

**Supporting Information for:**

**Thioanhydride/Isothiocyanate/Epoxide Ring Opening Terpolymerisation:  
Sequence selective enchainment of monomer mixtures and switchable  
catalysis**

**Dorothee Silbernagl,<sup>a</sup> Heinz Sturm,<sup>a</sup> Alex J. Plajer<sup>b,\*</sup>**

<sup>a</sup> BAM Bundesanstalt für Materialforschung und -Prüfung, Unter den Eichen 87, 12205 Berlin

<sup>b</sup> Institut für Chemie und Biochemie, Freie Universität Berlin, Fabeckstraße 34-36, 14195 Berlin; \*email:  
plajer@zedat.fu-berlin.de

## Table of contents

Section S1: Methods .....	3
Section S2: ROTERP procedure and details .....	4
Section S3: Polymer characterisation data corresponding to Table 1 .....	5
Section S4: $\epsilon$ DL ROP to PhNCS/PTA/BO ROTERP switch protocol.....	16

## Section S1: Methods

Solvents and reagents were obtained from commercial sources and used as received unless stated otherwise. If “dried solvents” were used these were obtained by different procedures. Toluene, EtOH, *n*-hexane, *n*-pentane and CH<sub>2</sub>Cl<sub>2</sub> were prepared by using an MBraun Solvent Purification System MB-SPS 800 filled with Al<sub>2</sub>O<sub>3</sub>. Et<sub>2</sub>O was dried over Na/benzophenone and THF was dried over K/benzophenone under argon. The CDCl<sub>3</sub> was dried over CaH<sub>2</sub> and d<sub>8</sub>-THF over sodium prior to vacuum transfer onto 4 Å sieves followed by three freeze pump thaw degassing cycles. <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and <sup>7</sup>Li NMR spectra were recorded by using a Jeol JNM-ECA 400II, Bruker Advance 600 and 700 MHz spectrometer. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} chemical shifts are referenced to the residual proton resonance of the deuterated solvents.

Epoxides, PhNCS, CS<sub>2</sub> and ε-DL were dried over calcium hydride at room temperature for 3 days, vacuum transferred (for ε-DL fractionally distilled under static vacuum) followed by three freeze pump thaw degassing cycles and stored inside an argon filled glovebox prior to use. Phtalic thioanhydride was synthesized according to the literature procedure and then purified by recrystallisation from <sup>t</sup>BuOMe followed by recrystallisation from CHCl<sub>3</sub> and two sublimation under dynamic vacuum at 90°C and was stored inside an argon filled glovebox prior to use.<sup>[1]</sup>

UV-visible spectra were collected on a Varian Cary 50 UV spectrometer.

Infrared spectra were measured using a Thermo-Nicolet Nexus 670 FTIR spectrometer with DuraSample IR accessory in total reflection at room temperature.

The molecular weight and polydispersity of the polymers were determined by a Waters 1515 gel permeation chromatography (GPC) instrument equipped with two linear PLgel columns (Mixed-C) following a guard column and a differential refractive index detector using tetrahydrofuran as the eluent at a flow rate of 1.0 mL/min at 30 °C and a series of narrow polystyrene standards for the calibration of the columns. Each polymer sample was dissolved in HPLC-grade THF (6 mg/mL) and filtered through a 0.20 µm porous filter frit prior to analysis.

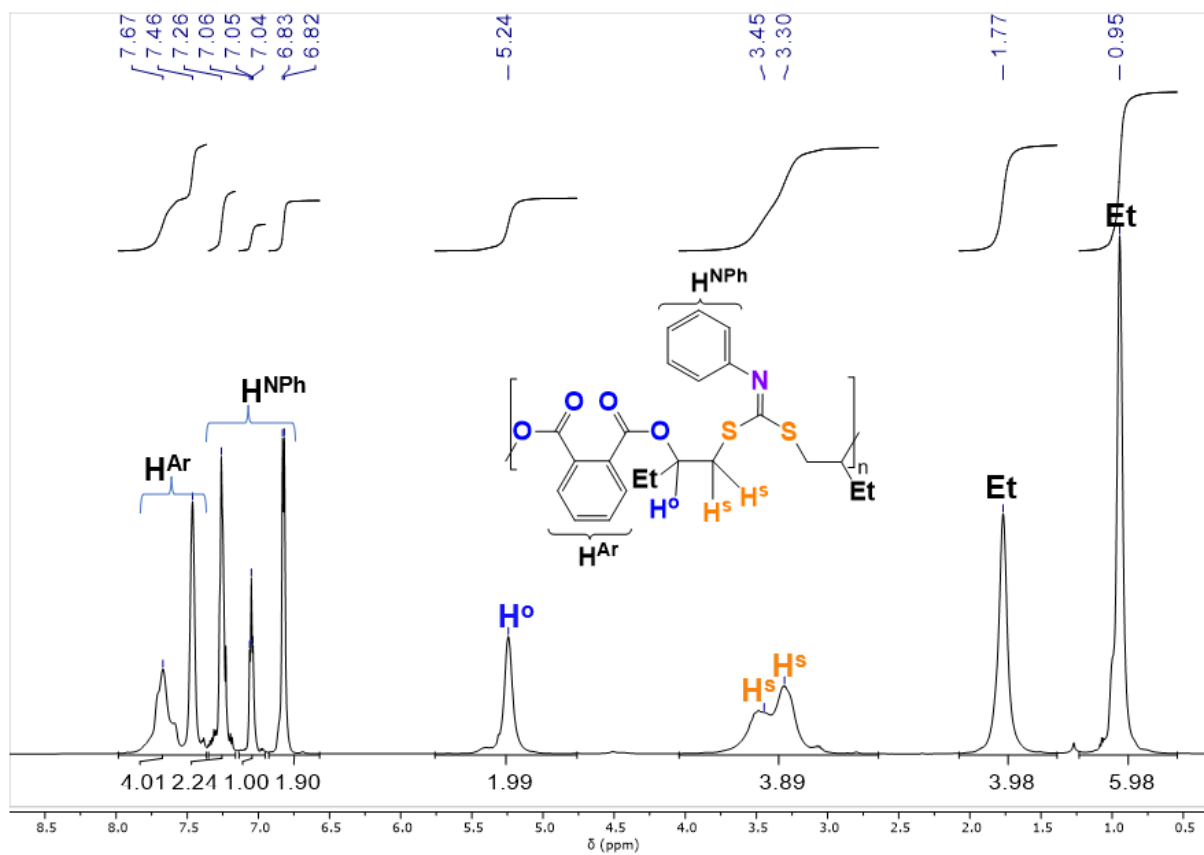
Polymer films for atomic force microscopy (AFM) were spun from a Vacuum Spin Coater (SCE 150). 50 µL of polymers in CH<sub>2</sub>Cl<sub>2</sub> (20 mg/mL) was dropped onto a silicon slice and the speed of the spin coater was then raised to 3000 r/min lasting for 1 min.

AFM measurements were performed with a MFP-3D Asylum instrument (Oxford Instruments Asylum Research Inc., Santa Barbara, CA, USA). Tapping mode images were done with a Pointprobe-Plus PPP-NCHR (Nanoworld AG, Neuchatel, Switzerland) with a resonance frequency of 319kHz and a spring constant of appr. 40N/m.

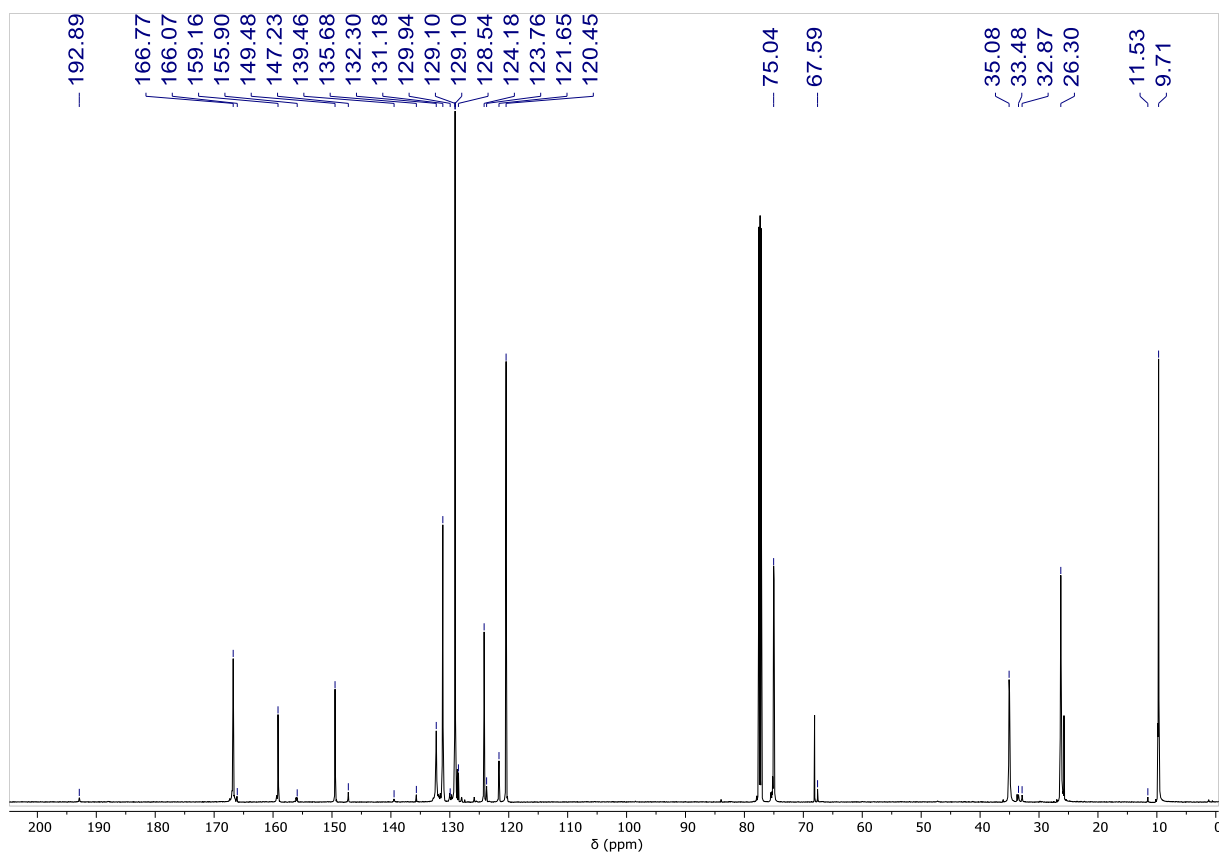
## Section S2: ROTERP procedure and details

**Terpolymerization protocol:** In an argon-filled glovebox, LiHMDS and BnOH was dissolved in butylene oxide and the mixture was transferred to a flame dried vial equipped with a flame dried stirrer bar and sealed with a melamine cap containing a Teflon inlay. PhNCS and PTA were then added and the vial was brought outside the glovebox and placed in a pre-heated oil bath at 80°C for the specified time. In cases where the reaction progress was monitored, the vial was rapidly cooled to room temperature with a dry ice cooling bath and brought inside an argon-filled glovebox before the aliquot was removed. At the specified end point of the reaction, the polymer was isolated by adding the polymerisation mixture to 200 mL of acidified MeOH (20  $\mu$ L concentrated HCl per 200 mL MeOH) resulting in the precipitation of the yellow product. After two further precipitations from DCM/MeOH and THF/pentane, the polymer was isolated by filtration and dried in a vacuum oven set to 60 °C.

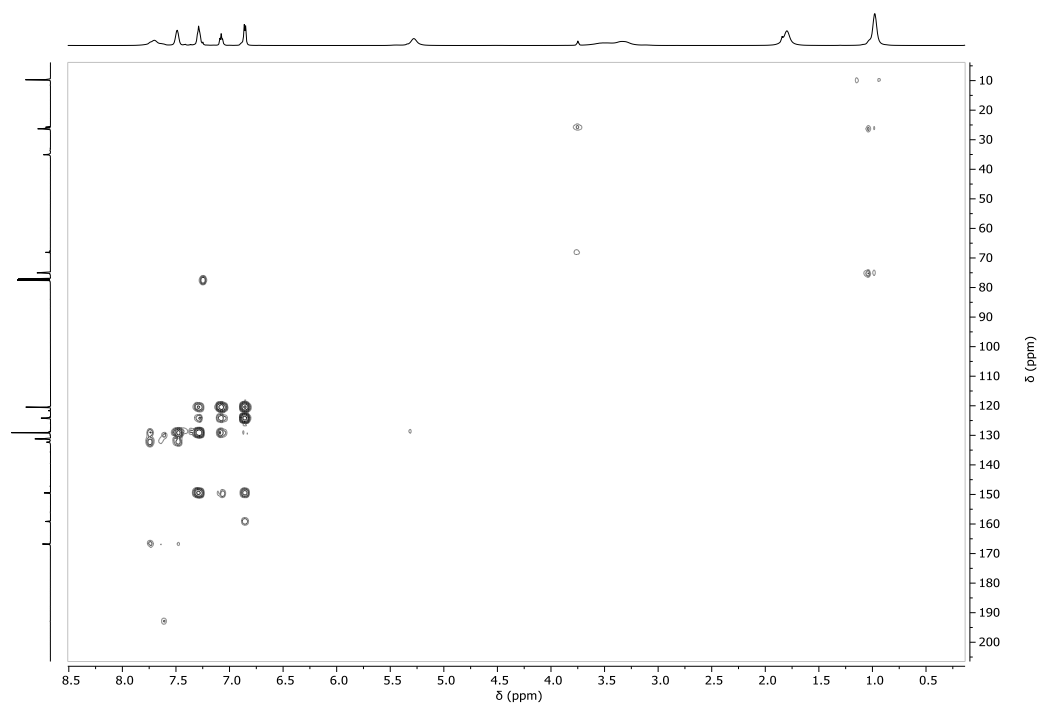
### Section S3: Polymer characterisation data corresponding to Table 1



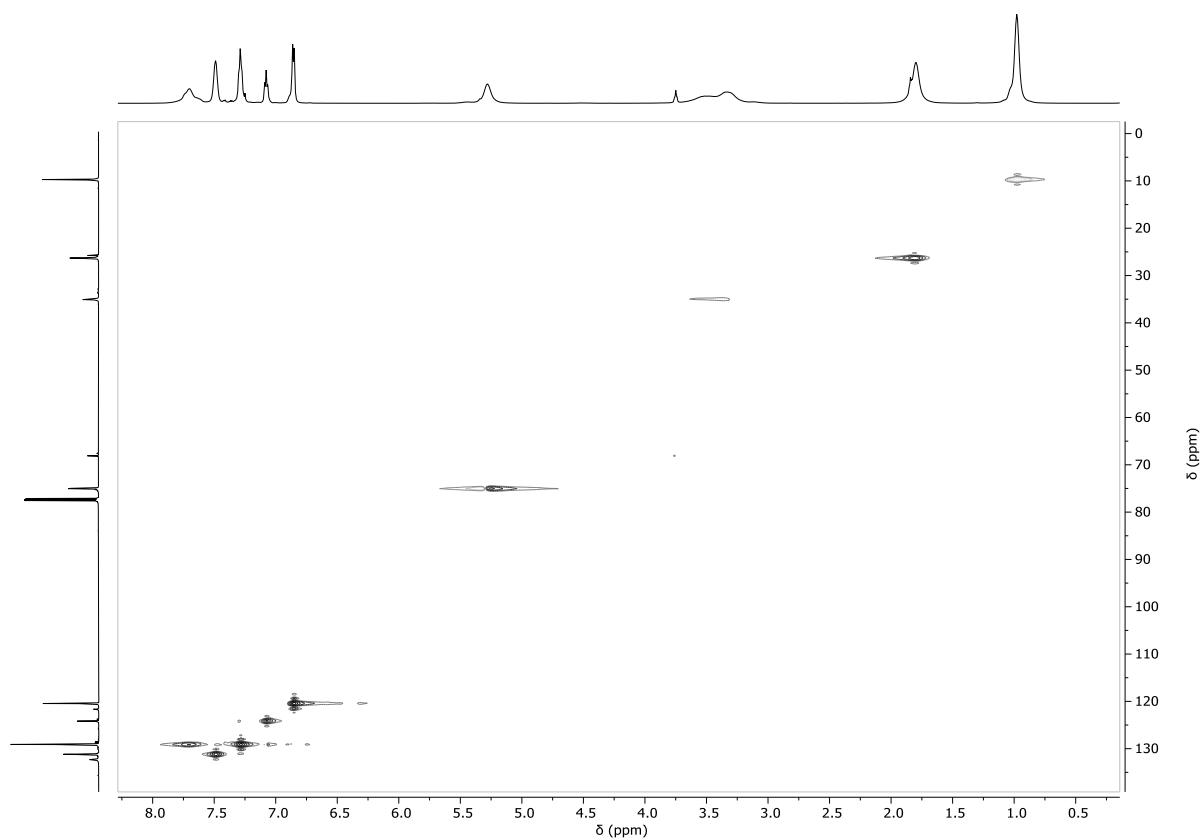
**Figure S 1:** <sup>1</sup>H NMR spectrum (500 MHz, CDCl<sub>3</sub>, 25°C) of terpolymer corresponding to table 1, run #4.



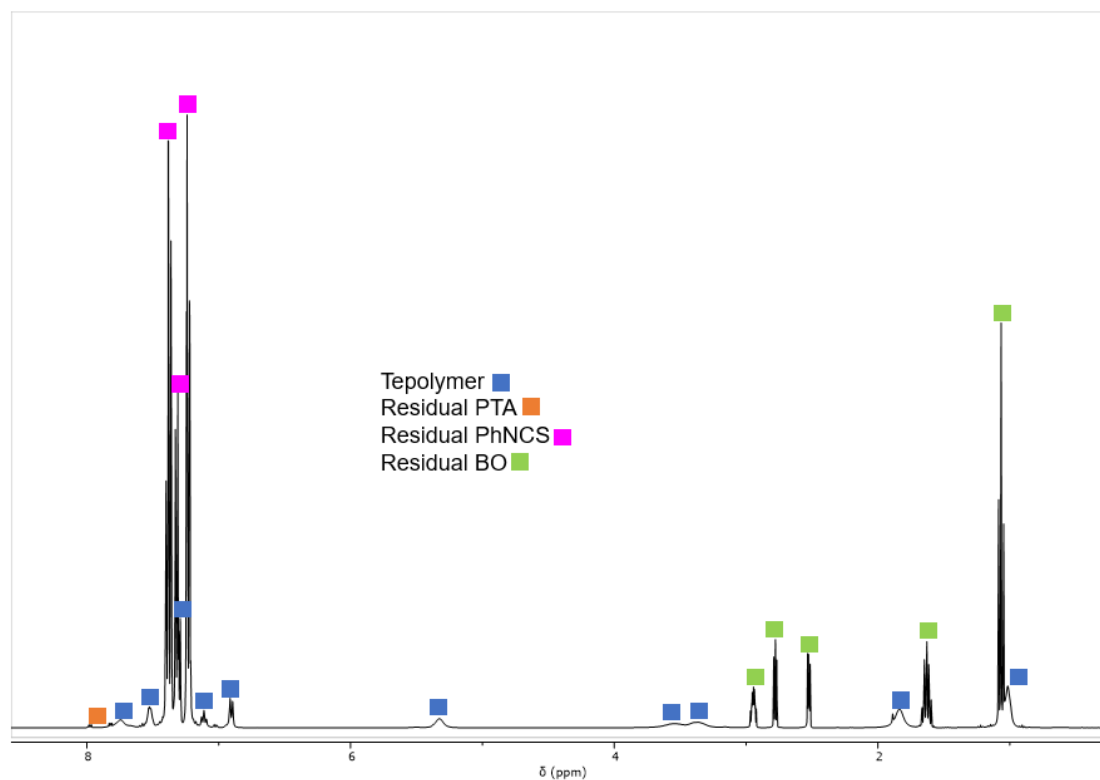
**Figure S 2:**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (126 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of terpolymer corresponding to table 1, run #4. Residual THF at 25.6 and 67.8 ppm.



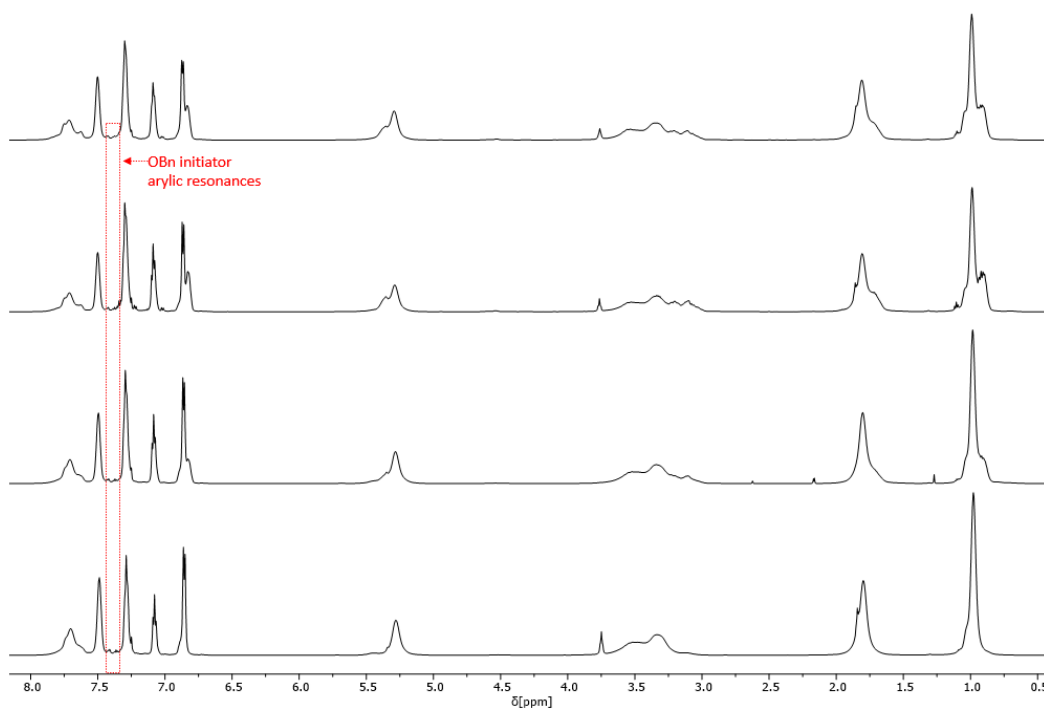
**Figure S 3:**  $^1\text{H} - ^{13}\text{C}$  HMBC NMR spectrum ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of terpolymer corresponding to table 1, run #4. Residual THF at 25.6 and 67.8 ppm.



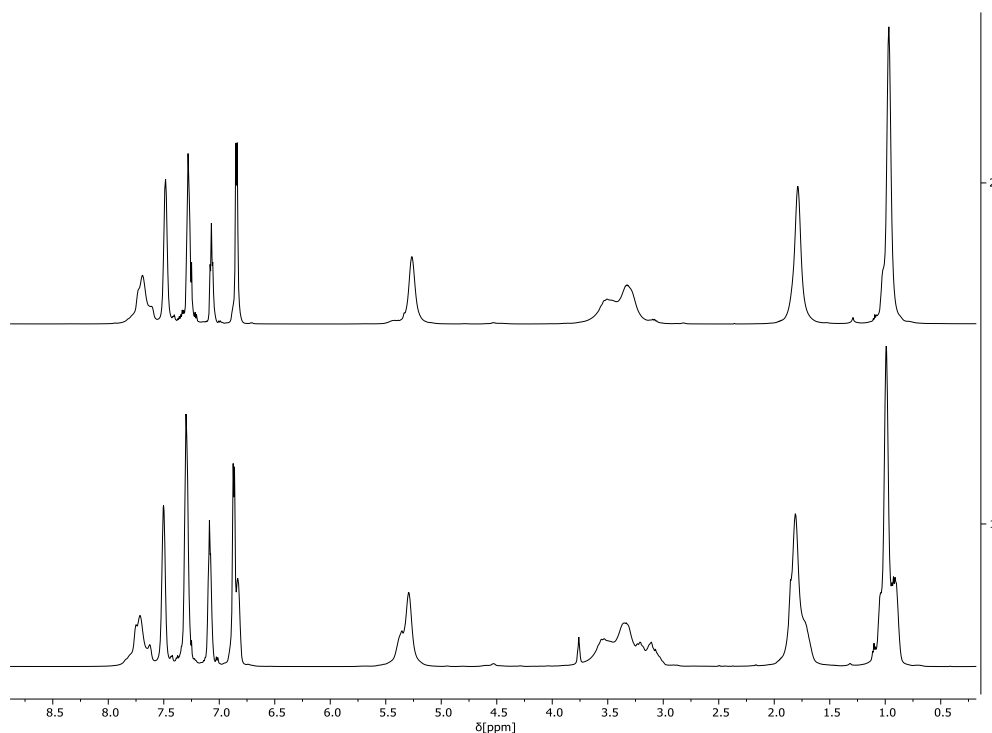
**Figure S 4:**  $^1\text{H} - ^{13}\text{C}$  HSQC NMR spectrum ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of terpolymer corresponding to table 1, run #4.



**Figure S4b:**  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ , 400 MHz) of crude reaction mixture corresponding to table 1, run #4.

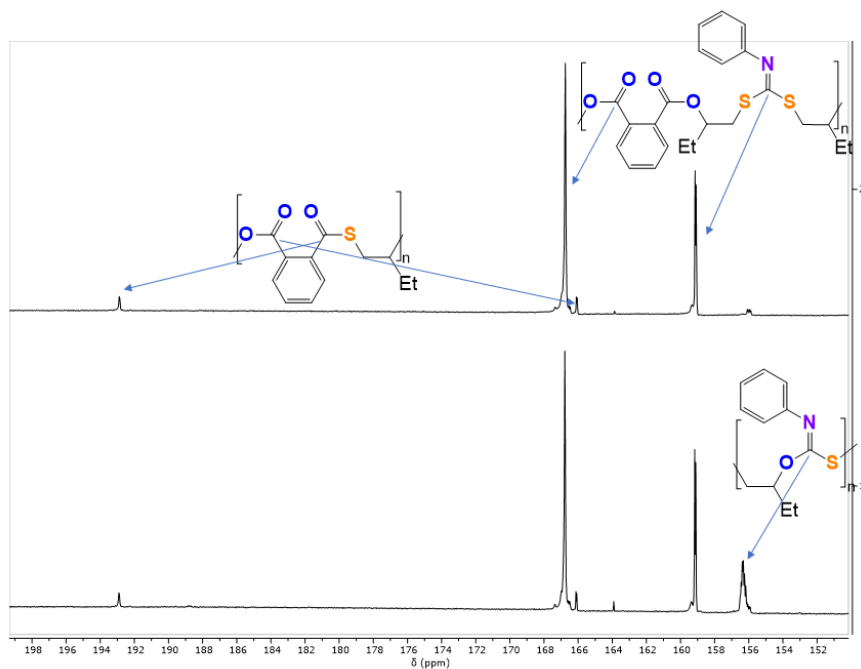


**Figure S 5:** Overlaid  $^1\text{H}$  NMR spectra (500 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of terpolymer corresponding (from top to bottom) to table 1, run #6, #7, #8, #4. Residual THF at 1.72 and 3.58 ppm.

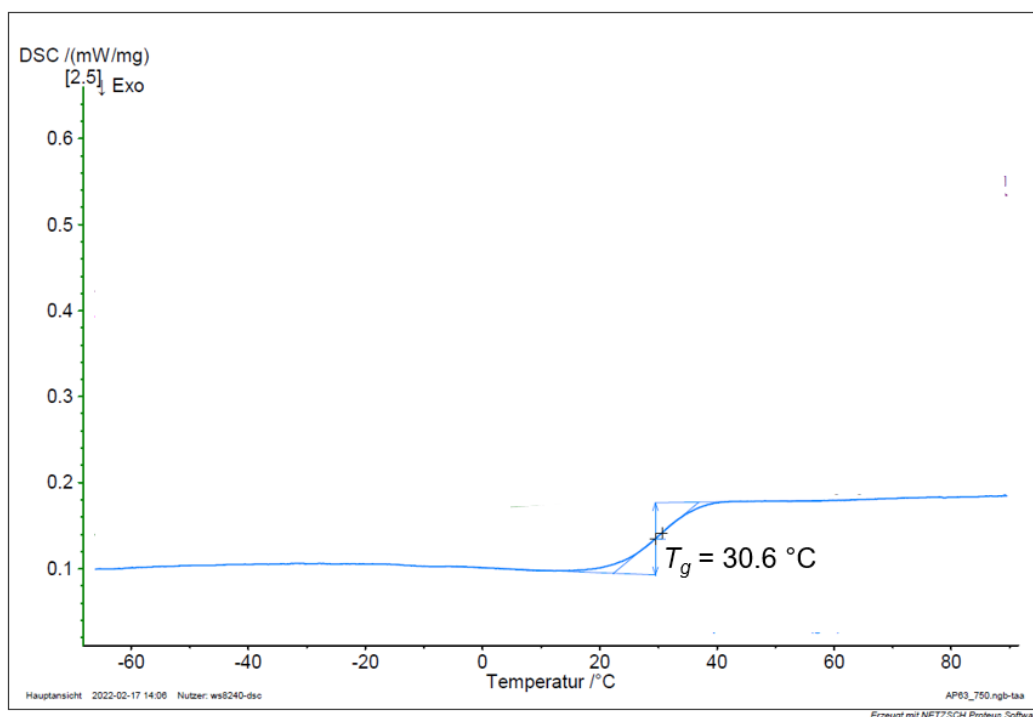


**Figure S 6:** Overlaid  $^1\text{H}$  NMR spectra (500 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of terpolymer corresponding to table 1, run #7 (top) before full PTA consumption and (bottom) at the end of reaction. Residual THF at 1.72 and 3.58 ppm.

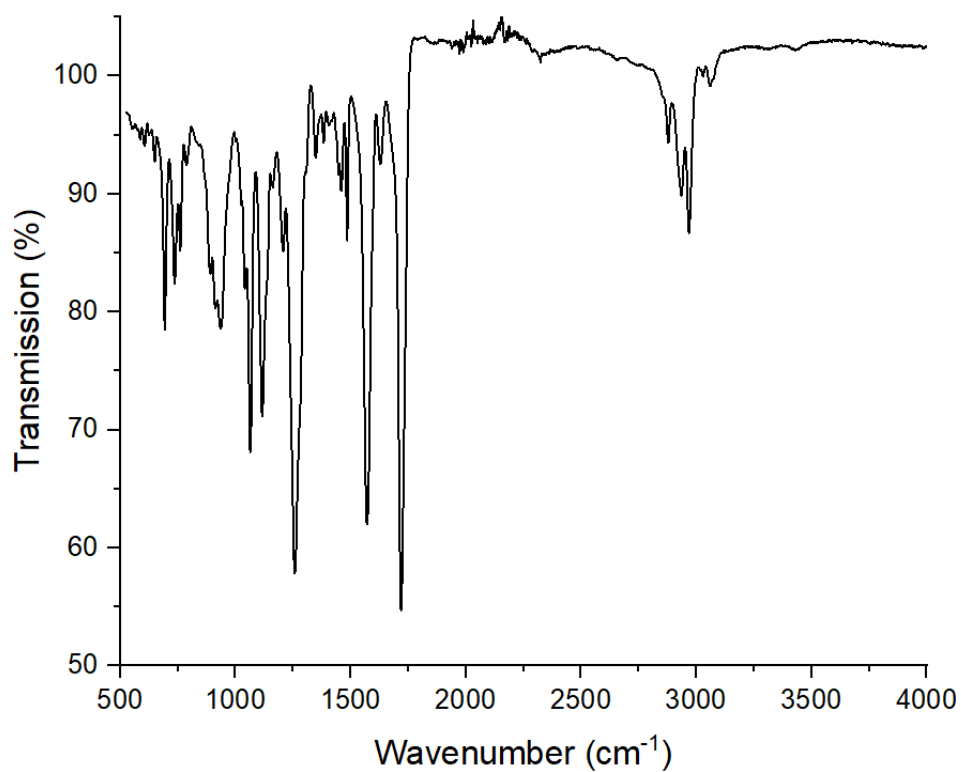




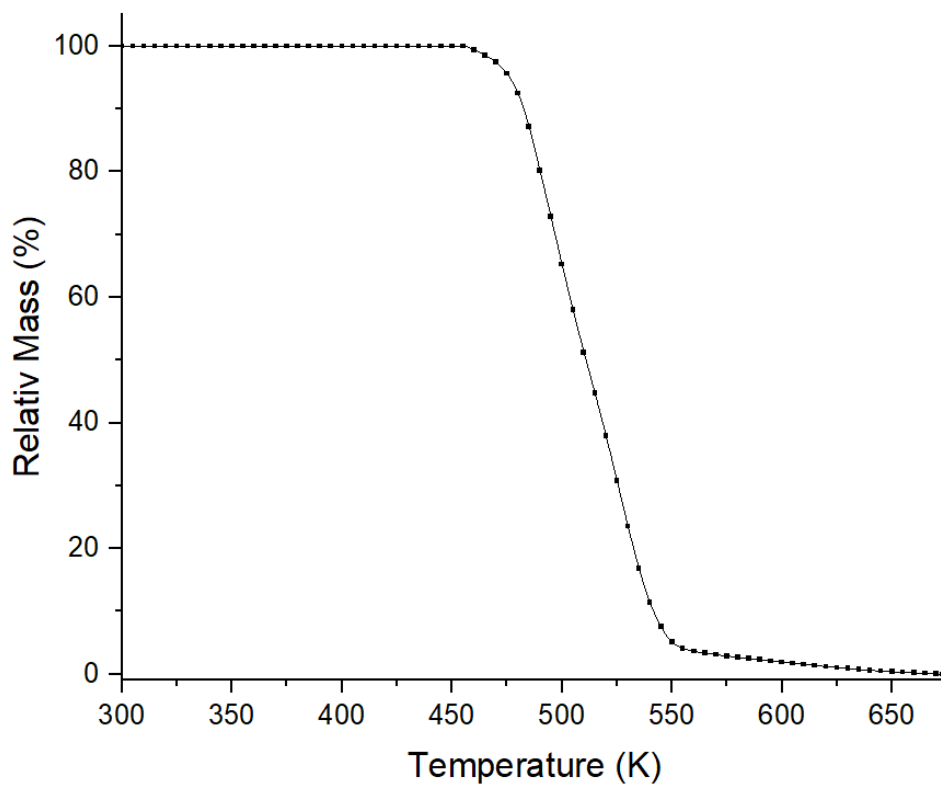
**Figure S 7:** Overlaid  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra (126 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of terpolymer corresponding to table 1, run #7 (top) before full PTA consumption and (bottom) at the end of reaction.



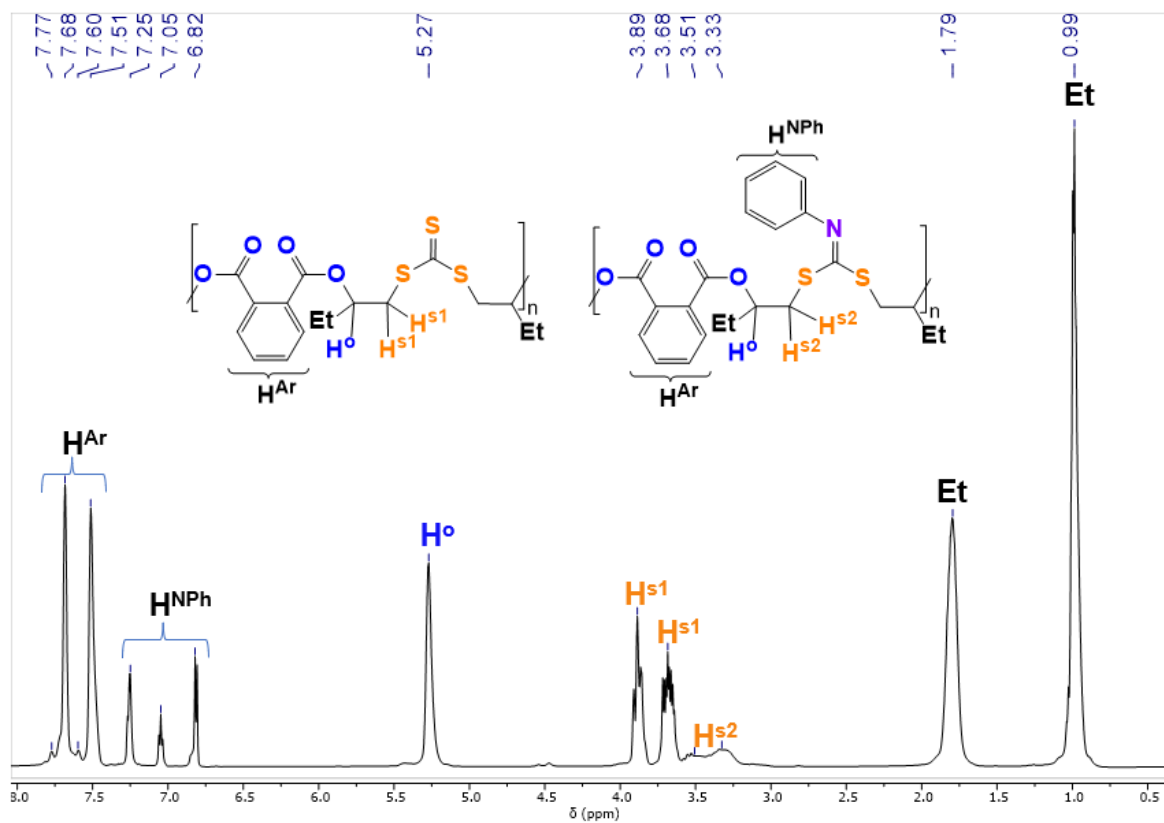
**Figure S 8:** DSC heating curve of terpolymer corresponding to table 1, run #4.



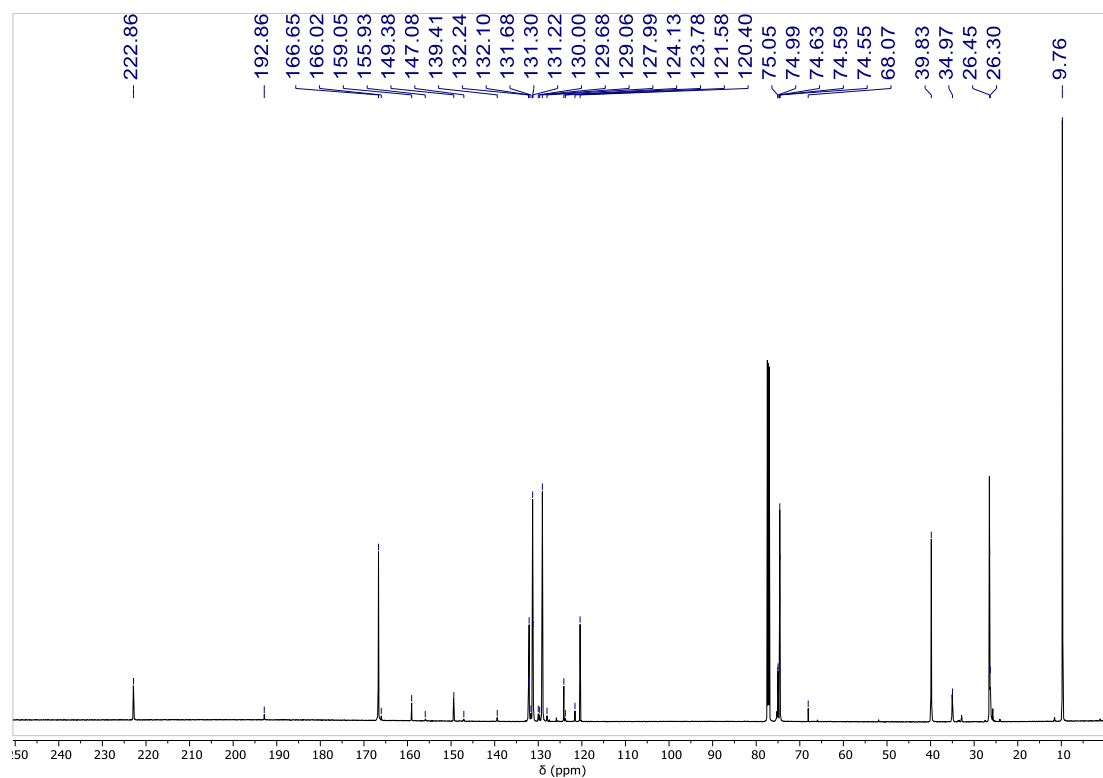
**Figure S 9:** FT ATR IR Spectrum of terpolymer corresponding to table 1, run #4.



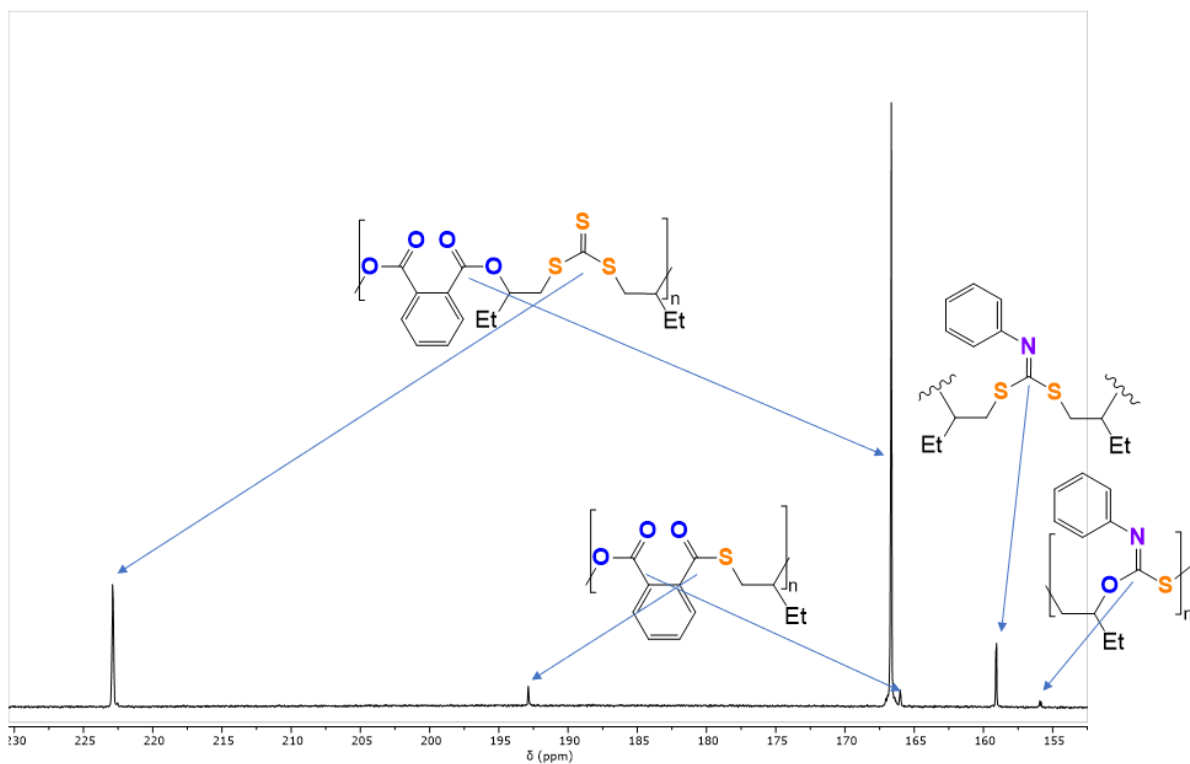
**Figure S 10:** TGA of terpolymer corresponding to table 1, run #4.



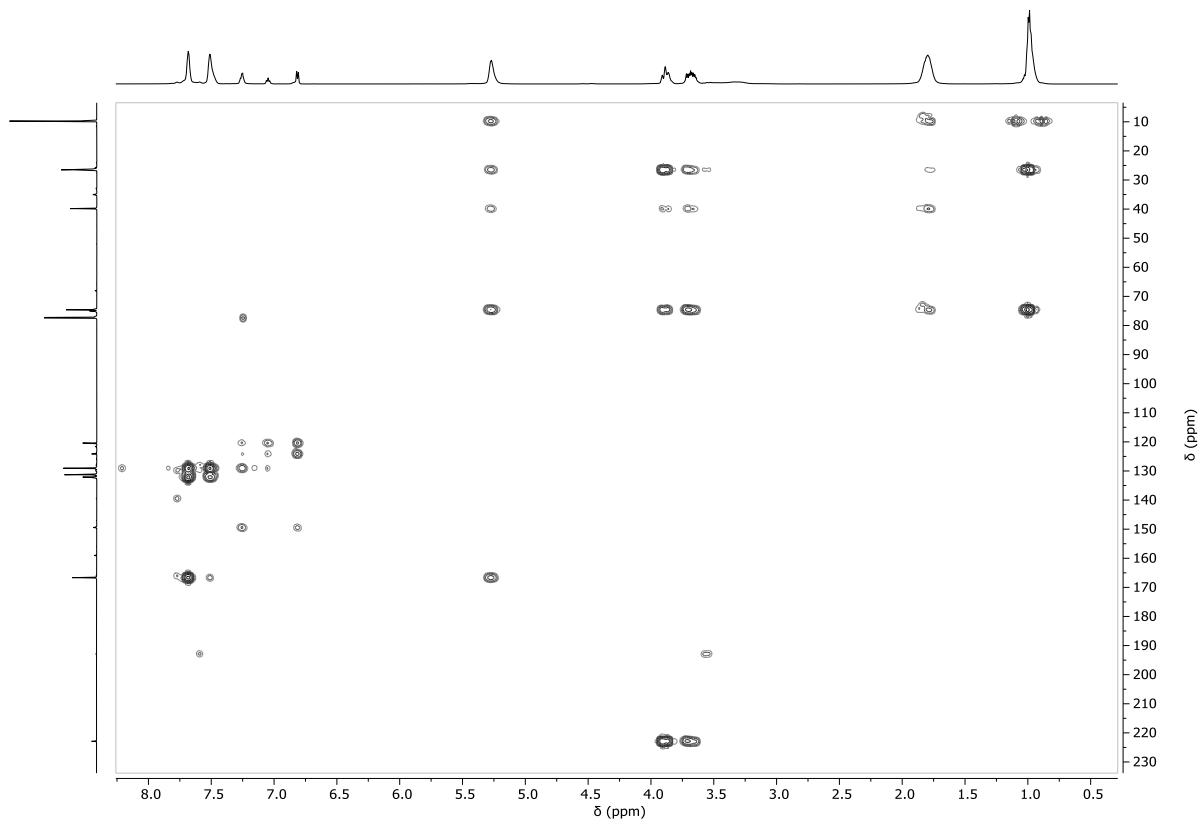
**Figure S 11:** <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>, 25°C) of terpolymer corresponding to table 1, run #11.



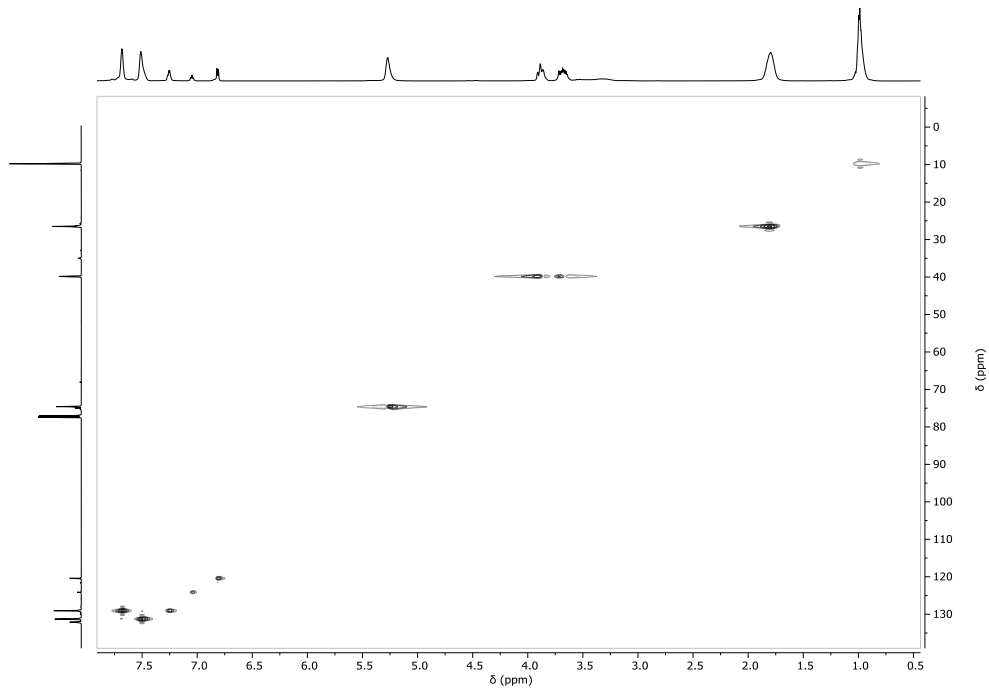
**Figure S 12:** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (126 MHz, CDCl<sub>3</sub>, 25°C) of terpolymer corresponding to table 1, run #11.



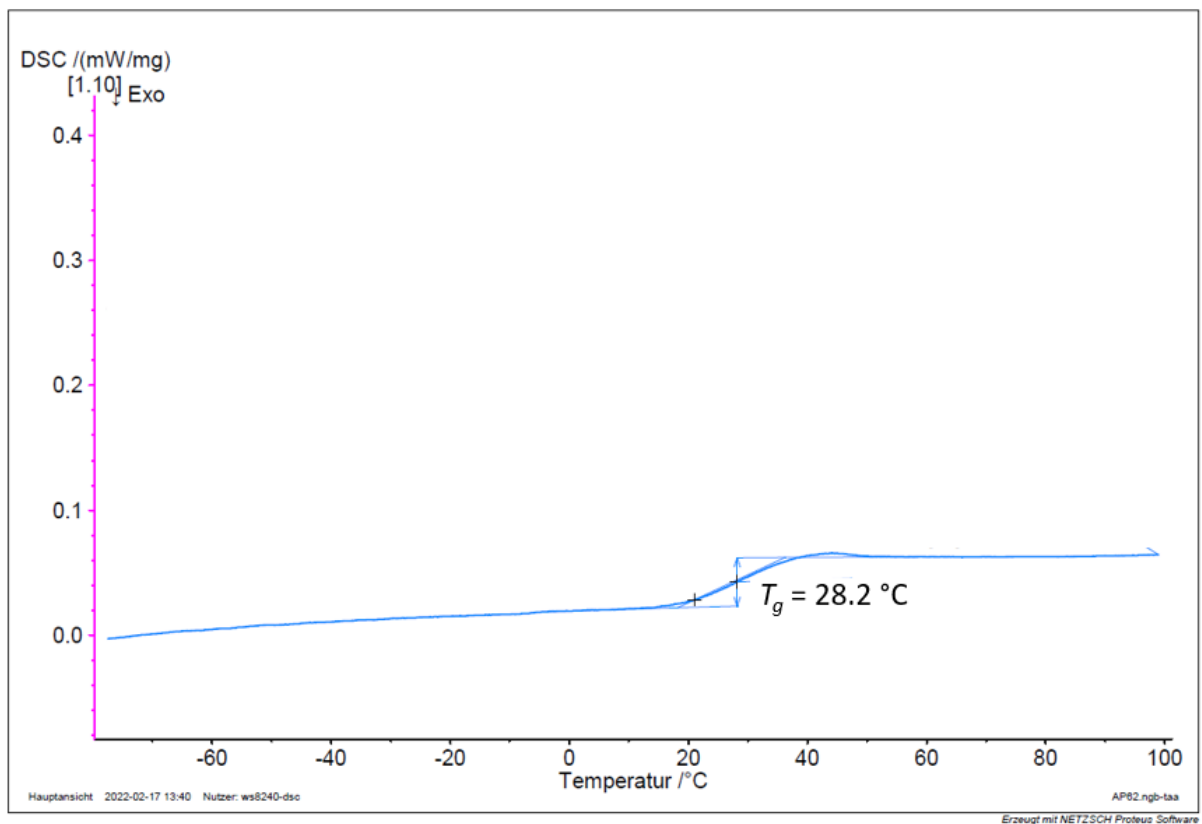
**Figure S 13:** Zoom into carbonyl region of the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (126 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of terpolymer corresponding to table 1, run #11.



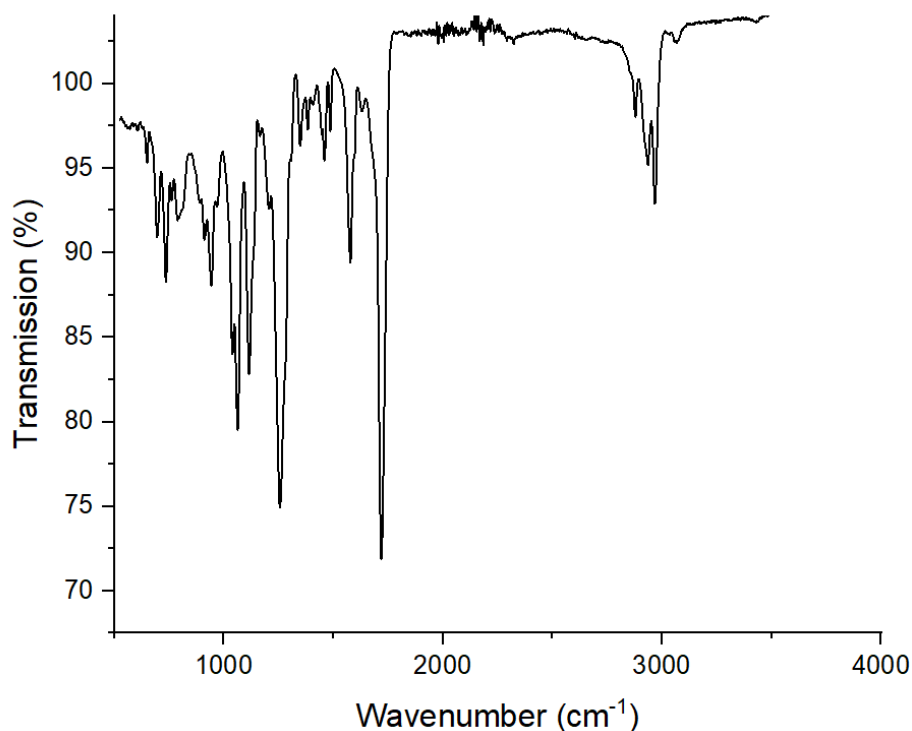
**Figure S 14:**  $^1\text{H} - ^{13}\text{C}$  HMBC NMR spectrum ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of terpolymer corresponding to table 1, run #11.



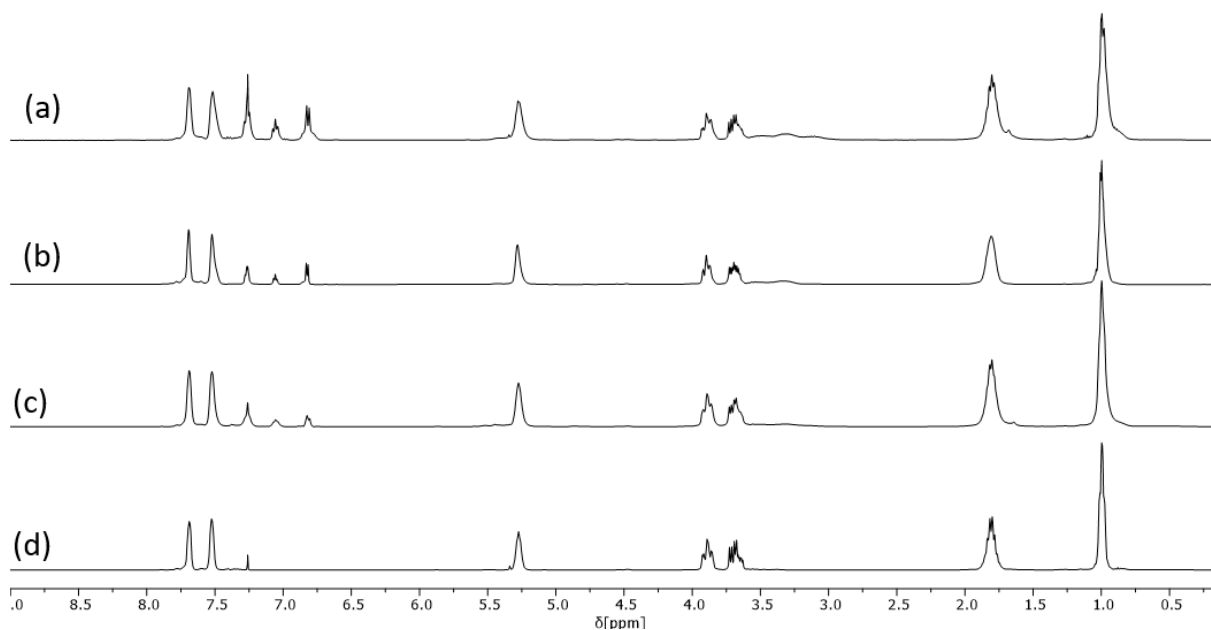
**Figure S 15:**  $^1\text{H} - ^{13}\text{C}$  HSQC NMR spectrum ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of terpolymer corresponding to table 1, run #11.



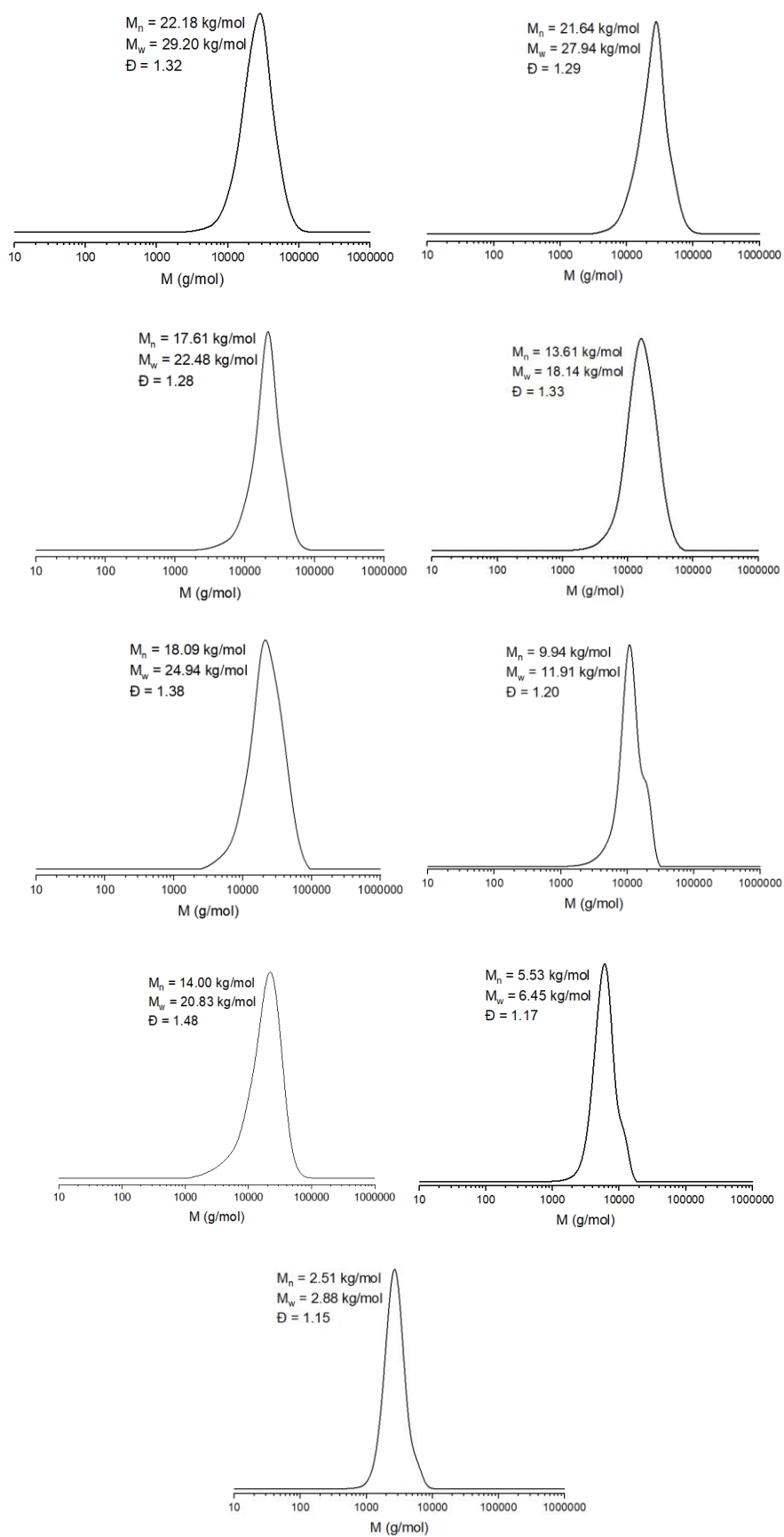
**Figure S 16:** DSC heating curve of terpolymer corresponding to table 1, run #9.



**Figure S 17:** FT ATRIR Spectrum of terpolymer corresponding to table 1, run 9.

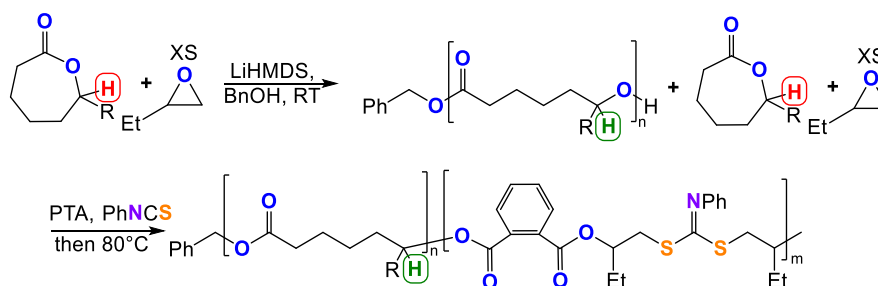


**Figure S 18:** Overlaid  $^1\text{H}$  NMR spectra (400 MHz,  $\text{CDCl}_3$ , 25 °C) of tetrapolymers obtain from 1 eq. LiOBn : 50 eq. PTA : 250 eq. BO : X eq.  $\text{CS}_2$  : Y eq. PhNCS. (a) X = 250, Y = 500; (b) X = 375, Y = 375; (c) X = 500, Y = 250; (d) X = 750, Y = 0. Heteroallene Incorporation during ROTERP by integration of the  $^1\text{H}$  NMR spectra: (a) 66%  $\text{CS}_2$ , 33 % PhNCS (heteroallene loading was 33%  $\text{CS}_2$  and 66% PhNCS); (b) 77%  $\text{CS}_2$ , 23% PhNCS (heteroallene loading was 50%  $\text{CS}_2$  and 50% PhNCS); (c) 84 %  $\text{CS}_2$ , 16 % PhNCS heteroallene loading was 66%  $\text{CS}_2$  and 16% PhNCS). In the case of (a), PhNCS/BO ROCOP after complete PTA consumption is inferred to cause monothiocarbonate links.



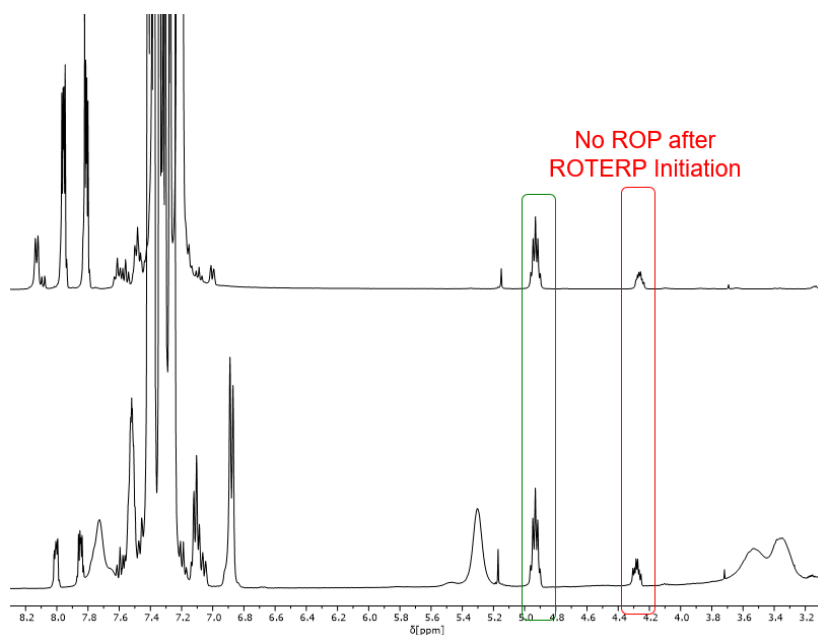
**Figure S 19:** GPC traces of Polymers reported in this study

## Section S4: $\epsilon$ DL ROP to PhNCS/PTA/BO ROTERP switch protocol



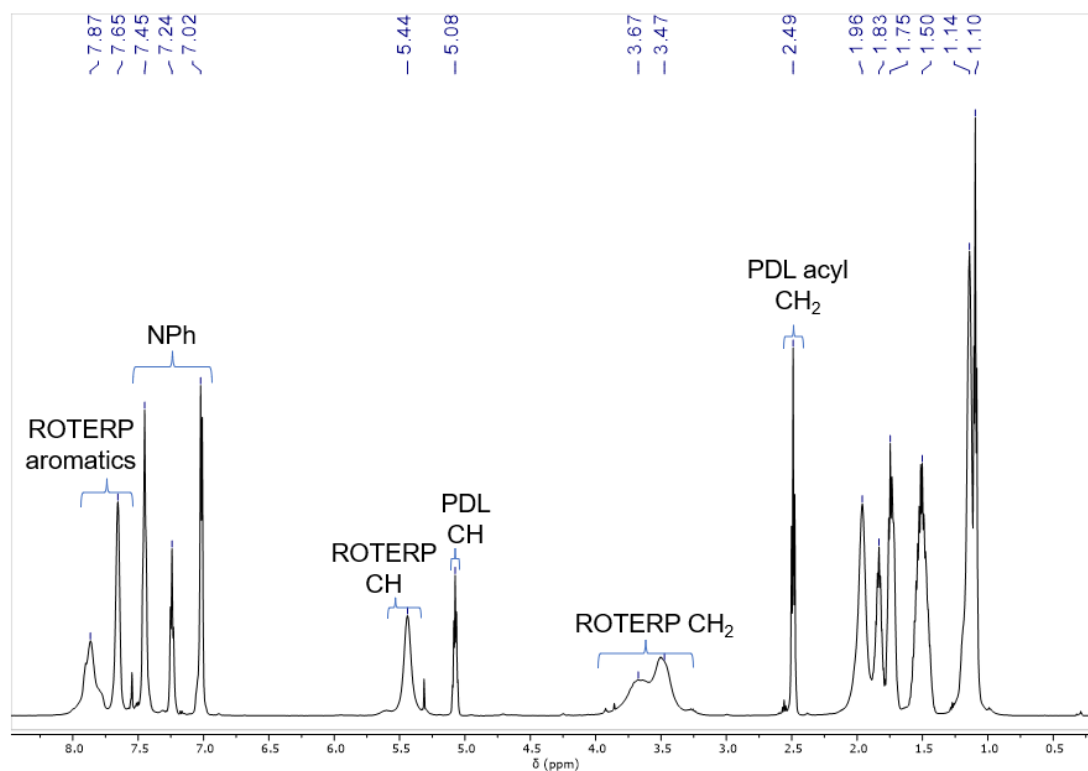
**Figure S 20:** Schematic showing  $\epsilon$ DL ROP to PhNCS/PTA/BO ROTERP to switchable catalysis.

**$\epsilon$ DL ROP into PhNCS<sub>2</sub>/PTA/BO ROTERP switch protocol:** In an argon-filled glovebox, LiHMDS (6.4 mg, 38.5  $\mu$ mol, 1 equiv.) was dissolved in butylene oxide (835.0  $\mu$ l, 693.5 mg, 9.6 mmol, 250 equiv.) and benzylalcohol (4.0  $\mu$ l, 4.2 mg, 36.5  $\mu$ mol, 1 equiv.) was added. The resulting mixture was stirred for 1 min and afterwards  $\epsilon$ -decalactone ( $\epsilon$ DL) (335.3  $\mu$ l, 327.3 mg, 19.3 mmol, 50 equiv.) was added and ROP was allowed to occur for 15 min. Afterwards PhNCS (3.4 mL, 28.8 mmol, 750 equiv.) and PTA (316.0 mg, 19.3 mmol, 50 equiv.) were added causing an immediate yellow discolouration of the mixture which was then allowed to react for 30 min at 80°C. The polymer was isolated by two consecutive precipitations from DCM/MeOH, followed by isolation by filtration and drying in a vacuum oven set to 60°C overnight.

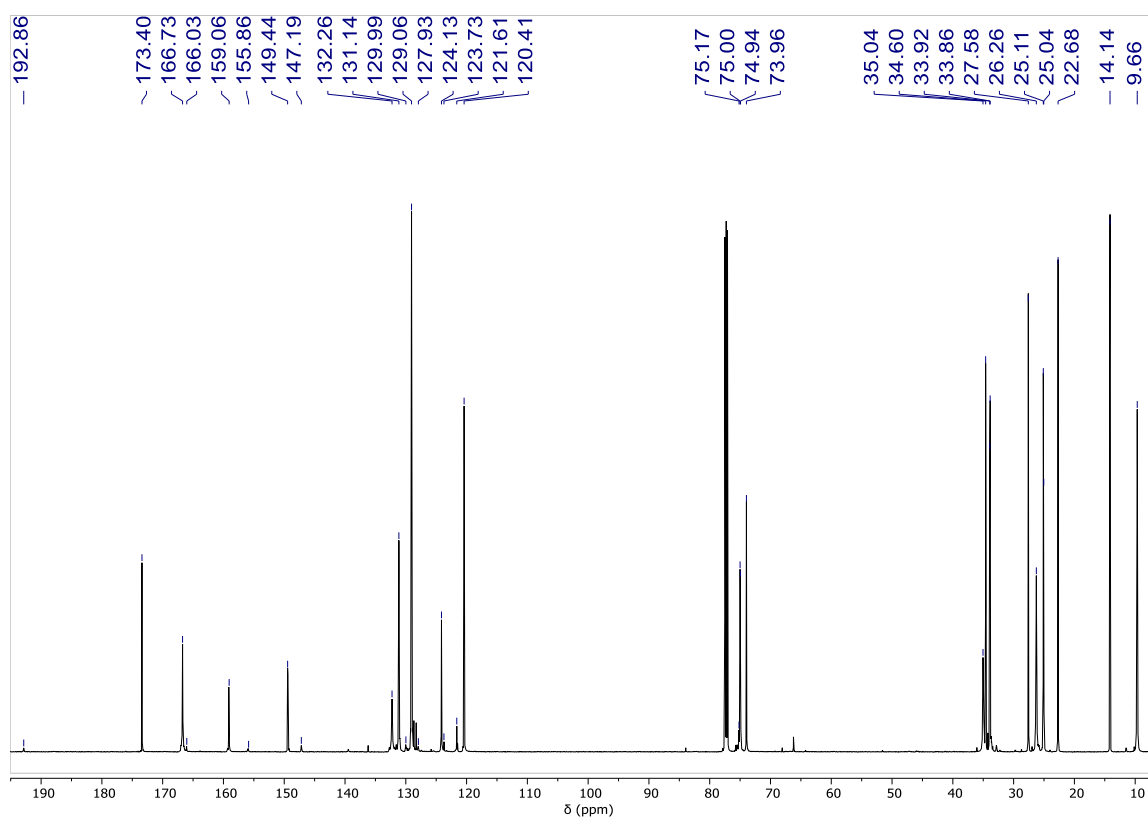


**Figure S 21:** <sup>1</sup>H NMR spectra (400 MHz, CDCl<sub>3</sub>, 25°C) of aliquots removed after ROP and ROTERP phases of switchable catalysis showing that no further ROP occurs after ROCOP and ROTERP initiation.

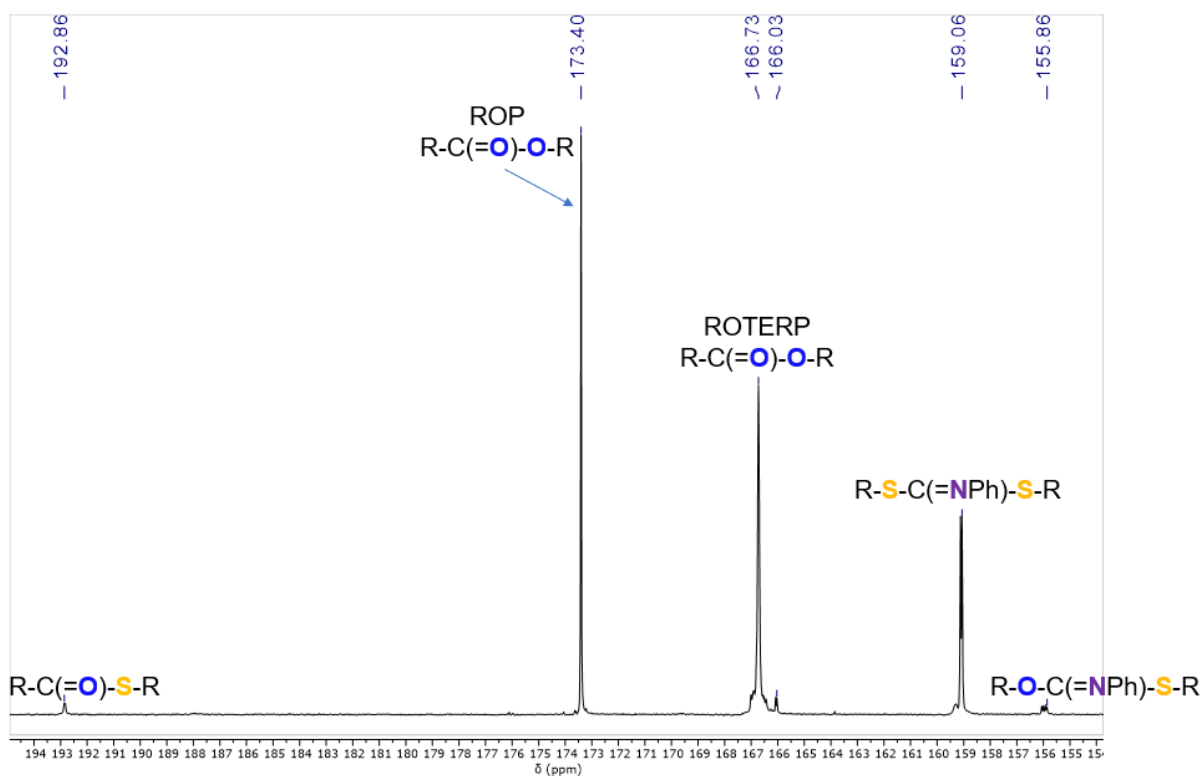




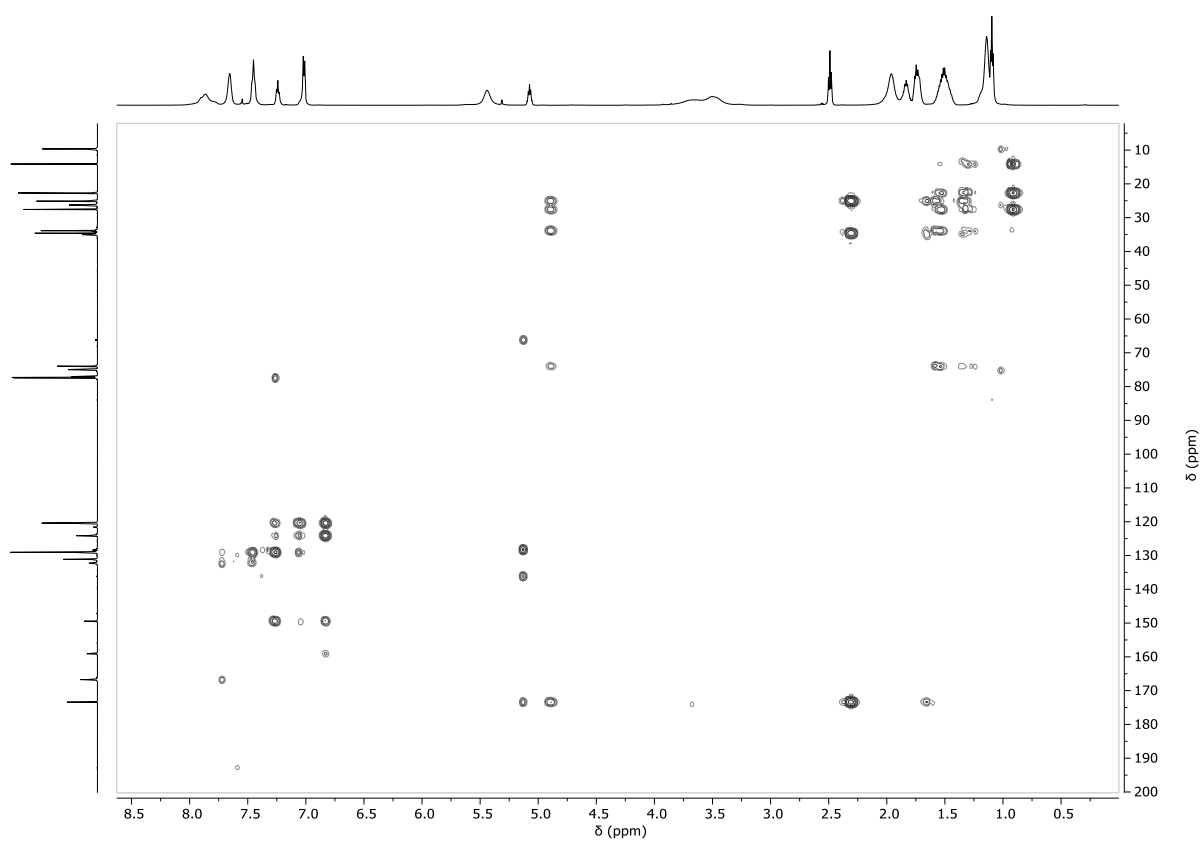
**Figure S 22:** <sup>1</sup>H NMR spectrum (500 MHz, CDCl<sub>3</sub>, 25°C) of εDL ROP to PTA/PhNCS/BO ROTERP polymer.



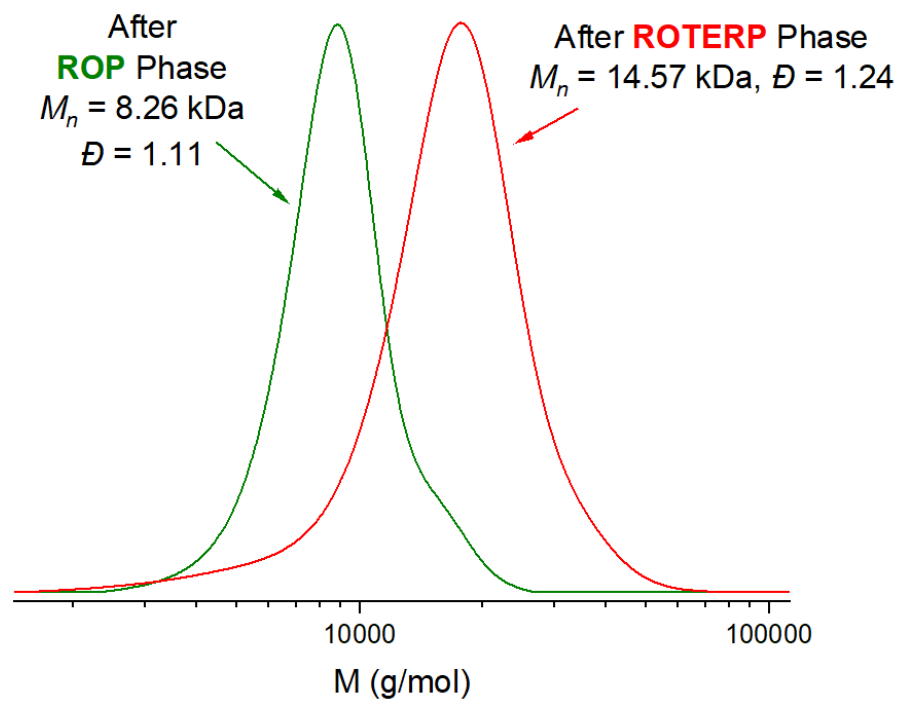
**Figure S 23:** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (126 MHz, CDCl<sub>3</sub>, 25°C) of εDL ROP to PTA/PhNCS/BO ROTERP polymer.



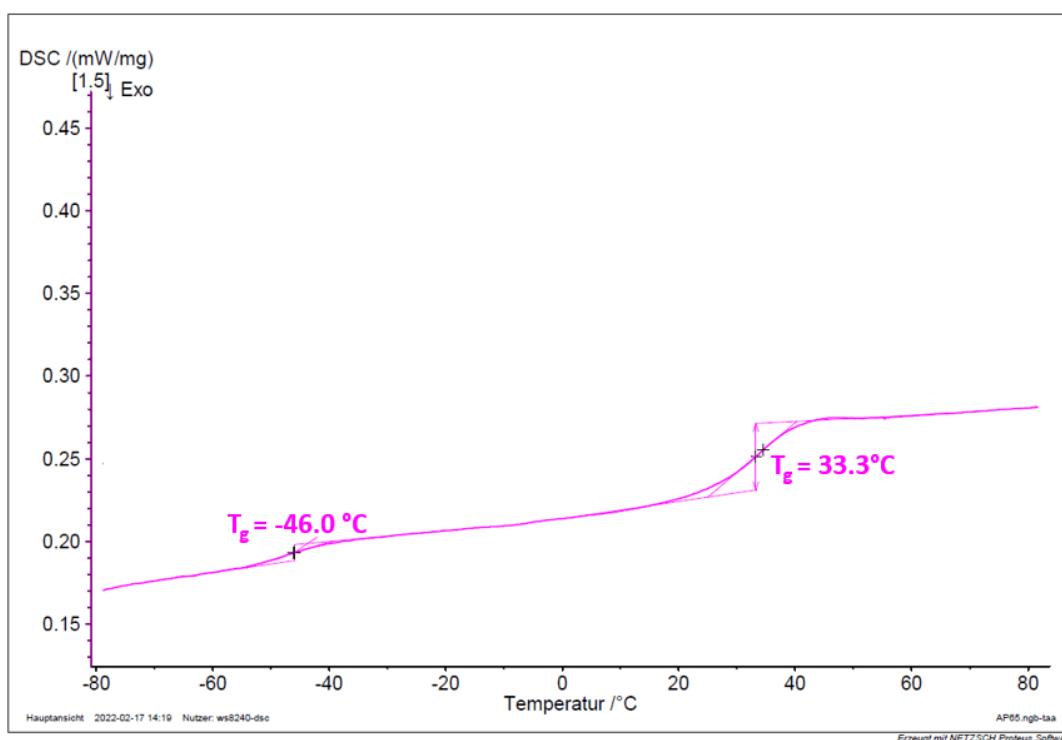
**Figure S 24:** Zoom into the carbonyl region of the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (126 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of  $\epsilon\text{DL}$  ROP to PTA/PhNCS/BO ROTERP polymer.



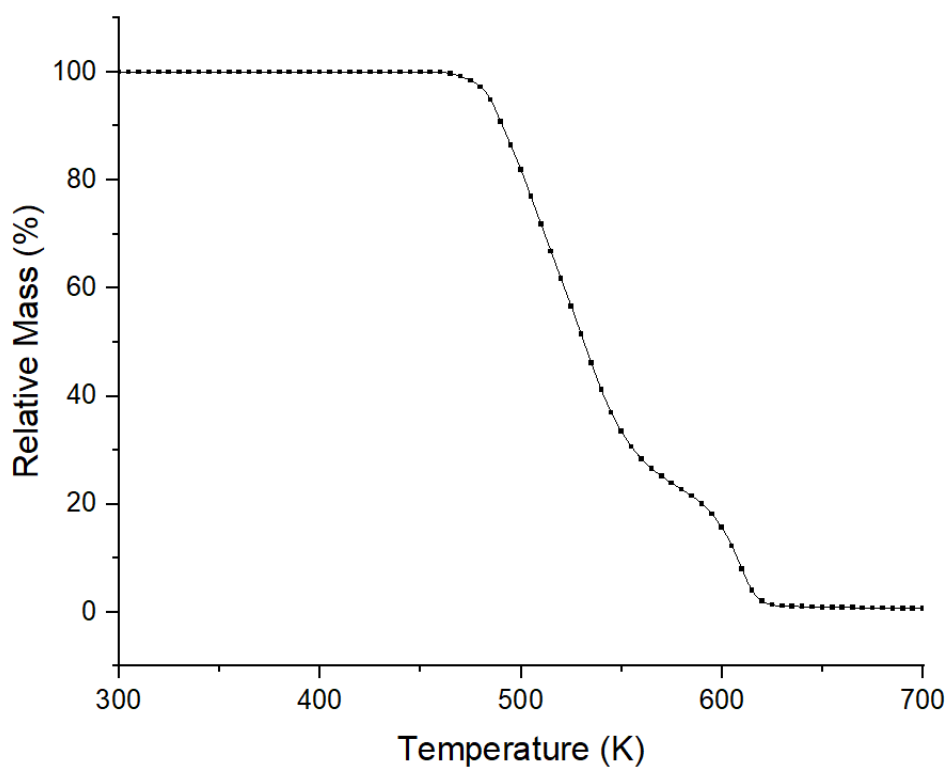
**Figure S 25:**  $^1\text{H} - ^{13}\text{C}$  HMBC NMR spectrum (126 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) of  $\epsilon\text{DL}$  ROP to PTA/PhNCS/BO ROTERP polymer.



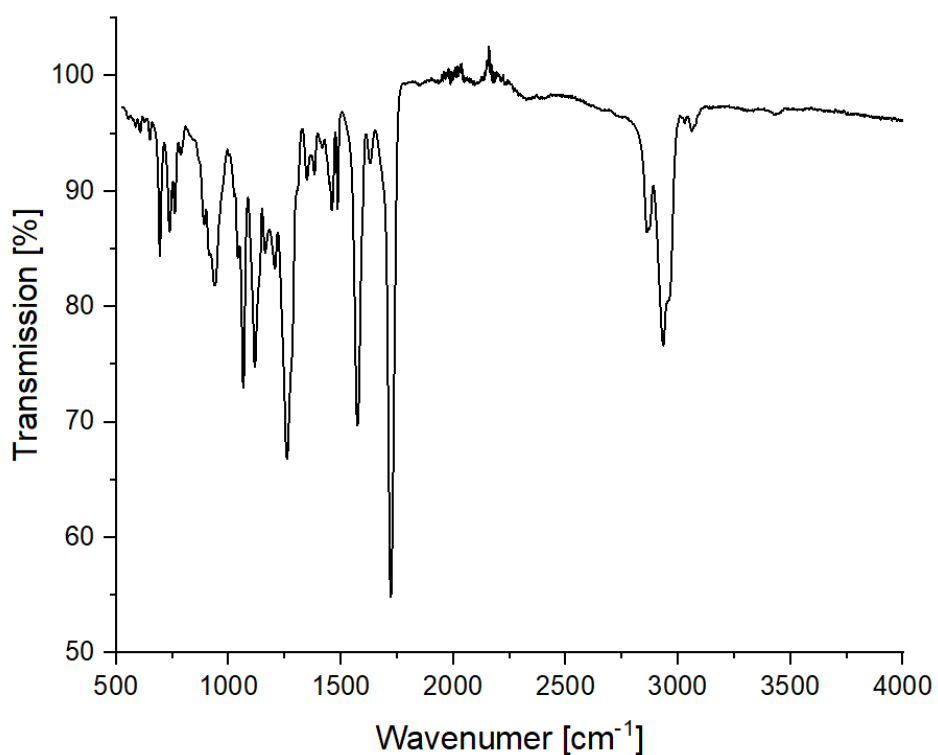
**Figure S 26:** Overlaid GPC traces of aliquots at the end of ROP (green) and ROTERP (red) phase.



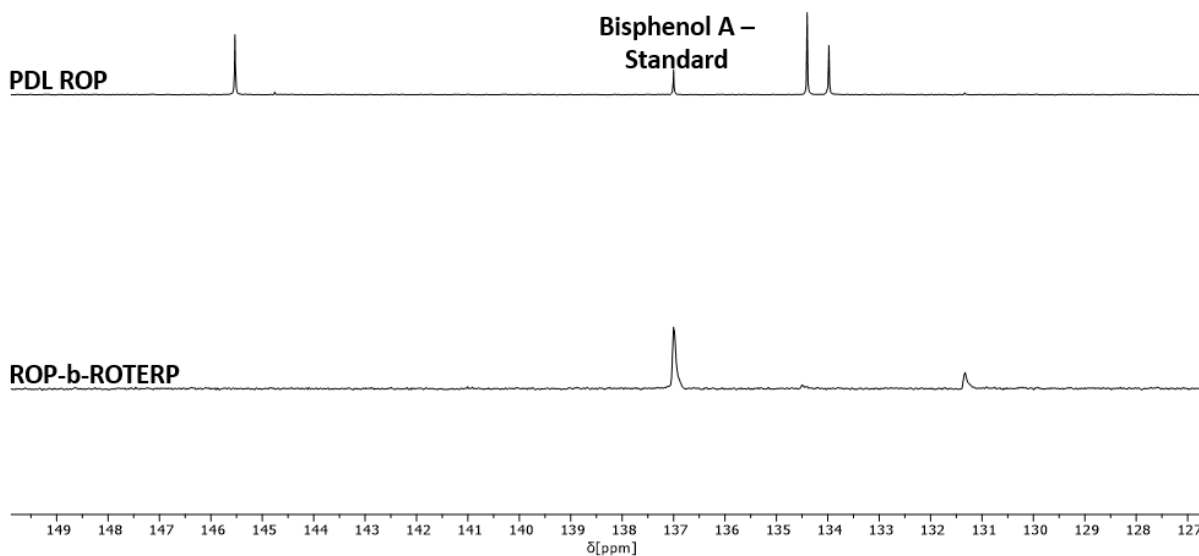
**Figure S 27:** DSC heating curve of  $\epsilon$ DL ROP to PTA/PhNCS/BO ROTERP polymer.



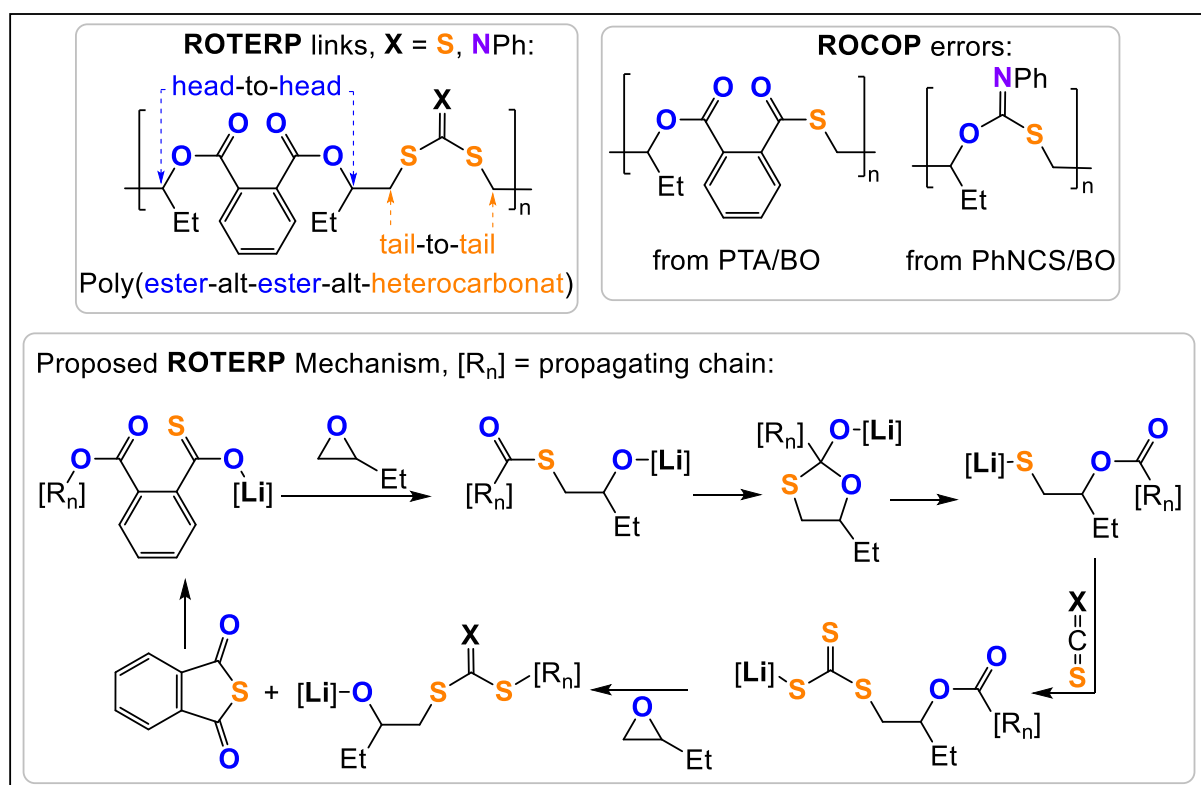
**Figure S 28:** TGA data of  $\epsilon$ DL ROP to CS<sub>2</sub>/BO ROCOP to PTA/CS<sub>2</sub>/BO ROTERP to CS<sub>2</sub>/BO ROCOP polymer.



**Figure S 29:** FT ATRIR spectrum of terpolymer corresponding to of  $\epsilon$ DL ROP to PTA/PhNCS/BO ROTERP polymer.



**Figure S 30:**  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) end-group analysis of polymers (top) before and (bottom) after ROTERP phase. Analysis has been performed as following: A polymer sample (20 mg) and stock solution (40  $\mu\text{L}$ , made of bisphenol A (400 mg), chromium(III)acetylacetonate (5.5 mg), and pyridine (10 mL)), in  $\text{CDCl}_3$  (0.5 mL), were mixed in an NMR tube. Excess 2-chloro-4,4,5,5-tetramethyldioxaphospholane (40  $\mu\text{L}$ ) was then added to the NMR tube and shaken. The mixture was allowed to react for 30 min before analysis by  $^{31}\text{P}\{^1\text{H}\}$  NMR.



**Figure S 31:** Summary of ROTERP and ROCOP as well as proposed ROTERP propagation mechanism.