

Supporting Information

Vinylidene-based polymers by Rh(I)-NHC catalyzed thiol-yne click polymerization: Synthesis, characterization and post- polymerization modification

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General Information. $[\text{Rh}(\mu\text{-Cl})(\text{coe})(\text{IPr})]_2$ ¹ and $[\text{RhCl}(\text{PPh}_3)_3]$ ² were prepared according to the literature procedure. Pyridine ($\rho = 0.978 \text{ g mL}^{-1}$, 99%), 3-chloroperbenzoic acid (MCPBA, 73%) and the monomers: 1,6-hexanedithiol ($\rho = 0.983 \text{ g mL}^{-1}$, 97%), 1,3-diethynylbenzene ($\rho = 0.949 \text{ g mL}^{-1}$, 97%) and 1,4-diethynylbenzene (95%), were purchased from Aldrich and used as received. Solvents were obtained oxygen- and water-free from a Solvent Purification System (Innovative Technologies).

The absolute molecular weight averages (M_n and M_w), polydispersity (PDI, M_w/M_n) and molecular weight distribution were determined by SEC-MALLS at the Chromatography and Spectroscopy Service of the ISQCH. SEC-MALLS analyses were carried out using a Waters 2695 instrument, equipped with three PL-Gel Mixed B LS columns fitted to a MALLS detector (MiniDawn Treos, Wyatt) and a differential refractive index detector (Optilab Rex, Wyatt). The polymer solutions in THF ($\approx 2.0 \text{ mg/mL}$) were filtered through a $0.45 \mu\text{m}$ PTFE membrane filter before being injected in the GPC systems. Data analysis was performed with ASTRA Software from Wyatt. Samples of **2a**, **2b** and **2b/h** were eluted at 35°C with THF at a flow rate of 1.0 mL/min . dn/dc values in THF were determined at 658 nm using the known concentration of the sample in THF and the assumption of 100% mass recovery.³ Accurately weighted sample of polymer (2.0 mg mL^{-1}) were dissolved in the minimum amount of chloroform to yield a clear solution (around 0.1 mL) and then the solution was taken to the required volume with THF. Low molecular weight samples of **2a** and **2b** were used for the determination of dn/dc . Samples of **2b/ox** were measured using the same methods except for the solvent that, in this case, was dimethylacetamide (DMAc) doped with 0.5% (w/v) of LiCl. A value of 0.158 mL g^{-1} was found for polymers **2a** and **2b**, 0.135 mL g^{-1} for **2b/h** (in THF), and 0.141 mL g^{-1} for **2b/ox** (in DMAc, 0.5% LiCl).

^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker AV-400 (400.16 MHz) and AV-300 (300.13 MHz) spectrometers. Chemical shifts are reported in ppm relative to tetramethylsilane and referenced to partially deuterated solvent resonances. Coupling constants (J) are given in Hertz. Spectral assignments were achieved by combination of ^1H - ^1H COSY, ^{13}C DEPT and APT, ^1H - ^{13}C HSQC and ^1H - ^{13}C HMBC experiments. Infrared spectra were recorded on a FT-IR Perkin-Elmer Spectrum 100 Spectrophotometer equipped with a Universal Attenuated Total Reflectance (UATR) accessory made by thallium bromide-iodide crystals (KRS-5), which allows the observation of the electromagnetic spectrum over the 4000-250 cm^{-1} region. Thermal gravimetric analyses were carried out on a TA Q-5000 TGA apparatus (TA Instruments). Samples were heated under nitrogen from room temperature to 800 $^{\circ}\text{C}$ at a rate of 10 $^{\circ}\text{C}/\text{min}$. Differential scanning calorimetry experiments were carried out on a DSC Q-20 apparatus (TA Instruments). Samples were heated under nitrogen from 20 $^{\circ}\text{C}$ to 160/220 $^{\circ}\text{C}$ at a rate of 10 $^{\circ}\text{C}/\text{min}$ and cooled to the initial temperature at the same rate. In some experiments this cycle was repeated several times. Field emission scanning electron microscopy (FE-SEM) images were recorded using Carl Zeiss MERLIN scanning electron microscope at the Microscopy Service Laboratory of the University of Zaragoza. The polymer samples were fixed onto glass and coated with gold.

Polymer Synthesis and Characterization. Thiol-yne click polymerization reactions were carried out under an atmosphere of argon using Schlenk techniques or glovebox. The reactions were monitored by ^1H NMR spectroscopy. Aliquots (0.1 mL) were taken from the reaction mixture at different reaction times and transferred to an NMR tube under argon. The solvent was removed under vacuum and the residue dissolved in CDCl_3 .[‡] The poor solubility of some isolated polymers in THF precludes the determination of the polymer molecular weight in this

solvent after precipitation, therefore SEC-MALS analysis was carried on aliquots (0.1 mL) of freshly made solution of the polymers in THF which were diluted to 2.0 mg/mL before analyses.⁴

Synthesis of polymer 2a. [Rh(μ -Cl)(coe)(IPr)]₂ (8.0 mg, 6.3 μ mol) was weighed in a Schlenk tube (25 mL) inside a glovebox. The catalyst was dissolved in degassed THF (2.5 mL) outside the glovebox and pyridine (5.1 μ L, 0.063 mmol) was added under an argon stream to give a yellow solution that was stirred for 5 min. Then, 1,6-hexanedithiol (**1**) (99.0 μ L, 0.628 mmol) and 1,3-diethynylbenzene (**a**) (86.0 μ L, 0.628 mmol) were sequentially added under an argon stream to give a red-orange solution that was stirred at room temperature for 24 h. The resulting orange-brown solution was brought to dryness under vacuum to give an oily residue, which was dried under vacuum for 48 h. The orange-brown residue was washed with THF (3 mL) to give the polymer as jelly-like needles, which were filtered under argon using cannula techniques, washed with THF (2 x 2 mL) and dried under vacuum for 48 h. Yield: 73 mg (42 %), orange needles. Bimodal distribution: $M_w = 4.22E+04$, $M_w/M_n = 1.78$ (80 %); $M_w = 4.70E+03$, $M_w/M_n = 1.11$ (20 %). ¹H NMR (400.16 MHz, CDCl₃, 298 K): δ 7.71 (m), 7.49 (dd, $J_{H-H} = 15.8$ and 7.8), 7.44 (m), 7.31 (m), 7.14 (m) (Ph), 6.60 (ABq, $J_{AB} = 12.0$), 6.57 (ABq, $J_{AB} = 12.0$) (=CH *trans*), 5.47, 5.44, 5.16, 5.14 (=CH₂), 2.79, 2.67 (m, S-CH₂-), 1.63, 1.40 (m, >CH₂). α/β -E ratio = 4.0. ¹³C{¹H} (100.62 MHz, C₆D₆, 298 K): δ 145.2, 145.0 (C=CH₂), 140.3, 140.00, 137.3 (C_q, Ph), 128.7, 128.5, 127.2 (Ph), 126.3, 126.0 (=CH *trans*), 125.9 (Ph), 125.7, 125.5 (=CH *trans*), 124.3 (Ph), 110.8, 110.7, 110.5 (C=CH₂), 32.5, 32.1, 29.31, 28.5, 28.4 (>CH₂). IR (ATR, cm⁻¹): ν (C=C), 1679 (s), 1594 (m).

Synthesis of polymer 2b. The polymer was prepared from [Rh(μ -Cl)(coe)(IPr)]₂ (4.0 mg, 3.1 μ mol), pyridine (2.6 μ L, 0.031 mmol), 1,6-hexanedithiol (**1**) (99.0 μ L, 0.628 mmol) and 1,4-

diethynylbenzene (**b**) (83.4 mg, 0.628 mmol) in THF (2.5 mL) at room temperature for 24 h following the procedure described above. Yield: 123 mg (71 %), orange-brown plates and needles. $M_w = 4.69 \times 10^4$, $M_w/M_n = 1.85$. ^1H NMR (400.16 MHz, CDCl_3 , 298 K): δ 7.52 (br s), 7.34 (ABq, $J_{AB} = 8.3$) (Ph), 6.59 (ABq, $J_{AB} = 16.0$), 6.58 (ABq, $J_{AB} = 16.0$), 6.55 (ABq, $J_{AB} = 14.0$) (=CH *trans*), 5.48, 5.45, 5.17, 5.16, 5.14 (=CH₂), 2.80, 2.67 (m, S-CH₂-), 1.63, 1.42 (m, >CH₂). α/β -E ratio = 4.0. $^{13}\text{C}\{^1\text{H}\}$ (75.46 MHz, C_6D_6 , 298K): δ 144.8, 144.7, 144.3 (C=CH₂), 140.2, 139.9, 138.1, 137.6, 137.4 (C_q, Ph), 132.6, 132.2, 127.5, 127.2 (Ph), 126.2, 126.0, 125.8, 125.6, 125.5, 125.3 (=CH *trans*), 111.7, 111.6, 110.8, 110.7, 110.4 (C=CH₂), 39.1, 32.2, 29.1, 28.6, 28.4, 28.2, 28.1 (>CH₂). IR (ATR, cm^{-1}): $\nu(\text{C}=\text{C})$, 1671 (s), 1586 (m).

Hydrogenation of 2b. Synthesis of polymer 2b/h. A solution of polymer **1b** in THF was prepared by copolymerization of 1,6-hexanedithiol and 1,4-diethynylbenzene (0.628 mmol) using the $[\text{Rh}(\mu\text{-Cl})(\text{coe})(\text{IPr})_2]$ (3.1 μmol)/pyridine (0.031 mmol) catalytic system following the procedure describe above. The solution was concentrated under vacuum almost to dryness and THF (2.5 mL) was added. This operation was repeated three times in order to remove the pyridine present in the reaction media. Then, $[\text{RhCl}(\text{PPh}_3)_3]$ (29.1 mg, 0.031 mmol) was added and the solution transferred to a medium pressure glass reactor which was pressurized to 5.5 bar of $\text{H}_2(\text{g})$ and stirred at 25 °C for 5 days (incomplete reduction of the vinylidene groups was observed at shorter reaction times). The resulting light orange solution was filtered through a short pad of silica gel and the solvent removed under vacuum to give an orange oil which was dried under vacuum for 48 h. Yield: 167 mg (96 %). $M_w = 2.19 \times 10^4$, $M_w/M_n = 2.59$. ^1H NMR (400.16 MHz, CDCl_3 , 298 K): δ 7.34 (m), 7.26 (m), 7.15 (m) (Ph), 6.57 (set of ABq, $J_{AB} \approx 16$) (=CH *trans*), 3.92 (m) (-CH), 2.85, 2.76, 2.63, 2.51, 2.30 (S-CH₂-), 1.56 (d, $J_{\text{H-H}} = 6.7$), 1.55 (d, $J_{\text{H-H}} = 7.0$) (-CH₃), 1.45, 1.32, 1.22 (>CH₂). $^{13}\text{C}\{^1\text{H}\}$ (75.46 MHz, CDCl_3 , 298K): 142.8, 132.1,

131.9, 128.5, 128.4, 127.5, 127.3, 127.1 (Ph), 125.6, 125.5 (=CH *trans*), 43.7 (-CH), 33.8, 31.2, 29.2, 28.5, 27.9, 24.5 (>CH₂), 22.6, 22.5 (-CH₃).

Oxidation of 2b. Synthesis of polymer 2b/ox. A solution of polymer **1b** in THF was prepared by copolymerization of 1,6-hexanedithiol and 1,4-diethynylbenzene (1.256 mmol) using the [Rh(μ -Cl)(coe)(IPr)]₂ (6.3 μ mol)/pyridine (0.063 mmol) catalytic system following the procedure describe above. The solution was concentrated under vacuum almost to dryness and CH₂Cl₂ (4 mL) was added. This operation was repeated twice to change the solvent. The solution was transferred to a flask and diluted to 10 mL. A solution of MCPBA (653 mg, 2.76 mmol) in CH₂Cl₂ (20 mL) was added dropwise at -20 °C and the mixture stirred at room temperature for 24 h. The resulting yellow solution was washed with a solution of NaOH (15%) (3 x 20 mL), H₂O (2 x 20 mL) and brine (2 x 20 mL). The organic phase was dried over MgSO₄ and then filtered. The solvent was removed under vacuum to give a pale yellowish solid, which was dried under vacuum. Yield: 328 mg (84 %). $M_w = 1.64E+04$, $M_w/M_n = 2.04$. ¹H NMR (300.13 MHz, CDCl₃, 298 K): δ 7.65-7.29 (m) (Ph), 7.06 (ABq, $J_{AB} \approx 16$) (=CH *trans*), 6.13, 6.06, 6.05 (=CH₂), 2.76, 2.60, 2.37 (m, S-CH₂-), 1.74, 1.57, 1.44, 1.35 (m, >CH₂). ¹³C{¹H} (75.46 MHz, CDCl₃, 298 K): δ 151.7, 151.6, 151.5 (C=CH₂), 135.4, 135.1 (C_q, Ph), 135.0 (=CH *trans*), 134.9 (C_q, Ph), 132.9, 132.7, 131.8 (Ph), 128.4 (=CH *trans*), 127.4, 127.2, 126.5 (Ph), 111.7, 111.6, 110.8, 110.7, 110.4 (C=CH₂), 53.8, 51.6 (S-CH₂-), 28.5, 28.3, 21.9, 21.4 (>CH₂). α/β -E ratio: 4.0. IR (ATR, cm⁻¹): ν (C=C), 1604 (m); ν (S=O), 1030 (s).

[‡] The underlined signals in the ¹H and ¹³C{¹H} NMR spectra are the more intense resonances of each type that correspond to the main sequence in the polymers.

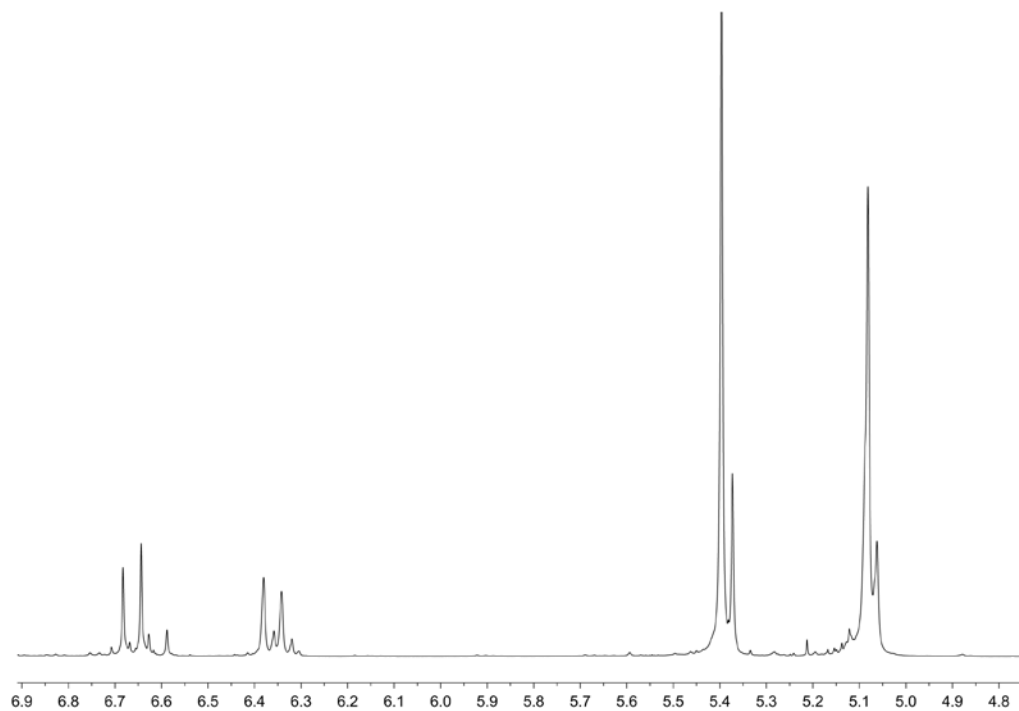


Figure S1. Vinyl region of the ^1H NMR spectrum of polymer **2b** in CDCl_3 .

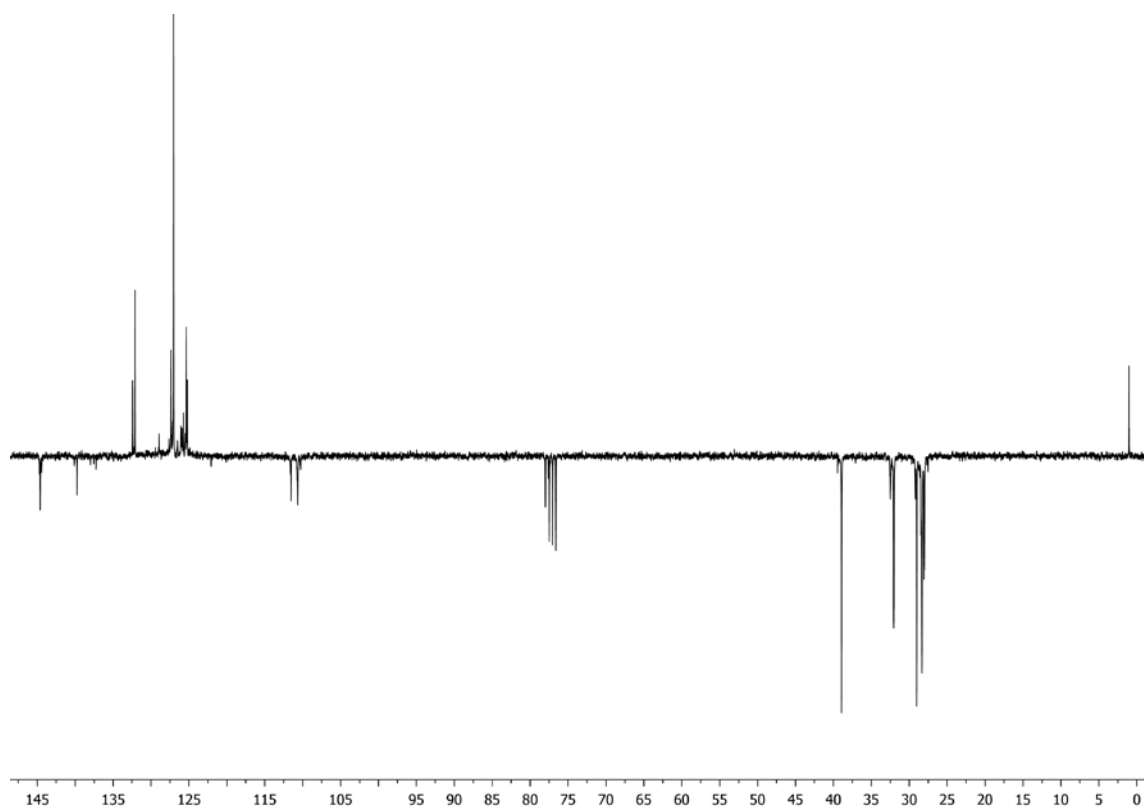


Figure S2. $^{13}\text{C}\{^1\text{H}\}$ -APT NMR spectrum of polymer **2b** in CDCl_3 .

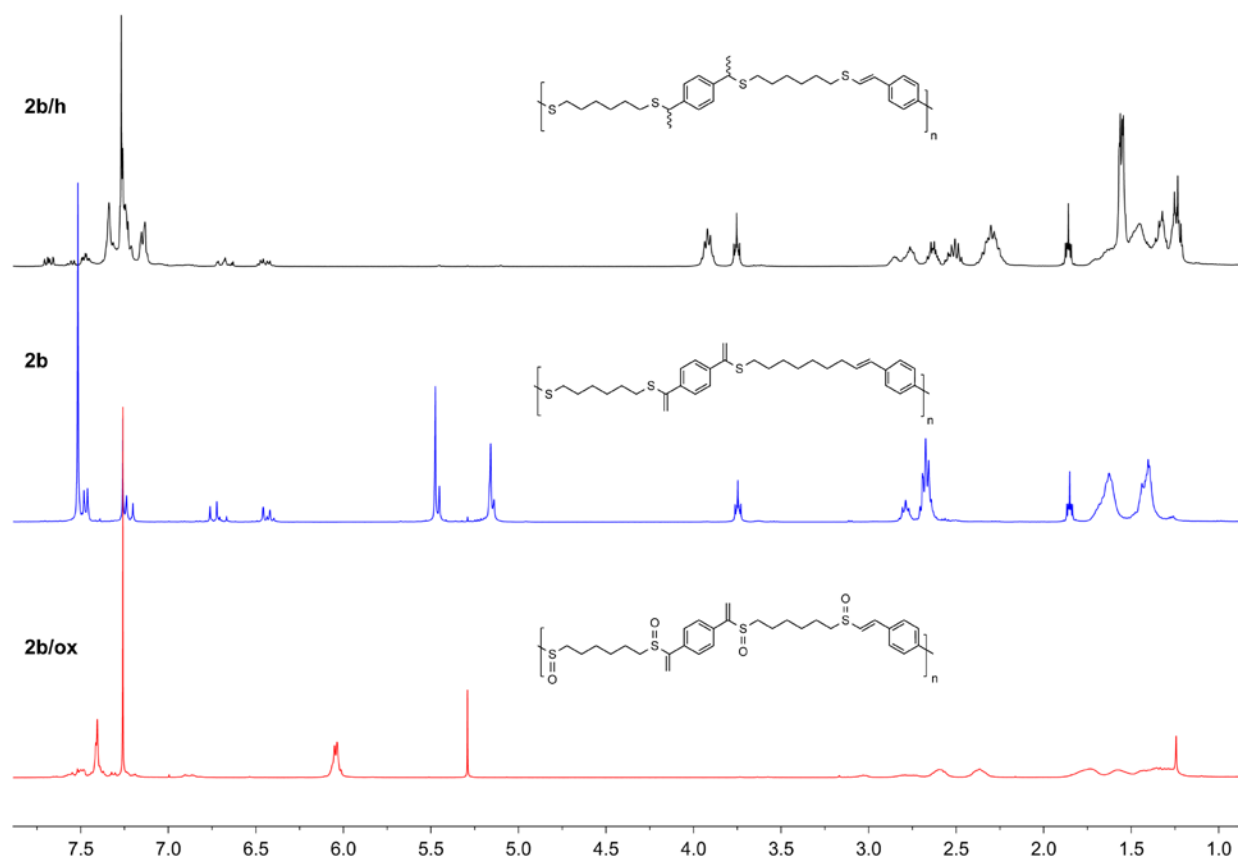


Figure S3. ^1H NMR spectra of polymers **2b**, **2b/h** and **2b/ox** in CDCl_3 .



Figure S4. Representative photographs of polymers **2a** (left) and **2b** (right) in THF solutions.

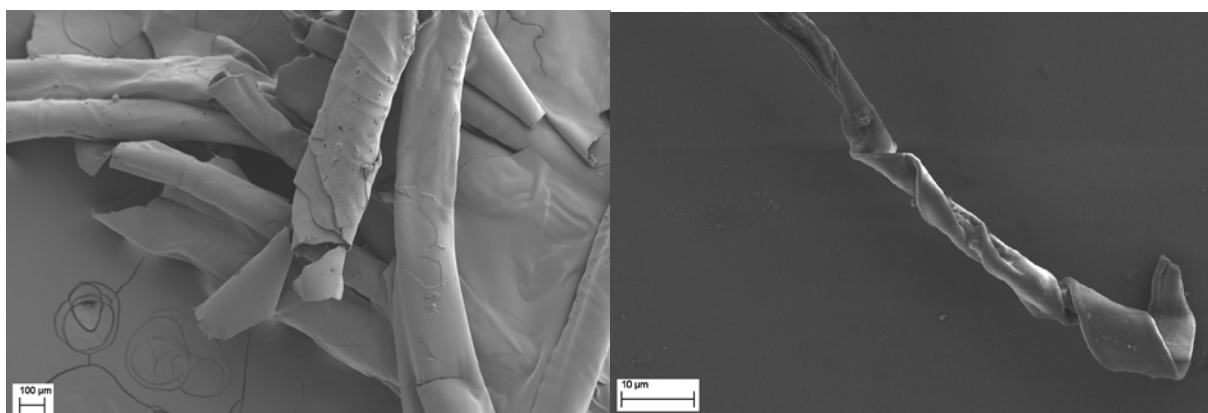


Figure S5. Representative FE-SEM images of polymer **2a**.

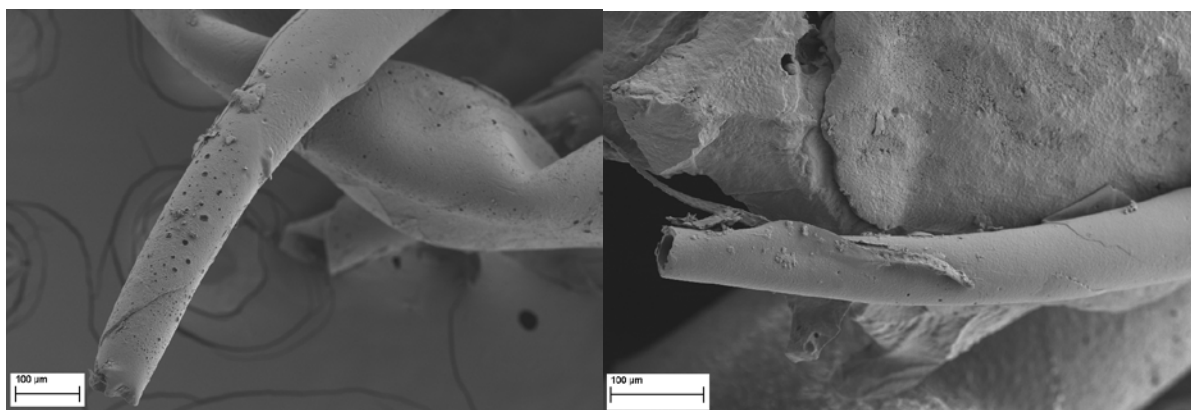


Figure S6. Representative FE-SEM images of polymer **2b**.

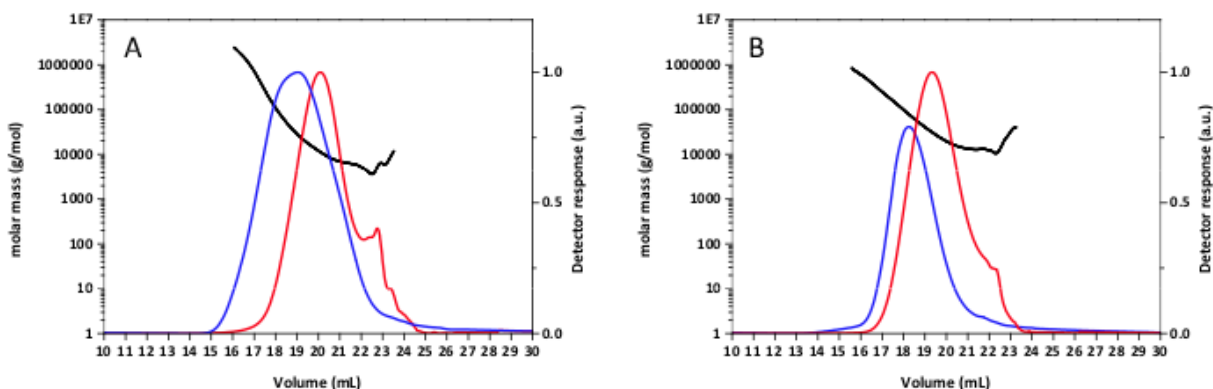


Figure S7. Light scattering (blue) and refractive index (magenta) chromatograms and MM (black) vs. elution volume (mL) plots: A) polymer **2a** (entry 1) and B) polymer **2b** (entry 3) prepared at 25 °C with 1 mol% of catalyst **1** for 24 h.

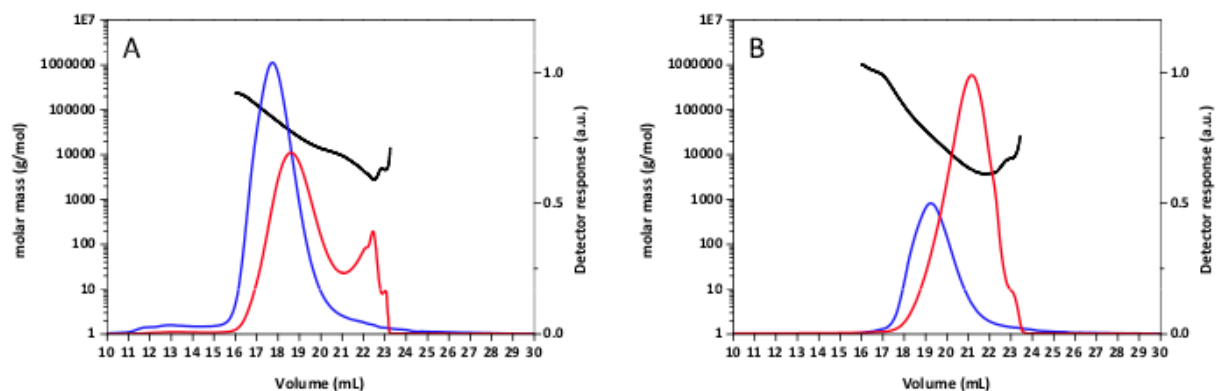


Figure S8. Light scattering (blue) and refractive index (magenta) chromatograms and MM (black) vs. elution volume (mL) plots: A) polymer **2a** (entry 2) and B) polymer **2b** (entry 5) prepared at 25 °C with 2 mol% of catalyst **1** for 24 h.

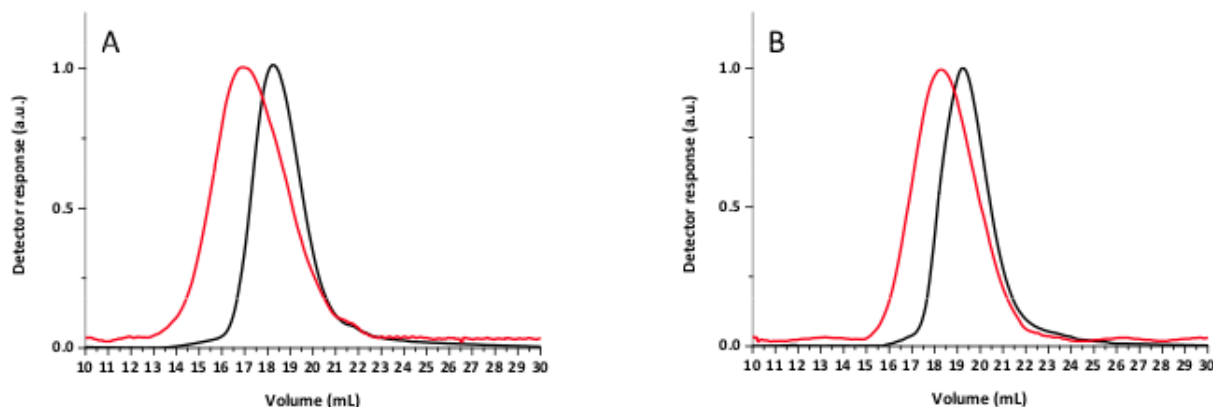


Figure S9. Light scattering chromatograms vs. elution volume (mL) plots for polymer **2b** prepared at 25 °C for 24 h (black line) or 48 h (red line). A) 1 mol% of catalyst **1** (entries 3 and 4), and B) 2 mol % of catalyst **1** (entries 5 and 6).

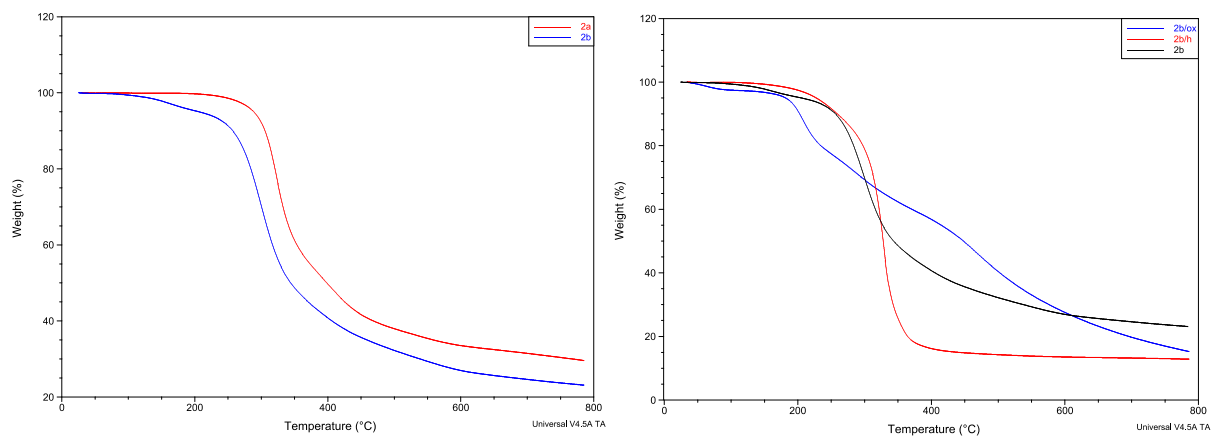


Figure S10. TGA thermograms of polymers **2a**, **2b**, **2b/h** and **2b/ox**.

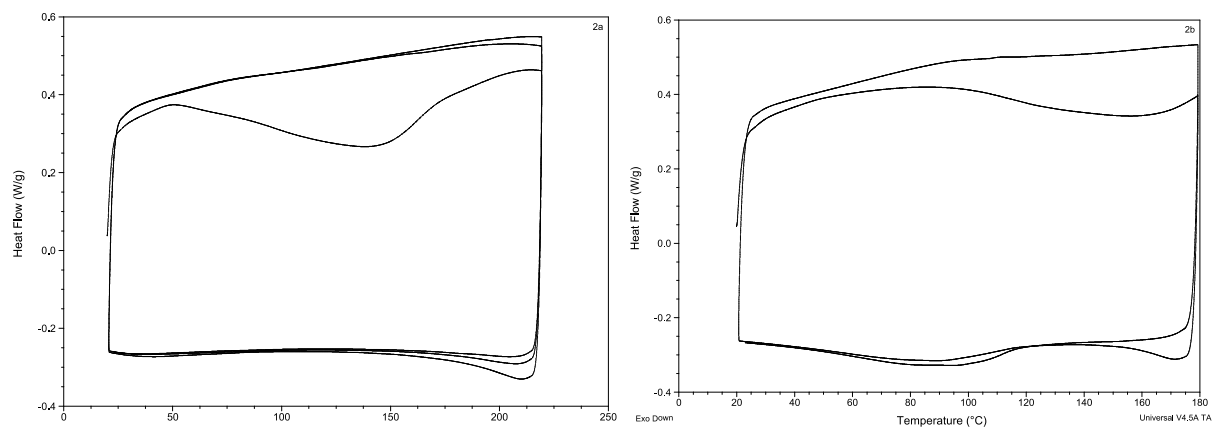


Figure S11. DSC thermograms of polymers **2a** and **2b**.

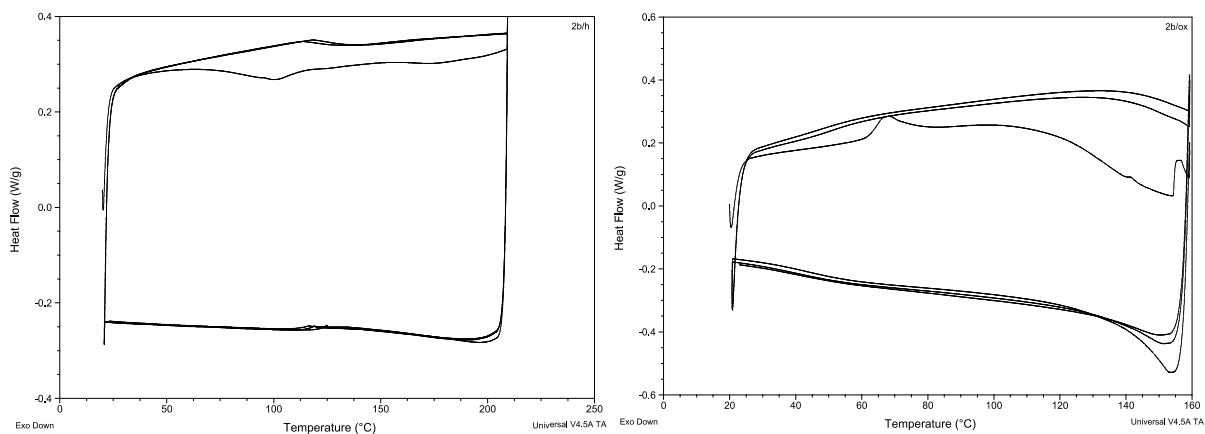


Figure S12. DSC thermograms of polymers **2b/h** and **2b/ox**.

Table S1. Thermal properties of polymers **2a**, **2b**, **2b/h** and **2b/ox** derived from ATG y DSC.

Polymer	T _{5%} (°C) ^a	Residue (%) ^b	T _{onset} (°C) ^c	T _{max} (°C) ^d	Other (°C) ^e	Exothermic process (°C)
2a	288	30	300	322	402	137
2b	206	23	266	299	165, 400	154
2b/h	288	13	302	330	257, 354	101
2b/ox	182	15	188 (24%), 274 (20%), 430 (41%)	208	67, ^f 291, 472	154

^a Temperature for which the weight loss is 5%; ^b Percentage of residue at 800 °C; ^c T_{onset} = onset of the decomposition processes. ^d T_{max} = temperature of the maximum in the weight loss rate. ^e Other maxima in the derivative thermogram. ^f Loss of solvent (THF).

References

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