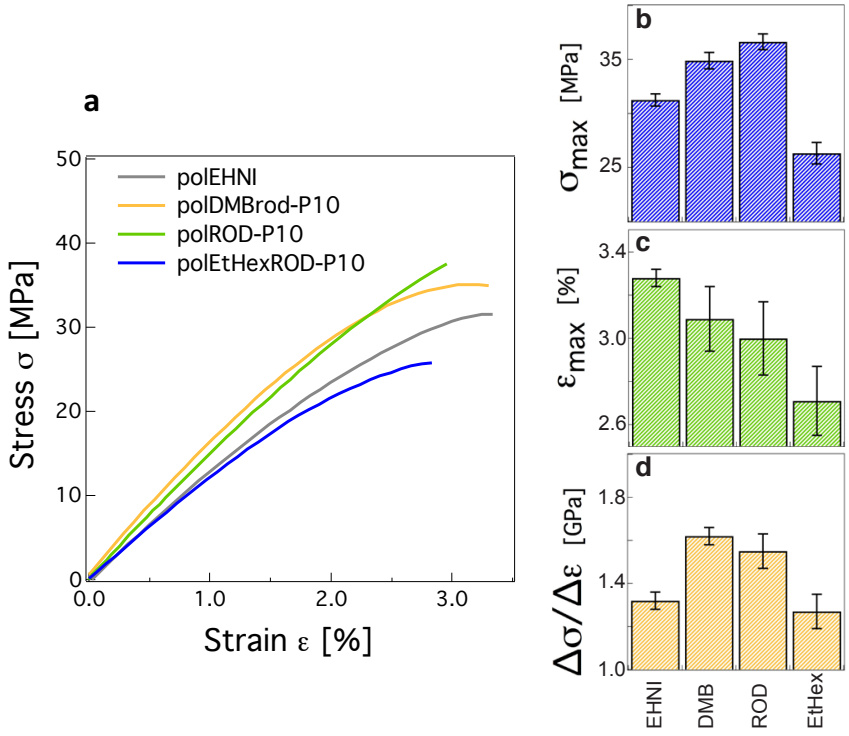


Figure S 8 (a) Tensile stress-strain curves measured at 25°C. One representative curve per composition is shown and the curves were cut at maximum stress for clarity. Also shown are averages of (b) maximum stress, (c) elongation at maximum stress, and (d) Young's modulus determined from the tensile tests. Experiments were conducted at least in triplets.

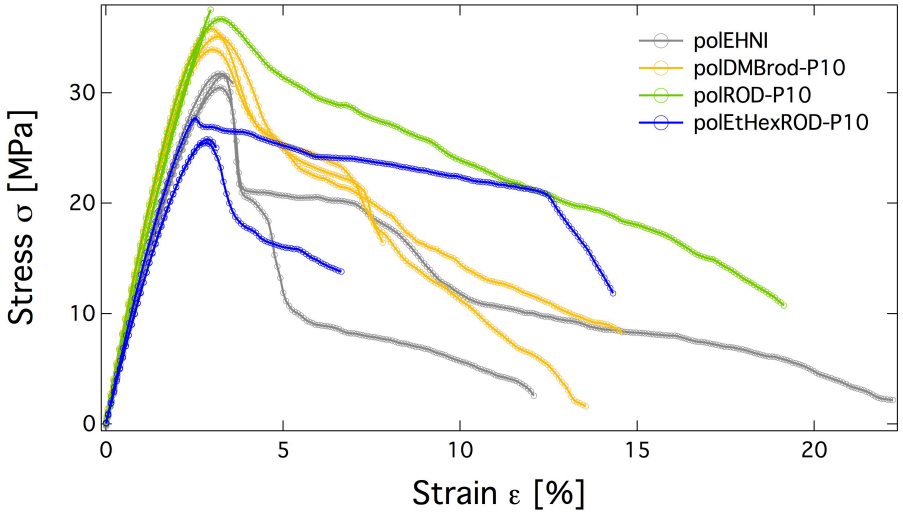


Figure S 9 Tensile stress-strain-curvature derived from DMA experiments at 25°C.

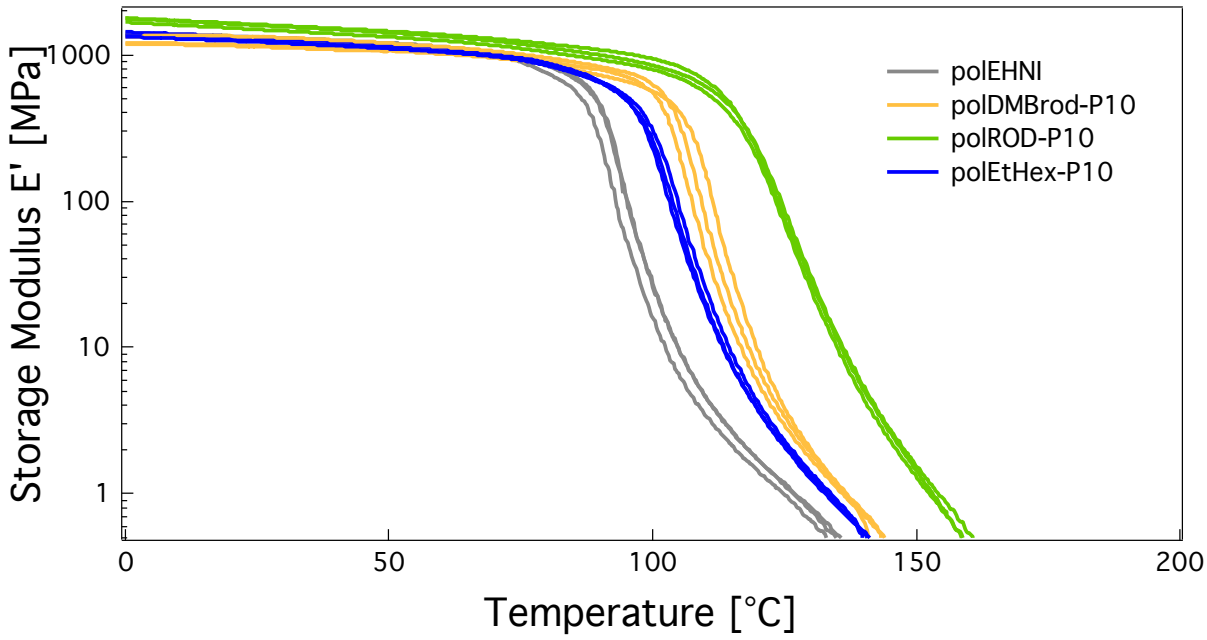


Figure S 10 Temperature dependence of storage modulus E' obtained via DMA experiments on 0.12 ± 0.01 mm hot-pressed films of all polymer samples

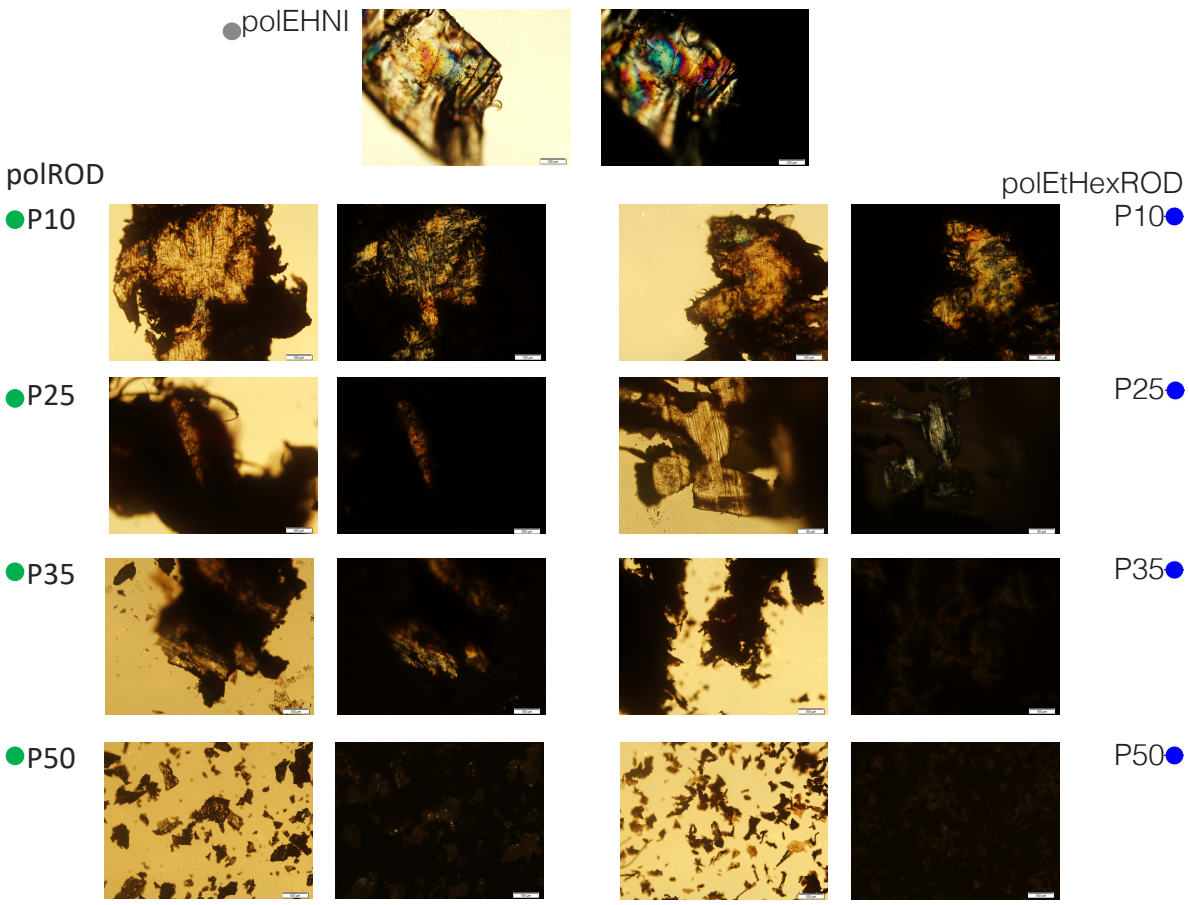


Figure S 11 Photographs of transmission and cross-polarized light microscopy of polymers obtained from precipitation. (Scale bar all 100 μm, except **polEtHexROD-P25** is 50 μm and **polROD-P25** is 200 μm.)

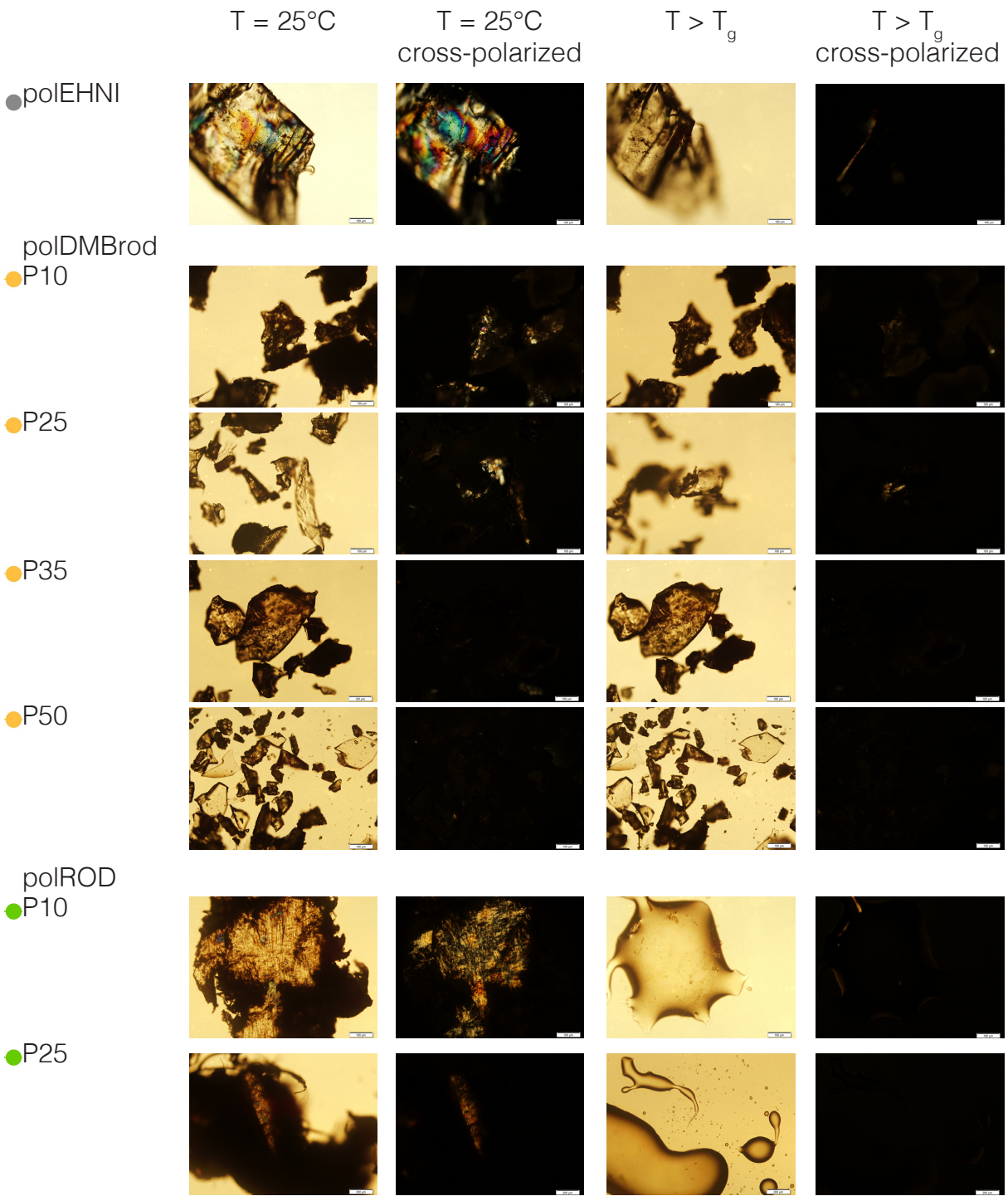


Figure S 12 Photographs of transmission and cross-polarized light microscopy of polymers obtained from precipitation. Pictures taken below and above 250°C. Scale bar all: 100 μm (except polROD-P25 is 200 μm).

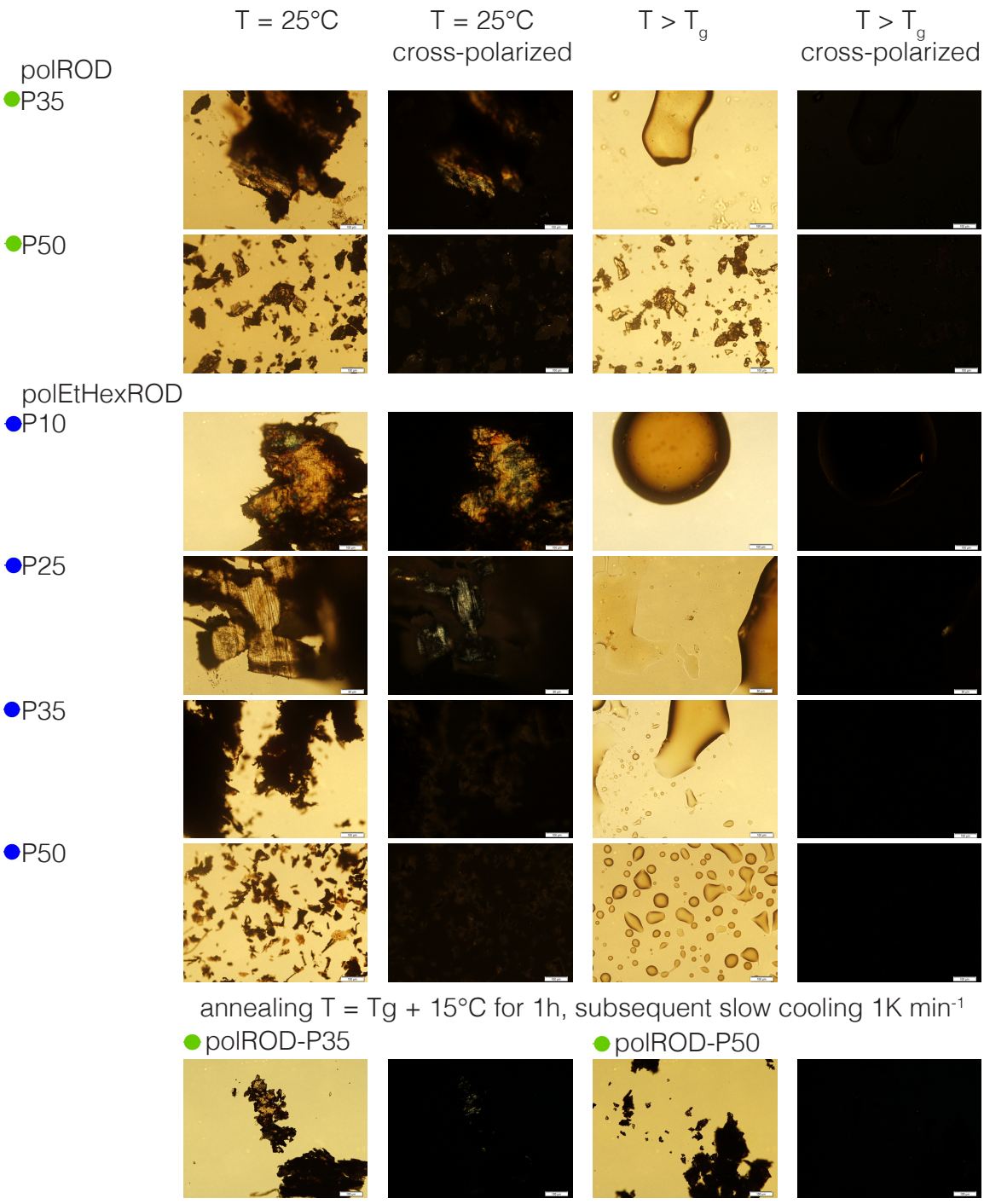


Figure S 13 Photographs of transmission and cross-polarized light microscopy of polymers obtained from precipitation. Pictures taken below and above 250°C. Scale bar all 100 µm, except **polEtHexROD-P25** is 50 µm