Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Electronic Supplementary Information for

Organopolymerization of Tulipalin B: A Hydroxyl-Functionalized Methylene Butyrolactone

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Materials, Reagents, and Methods

All manipulations with air- and moisture-sensitive chemicals and reagents were performed using standard Schlenk techniques on a dual-manifold line, on a high-vacuum line, or in an inert gas (Ar or N_2)-filled glovebox. NMR-scale reactions were conducted in Teflon-valve-sealed J. Young-type NMR tubes. NMR (^{1}H and ^{13}C) spectra were recorded on a Varian Inova 400 MHz or 500 MHz spectrometer. Chemical shifts for ^{1}H and ^{13}C spectra were referenced to internal solvent resonances and are reported as parts per million relative to $SiMe_4$. DMSO-d_6 was dried over CaH_2 overnight and vacuum-distilled. HPLC-grade organic solvents were first sparged extensively with nitrogen during filling 20 L solvent reservoirs and then dried by passage through activated alumina (for Et_2O, THF, and CH_2Cl_2) followed by passage through Q-5 supported copper catalyst (for toluene and hexanes) stainless steel columns. HPLC-grade DMF was degassed and dried over CaH_2 overnight, followed by vacuum distillation (CaH_2 was removed before distillation).

The superbase phosphazene, 1-*tert*-butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)phosphoranylidenamino]-2λ^5,4λ^5-catenadi(phosphazene) (^{t}Bu-P_4), was purchased from Sigma-Aldrich as a 1.0 M solution in hexanes; the solvent was removed under vacuum prior to use. BHT-H (2,6-di-*tert*-butyl-4-methylphenol) was purchased from Alfa Aesar and recrystallized from hexanes prior to use. Azobisisobutyronitrile (AIBN) was purchased from Sigma-Aldrich and recrystallized from methanol before use. NHC catalyst 1,3-di-*tert*-butylimidazol-2-ylidene (I^{t}Bu) and α-methylene-γ-butyrolactone (MBL) were purchased from TCI America, and selenium dioxide was purchased from Alfa Aesar Chemical Co. All other commercial reagents were used as received. NHC catalyst 1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-ylidene (TPT)[1] was prepared according to literature procedures.

Preparation of β-Hydroxy-α-Methylene-γ-Butyrolactone ($_\beta$HMBL). Literature procedures[2] were modified for the preparation of $_\beta$HMBL from MBL. To a solution of MBL (5.0 mL, 45.6 mmol) in dioxane (50 mL) was added SeO_2 (7.0 g, 63.1 mmol) and the reaction mixture was stirred at 80 ºC for 10 h. The resulting mixture was concentrated and the crude product was purified by flash chromatography on silica gel (CH_2Cl_2) to give $_\beta$HMBL (1.5 g, 30% yield) as a pale yellow liquid at room temperature. Seven batches of the resulted $_\beta$HMBL were collected for further purification by distillation at 50 ºC/10^{-5} Torr to give $_\beta$HMBL (10.2 g) as colorless crystals at –40 ºC, which melts at room temperature.

^{1}H NMR (400 MHz, $CDCl_3$) for $_\beta$HMBL: δ 6.37 (d, J = 2.1 Hz, 1H), 6.02 (d, J = 1.8 Hz, 1H), 4.95–4.90 (m, 1H), 4.48 (dd, J = 10.0, 3.6 Hz, 1H), 4.15 (dd, J = 10.0, 3.6 Hz, 1H), 3.86 (d, J = 5.7 Hz, 1H).

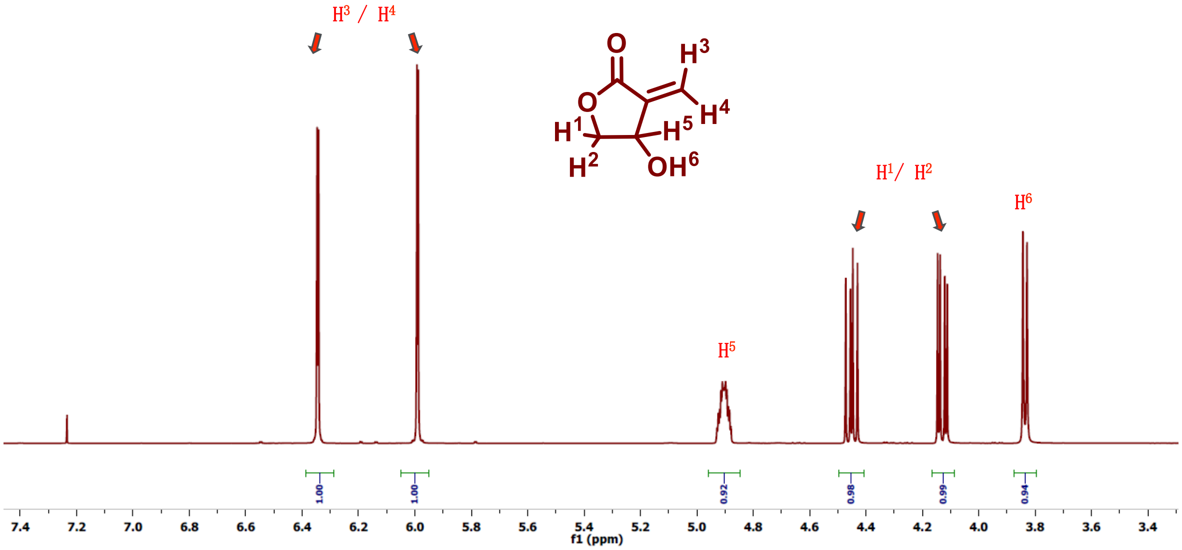

Figure S1. ^{1}H NMR (400 MHz, CDCl$_3$, 25 ºC) spectrum of $_\beta$HMBL.

General Polymerization Procedures

Polymerizations were performed either in 25 mL flame-dried Schlenk flasks interfaced to a dual-manifold Schlenk line for runs using external temperature bath, or in 20 mL glass reactors inside the glovebox for room temperature (~25 °C) runs. The reactor was charged with a predetermined amount of solvent and initiator. After equilibration at the desired polymerization temperature for 10 min, the polymerization was initiated by rapid addition of 200 mg monomer via a gastight syringe. After a measured time interval, a 0.1 mL aliquot was taken from the reaction mixture *via* syringe and quickly quenched into a 1.5 mL septum cap sealed vial containing 0.6 mL of "wet" CDCl$_3$ stabilized by 250 ppm of BHT-H; the quenched aliquots were later analyzed by ^{1}H NMR to obtain monomer conversion data. The remaining bulk polymerization reaction was immediately quenched after the removal of the last aliquot by addition of 5.0 mL of 5% HCl-acidified methanol. The quenched mixture was precipitated into 50 mL of cold methanol, filtered, washed with methanol to remove any unreacted monomer, and dried in a vacuum oven at 50 °C to a constant weight.

Polymer Characterization

Polymer number-average molecular weights (M_n) and molecular weight distributions ($Đ = M_w/M_n$) were measured by gel permeation chromatography (GPC) analyses carried out at 40 °C and a flow rate of 1.0 mL min^{-1}, with DMF (0.02 mol/L LiBr) as the eluent, on a Waters University 1500 GPC instrument equipped with four PLgel 5 μm mixed-C columns (Polymer Laboratories; linear range of molecular weight = 200–2,000,000) and calibrated using 10 PMMA standards. Chromatograms were processed with Waters Empower software (version 2002).

Glass transition temperatures (T_g) of the polymers were measured by differential scanning calorimetry (DSC) on a Q20 DSC, TA Instruments. Polymer samples were first heated to 180 °C at 20°C/min, equilibrated at this temperature for 4 min, cooled to −80 °C at 10 °C/min, and reheated to 250 °C at 10 °C/min. All T_g values were obtained from the second scan after the thermal history was removed from the first scan. Maximum rate decomposition temperatures (T_{max}) and decomposition onset temperatures (T_{onset}) of the polymers were measured by thermal gravimetric analysis (TGA) on a Q50 TGA Thermogravimetric Analyzer, TA Instrument. Polymer samples were heated from 20 °C to 700 °C at a rate of 20 °C/min. FT-IR spectra were recorded on a Nicolet iS-50 FT-IR spectrometer for powder samples.

The low molecular weight sample was analyzed by matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF MS). The experiment was performed on an Ultraflex MALDI-TOF mass spectrometer (Bruker Daltonics) operated in positive ion, reflector mode using a Nd:YAG laser at 355 nm and 25 kV accelerating voltage. The sample (1 μl) was mixed with 1μl of 2,5-dihydroxy benzoic acid (DHB, 10 mg/ml in 50% ACN, 0.1% TFA). The mixture was spotted on the MALDI target and allowed to air dry. External calibration was done using a peptide calibration mixture (4−6 peptides) on a spot adjacent to the sample. The raw data were processed in the FlexAnalysis software (version 2.4, Bruker Daltonics).

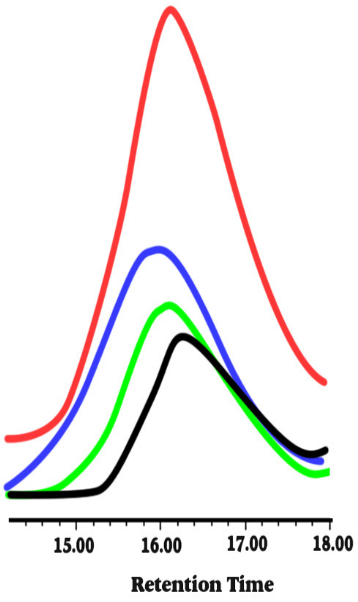

Figure S2. Representative GPC traces of the polymers produced by I^{t}Bu (red), ^{t}Bu-P$_4$ (blue), TPT (green), and AIBN (black).

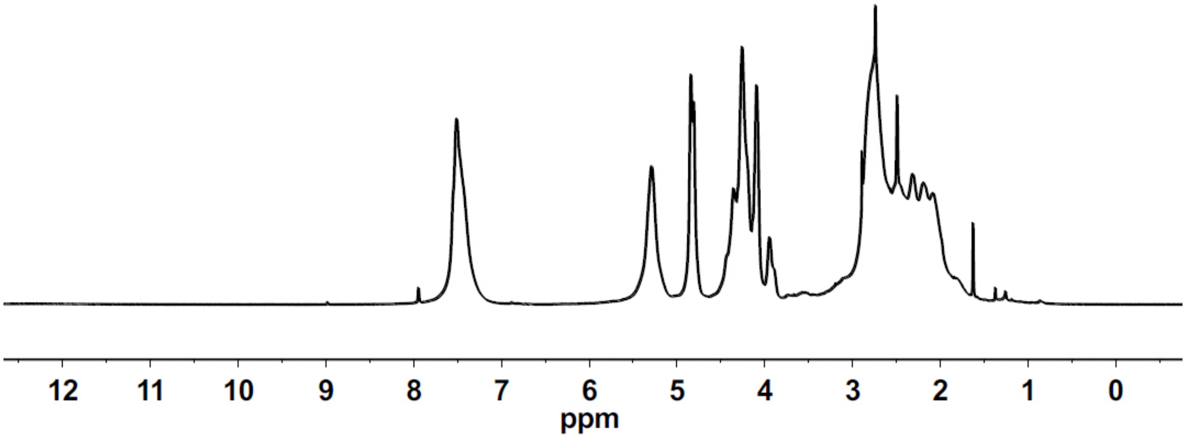

Figure S3. ^{1}H NMR (DMSO-d_6, 500 MHz, 80 °C) spectrum of the polymer produced by I^{t}Bu.

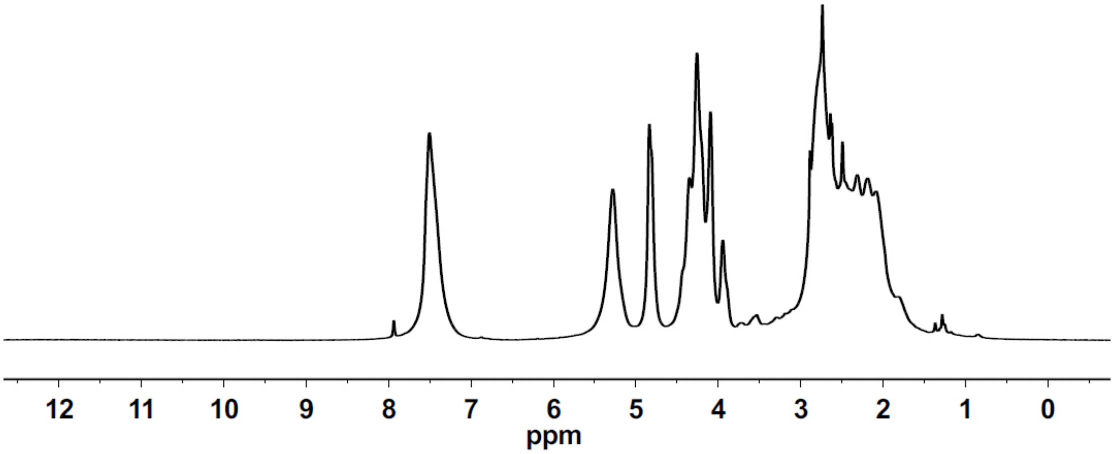

Figure S4. ^{1}H NMR (DMSO-d_6, 500 MHz, 80 °C) spectrum of the polymer produced by ^{t}Bu-P$_4$.

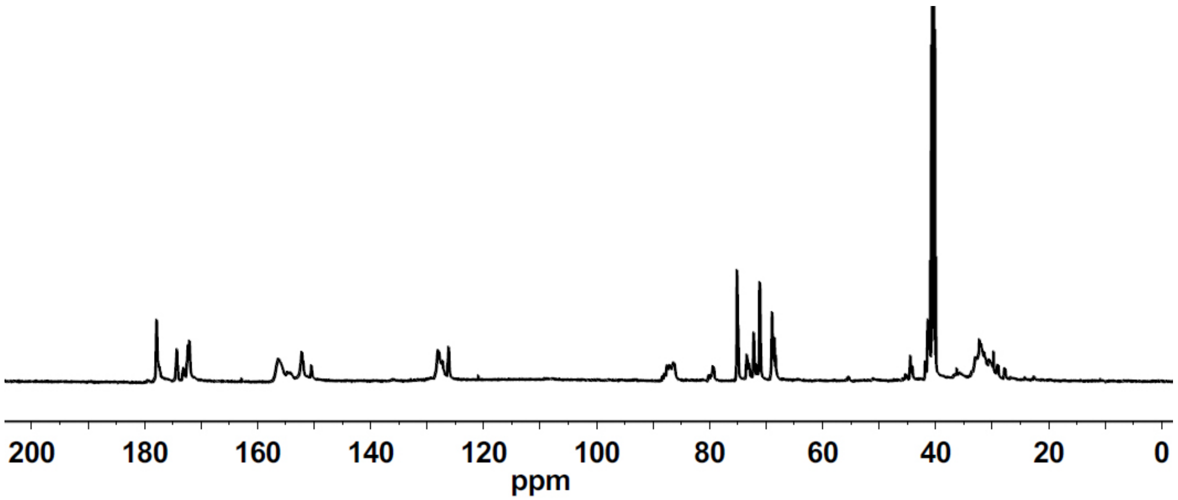

Figure S5. ^{13}C NMR (DMSO-d_6, 125 MHz, 80 °C) spectrum of the polymer produced by I^{t}Bu.

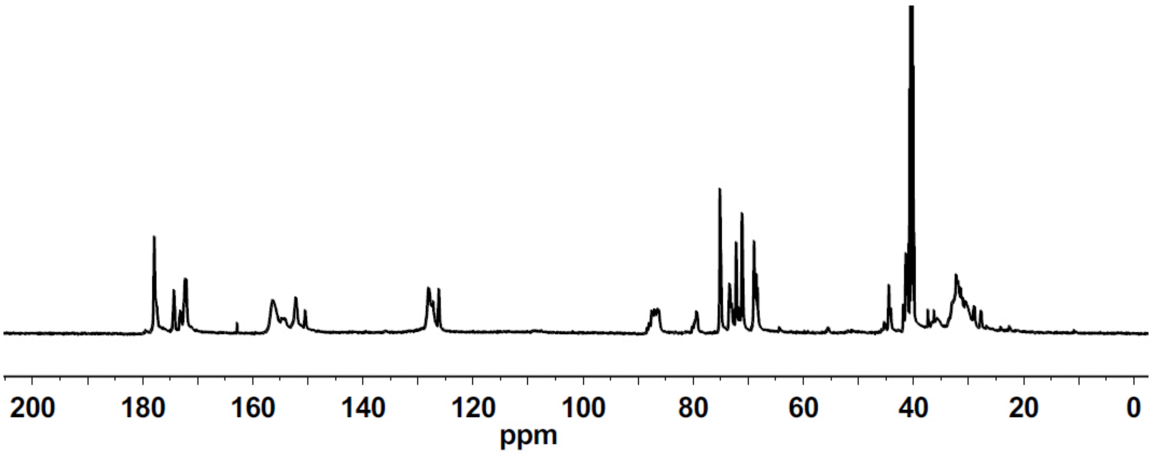

Figure S6. ^{13}C NMR (DMSO-d_6, 125 MHz, 80 °C) spectrum of the polymer produced by ^{t}Bu-P$_4$.

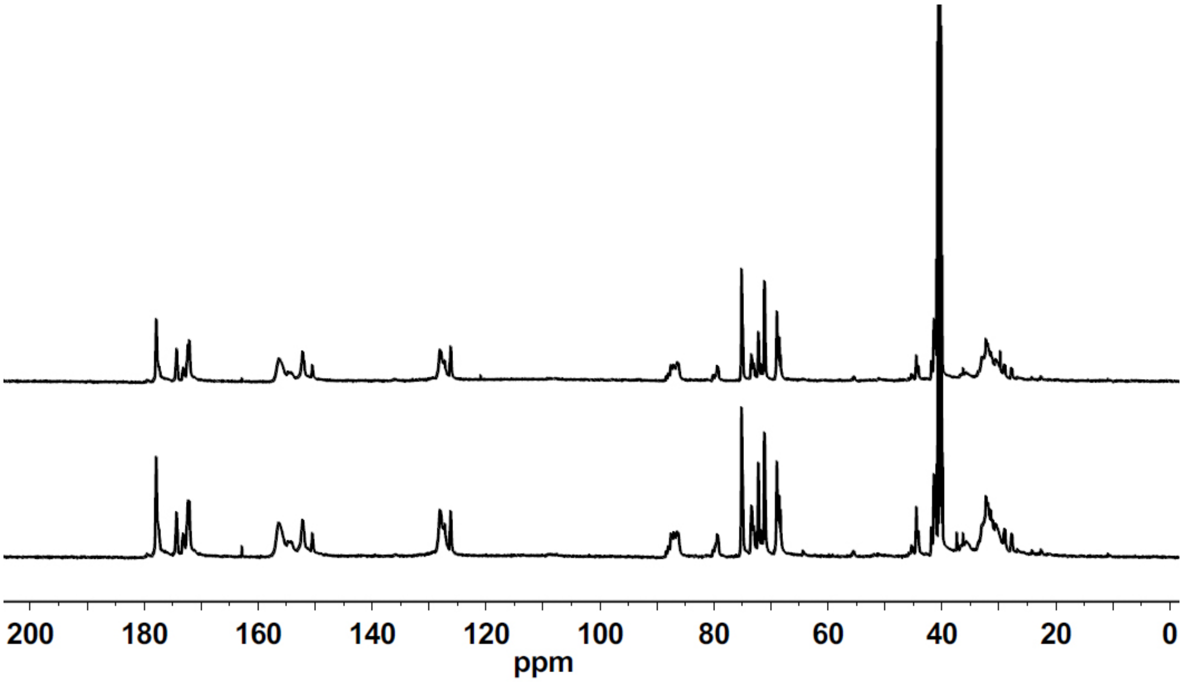

Figure S7. Overlay of ^{13}C NMR (DMSO-d_6, 125 MHz, 80 °C) spectra of the polymers produced by I^{t}Bu (top) and ^{t}Bu-P$_4$ (bottom).

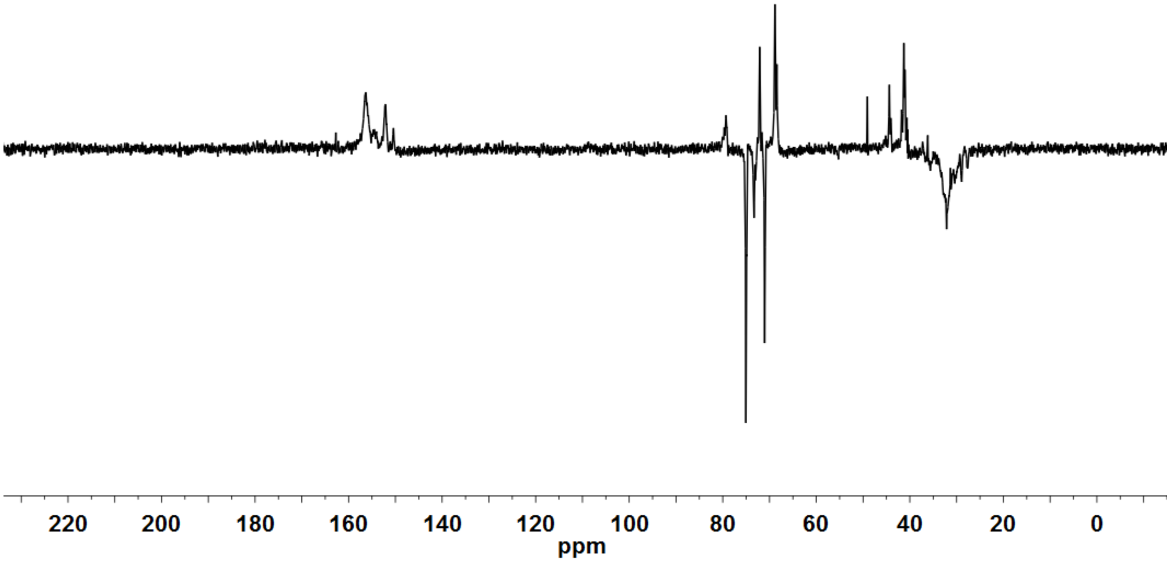

Figure S8. 135-DEPT (DMSO-d_6, 125 MHz, 80 °C) spectrum of the polymer produced by I^{t}Bu.

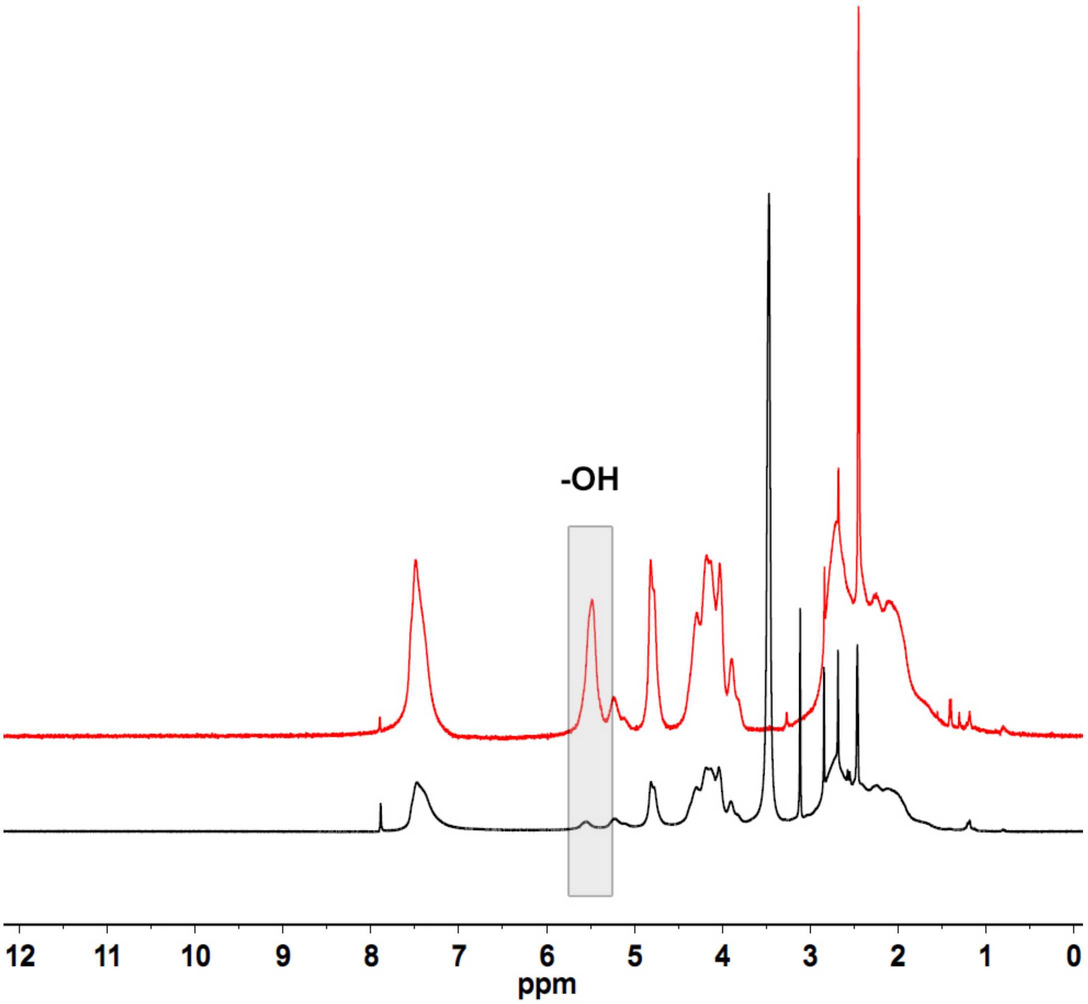

Figure S9. ^{1}H NMR (DMSO-*d*$_6$, 400 MHz, 25 °C) spectrum of the polymer produced by I^{t}Bu before (top, red) and after (bottom, black) addition of D_2O.

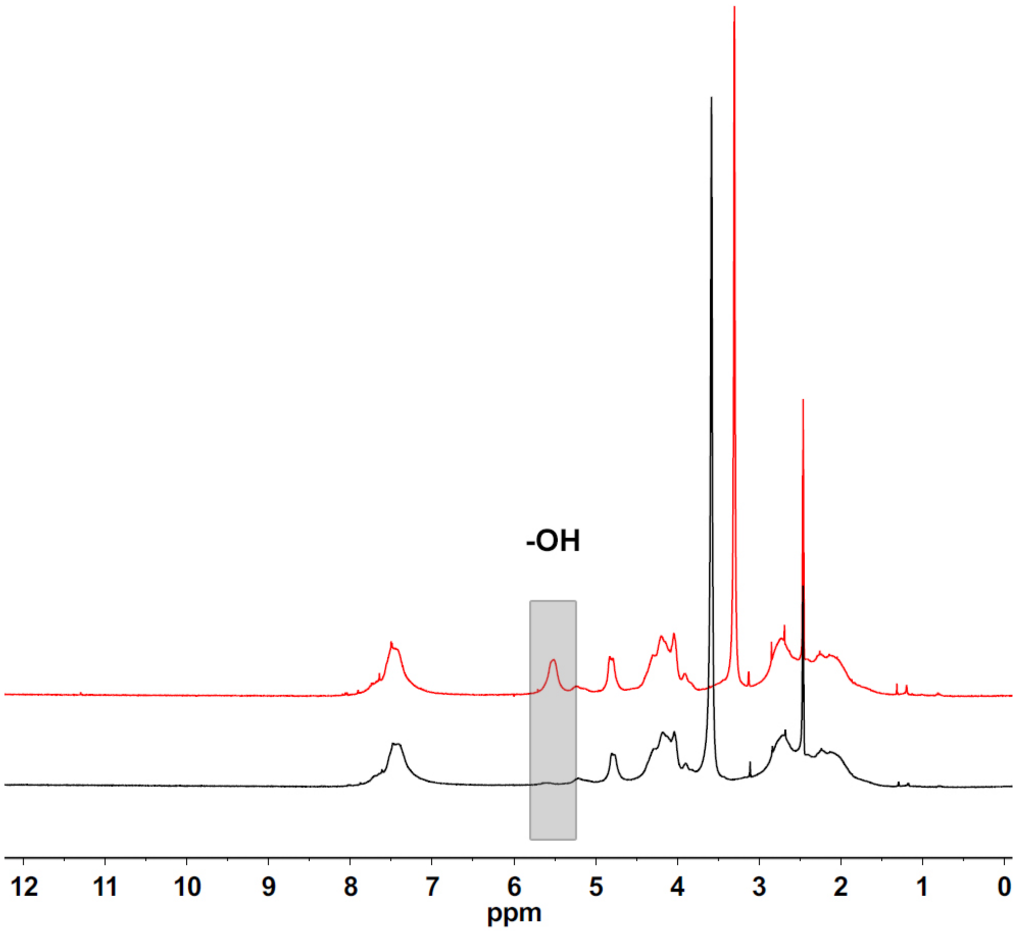

Figure S10. ^{1}H NMR (DMSO-d_6, 400 MHz, 25 °C) spectrum of the polymer produced by TPT before (top, red) and after (bottom, black) addition of D_2O.

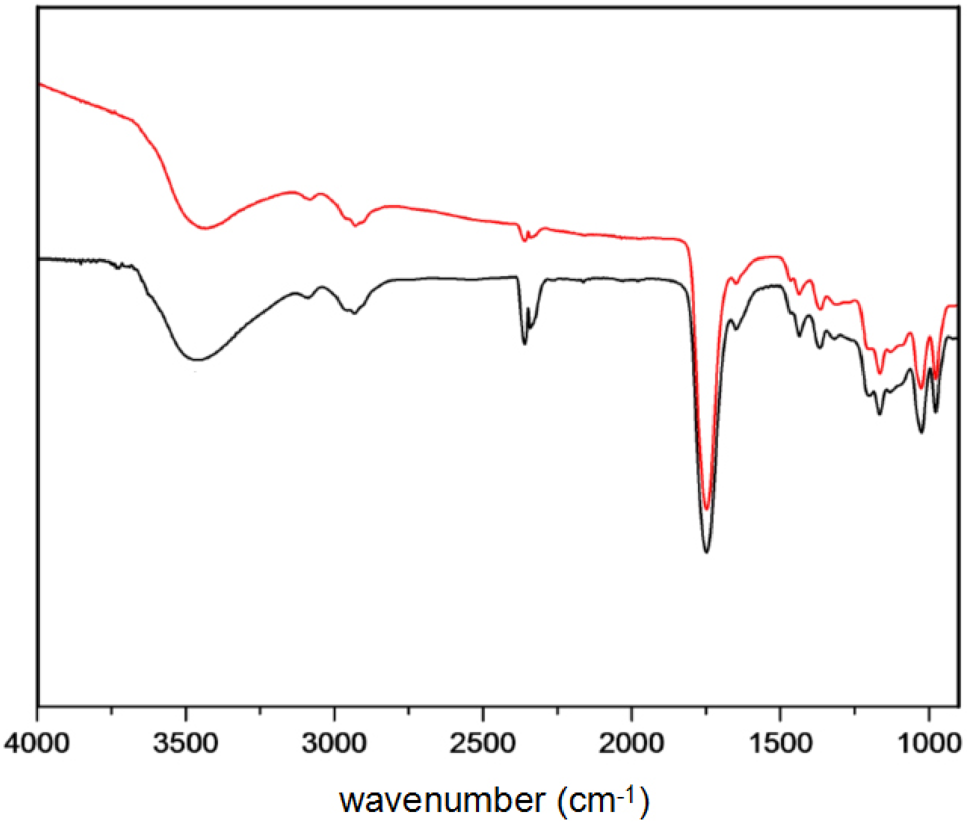

Figure S11. FT-IR spectra of the polymers produced by I^{t}Bu (red) and ^{t}Bu-P$_4$ (black).

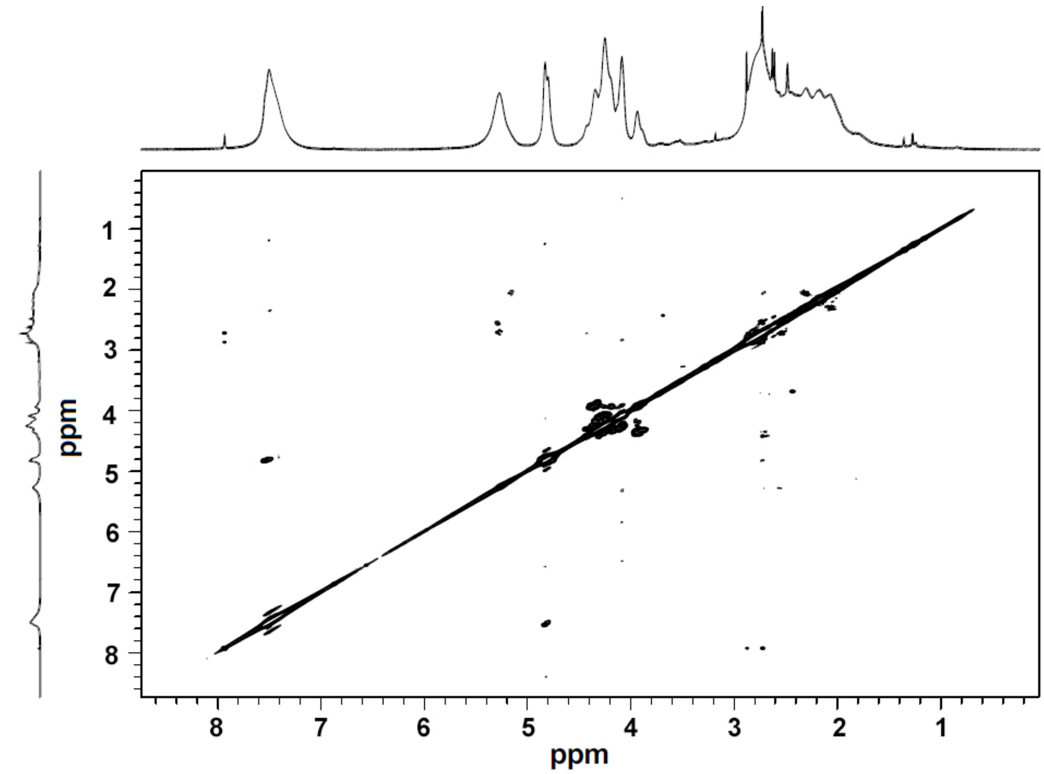

Figure S12. ^{1}H-^{1}H gCOSY (DMSO-d_6, 500 MHz, 80 °C) spectra of the polymer produced by I^{t}Bu.

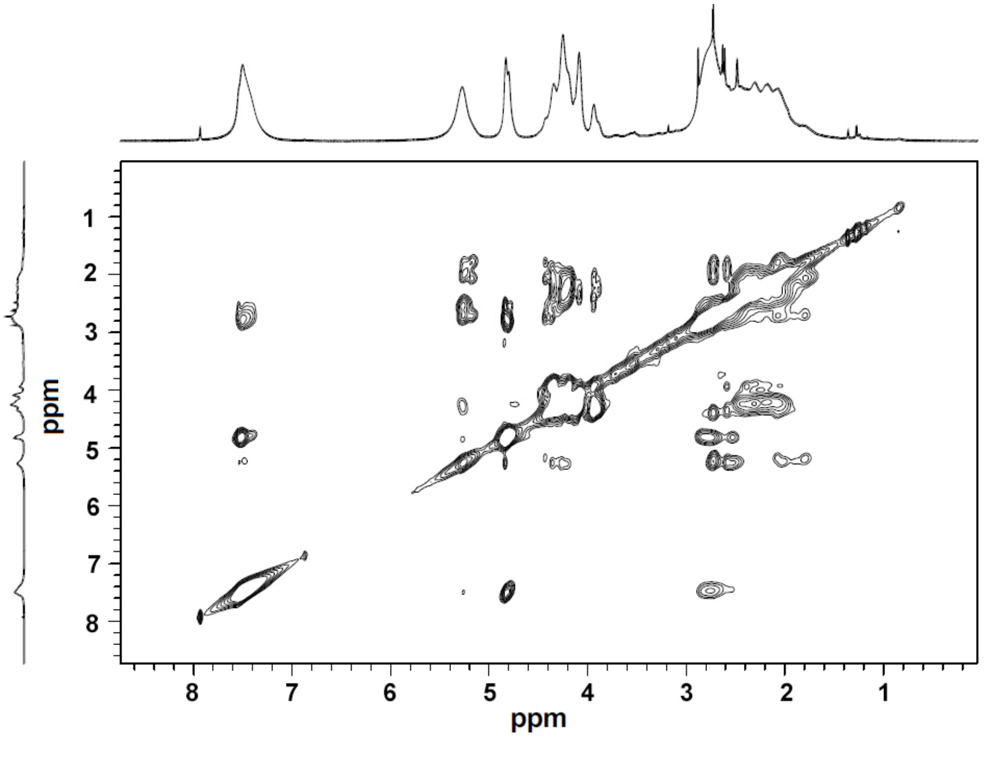

Figure S13. ^{1}H-^{1}H zTOCSY (DMSO-d_6, 500 MHz, 80 °C) spectra of the polymer produced by I^{t}Bu.

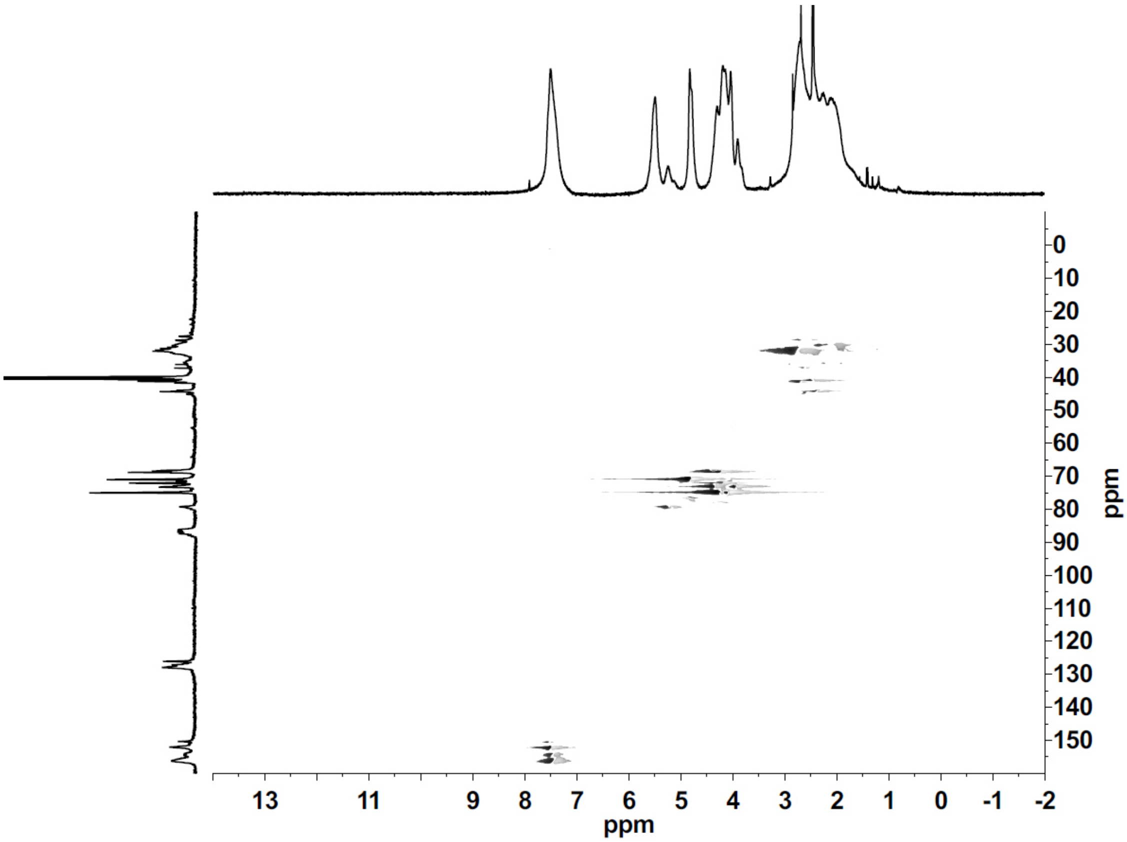

Figure S14. ^{1}H-^{13}C gHMQC (DMSO-d_6, 500 MHz, 80 °C) spectra of the polymer produced by I^{t}Bu.

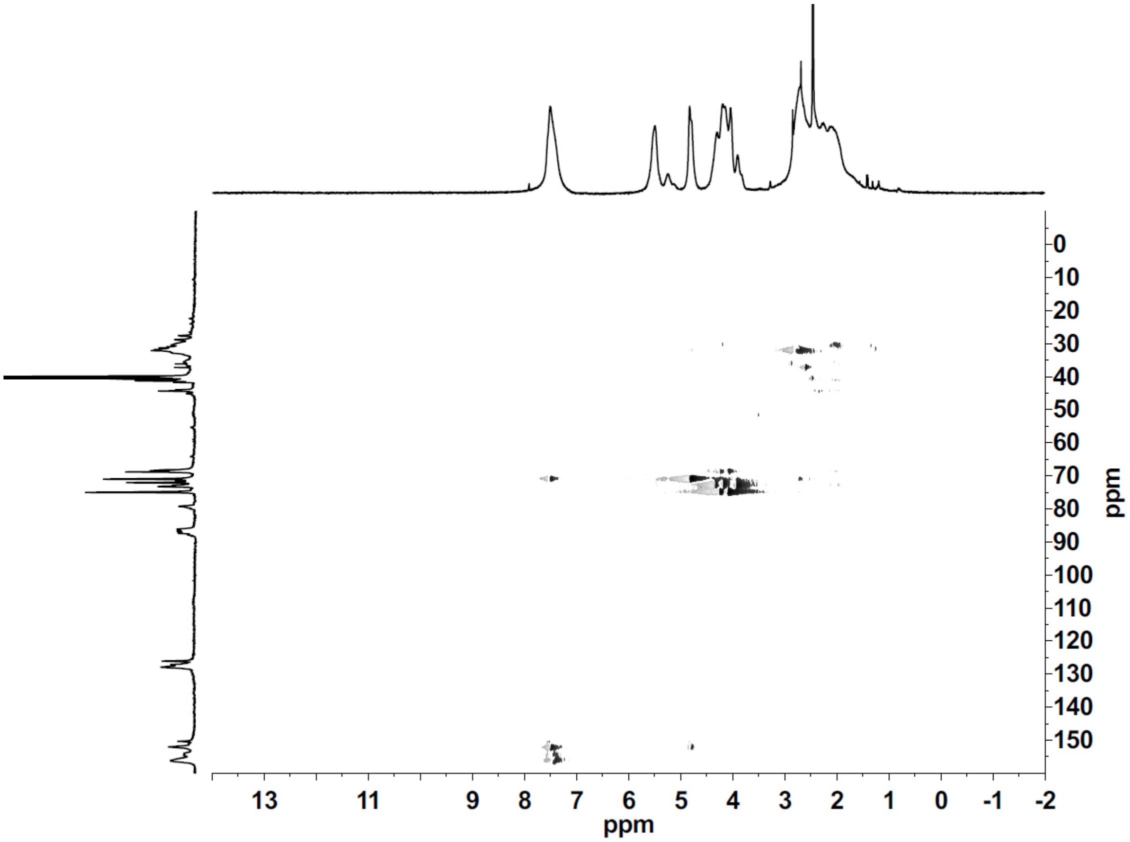

Figure S15. ^{1}H-^{13}C gHMQC-TOCSY (DMSO-d_6, 500 MHz, 80 °C) spectra of the polymer produced by I^{t}Bu.

References

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(1) (a) Enders, D.; Breuer, K.; Raabe, G.; Runsink, J.; Teles, J. H.; Melder, J. P.; Ebel, K.; Brode, S. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1021−1023. (b) Enders, D.; Breuer, K.; Kallfass, U.; Balensiefer, T. *Synthesis* **2003**, 1292–1295.

(2) Mendgen, T.; Scholz, T.; Klein, C. D. *Bioorg. Med. Chem. Lett.* **2010**, *20*, 5757–5762.