SUPPORTING INFORMATION

γ-Thiobutyrolactone - Ethylene Carbonate Decarboxylative Copolymerization, an Original Pathway to Prepare Aliphatic Oxidizable Poly(γ-thioether ester)

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γ-thiobutyrolactone

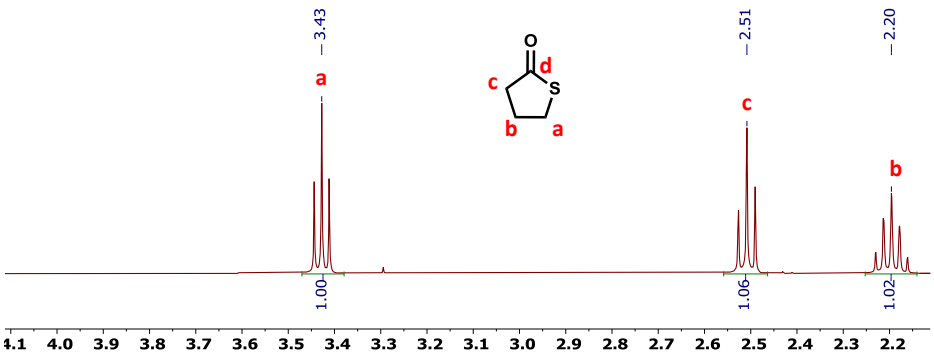


Figure S 1. ^{1}H NMR spectrum of TBL in DMSO-d_6 at room temperature

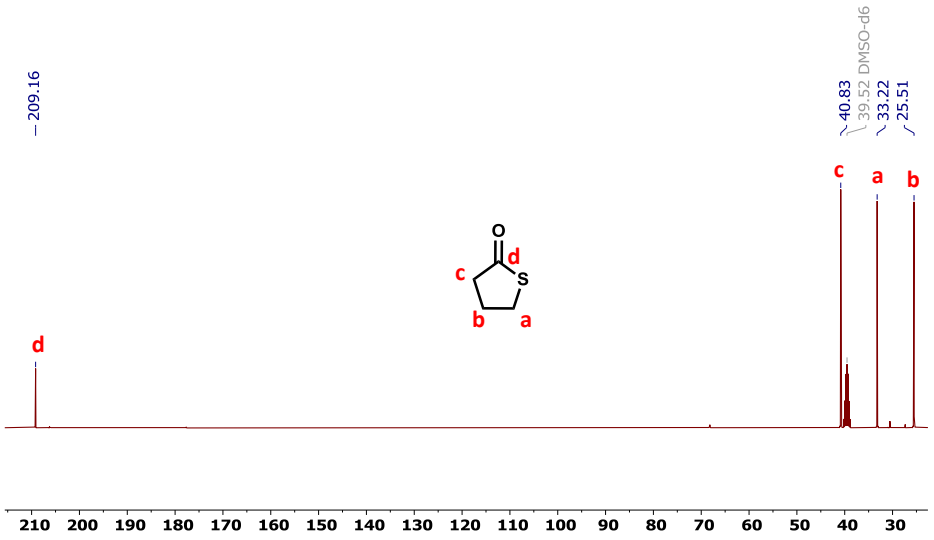


Figure S 2. ^{13}C NMR spectrum of TBL in DMSO-d_6 at room temperature

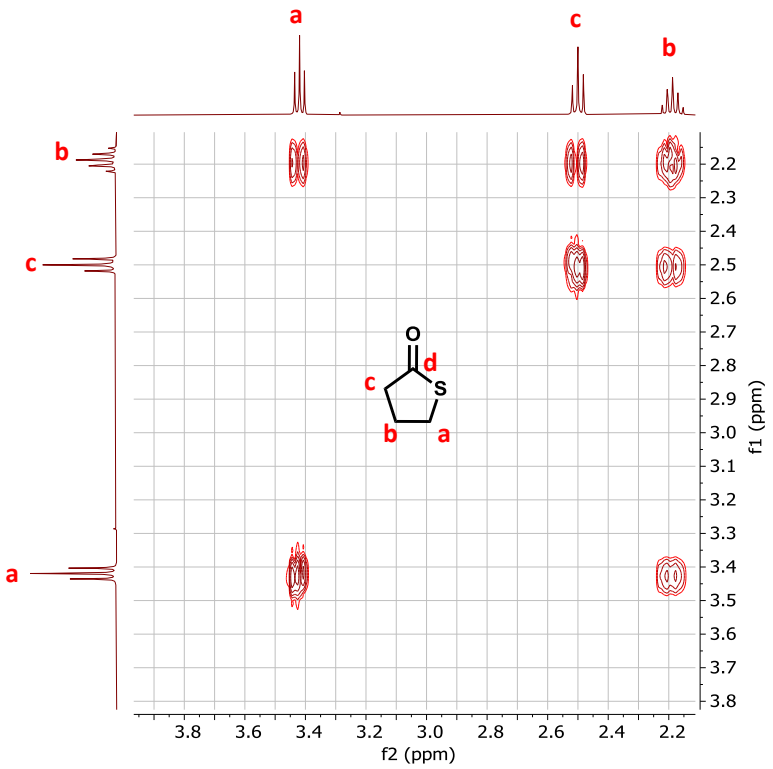


Figure S 3. COSY NMR spectrum of TBL in DMSO-d_6 at room temperature

Ethylene carbonate

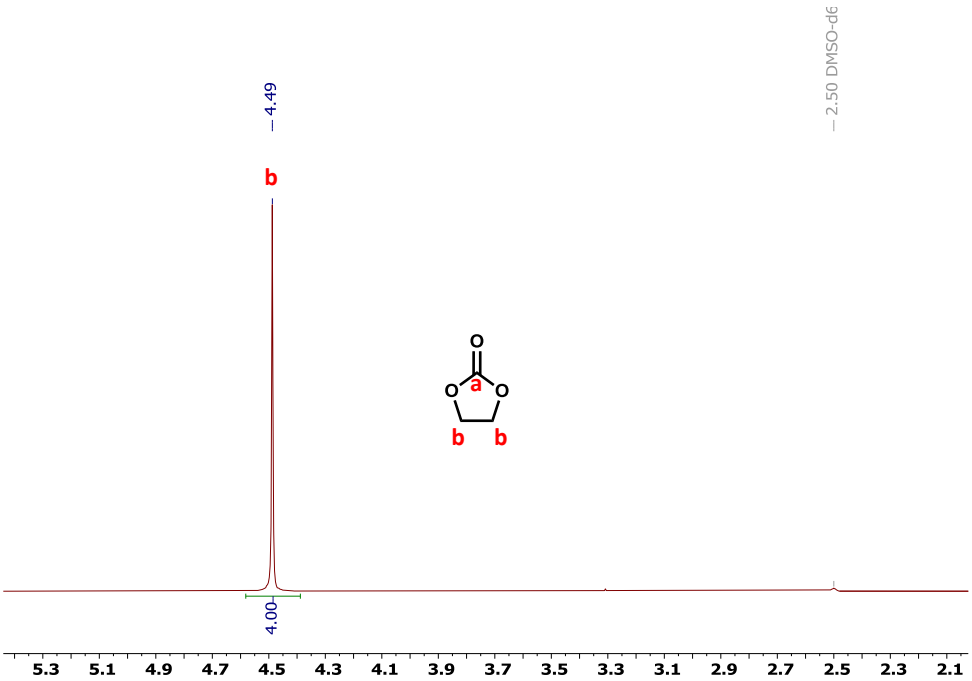


Figure S 4. ^{1}H NMR spectrum of ethylene carbonate in DMSO-d_6 at room temperature.

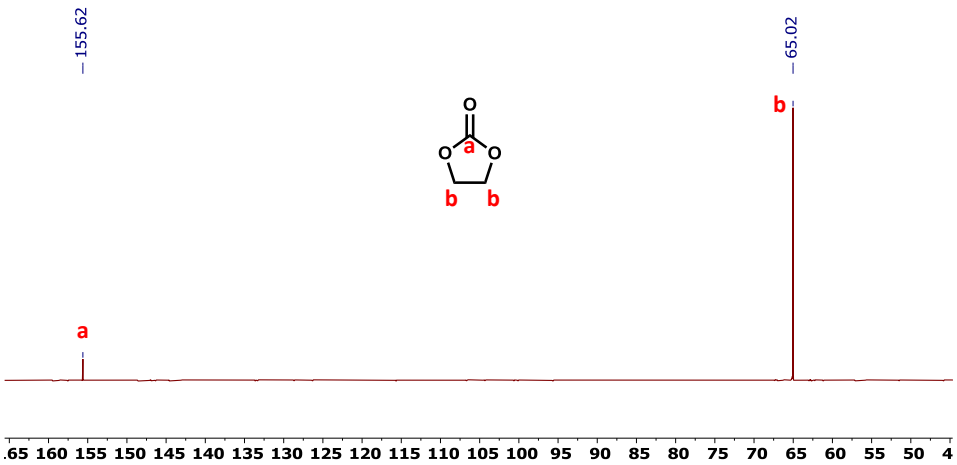


Figure S 5. ^{13}C NMR spectrum of ethylene carbonate in DMSO-d_6 at room temperature

Poly(thioether-*alt*-ester)

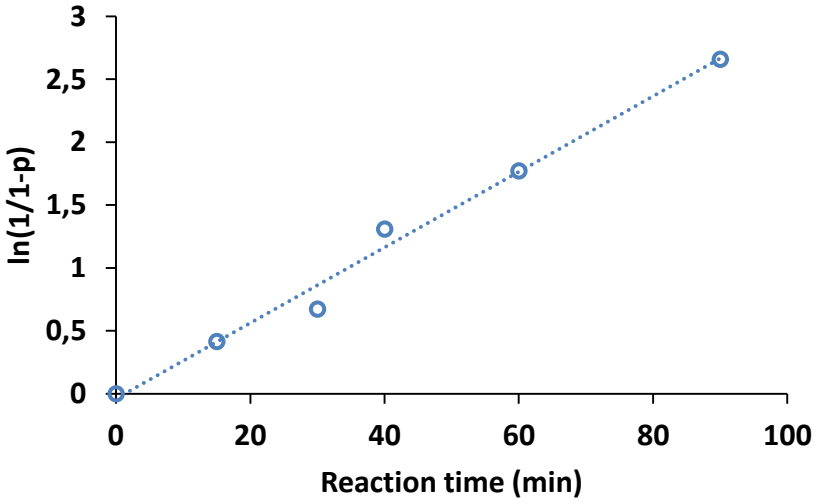


Figure S 6. Kinetic study of the synthesis of PTE using benzyl alcohol and *t*BuP4 as initiating system in bulk at 100°C (Table 1, run 7): ln(1/1-p) = f(t)

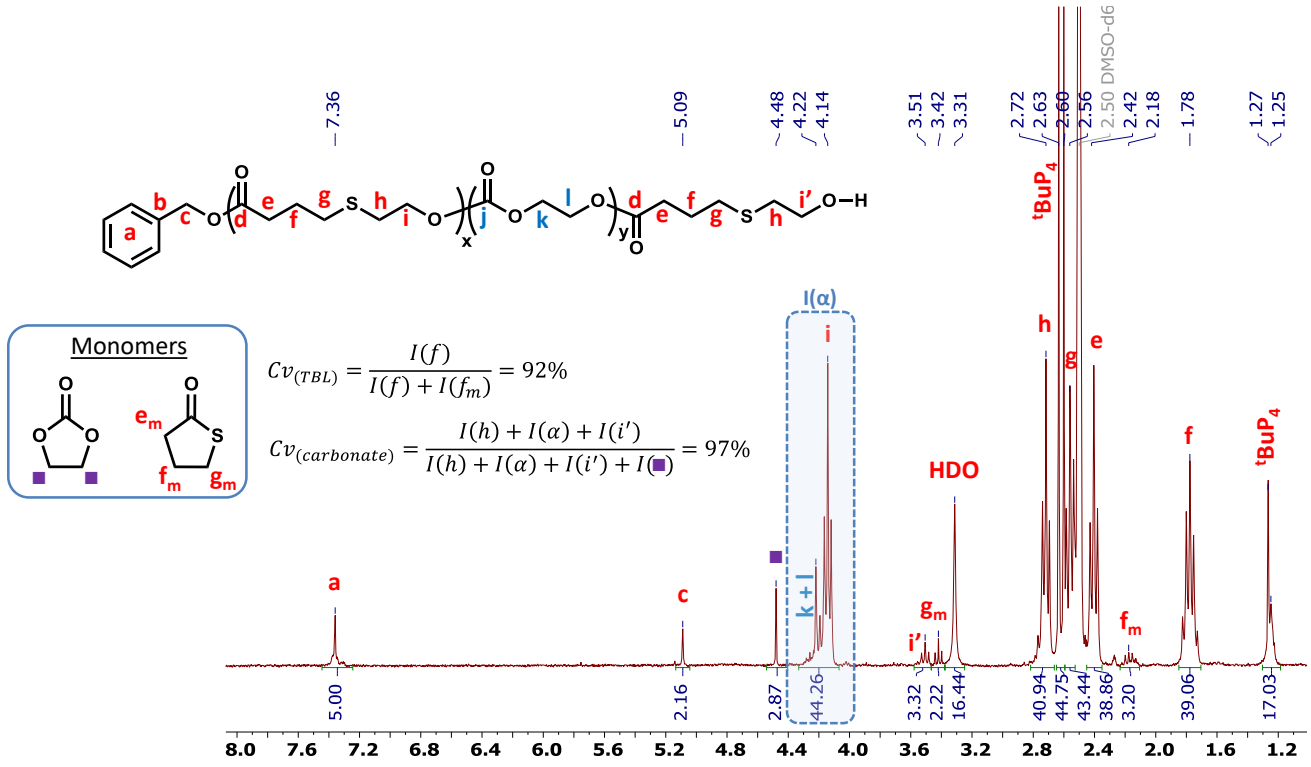


Figure S 7. ^{1}H NMR spectrum of the reaction medium of the alternating copolymerization of TBL and ethylene carbonate initiated by benzyl alcohol - ^{t}BuP$_4$ in bulk at 100°C after 3 h (Table 1, run 8)

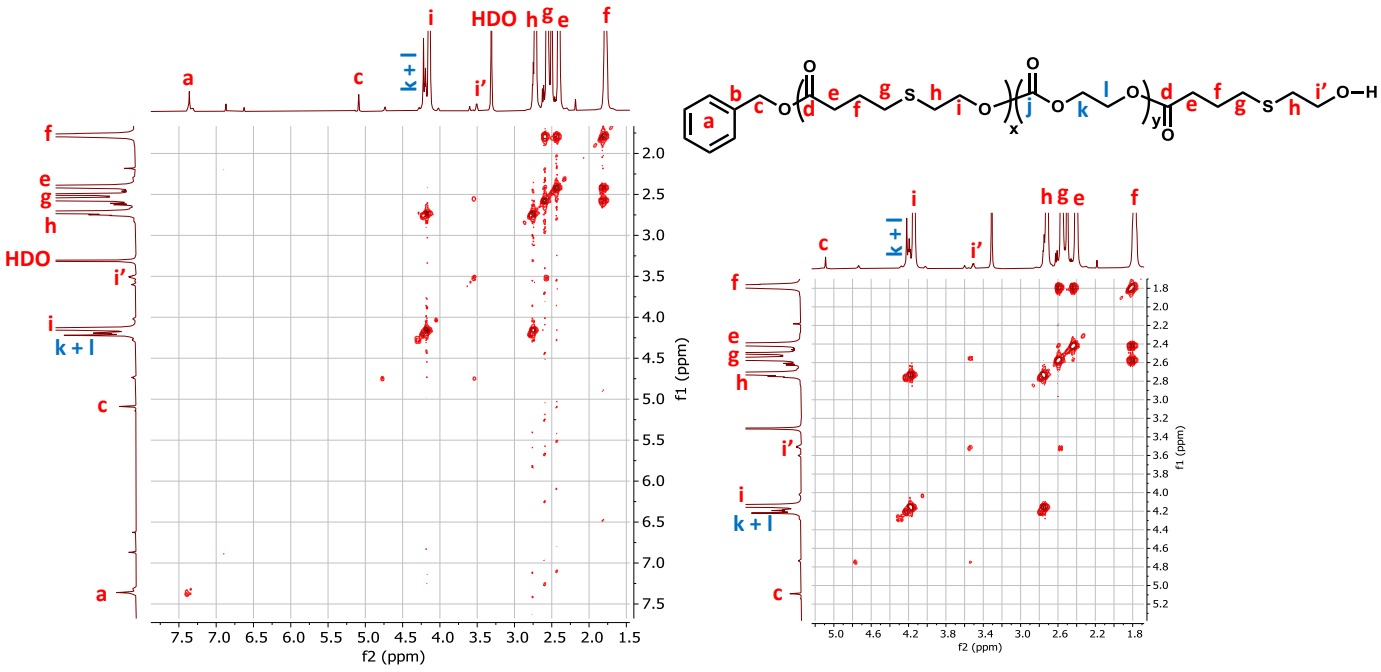


Figure S 8. COSY NMR spectrum of PTE in DMSO-d_6 at room temperature (Table 1, run 8)

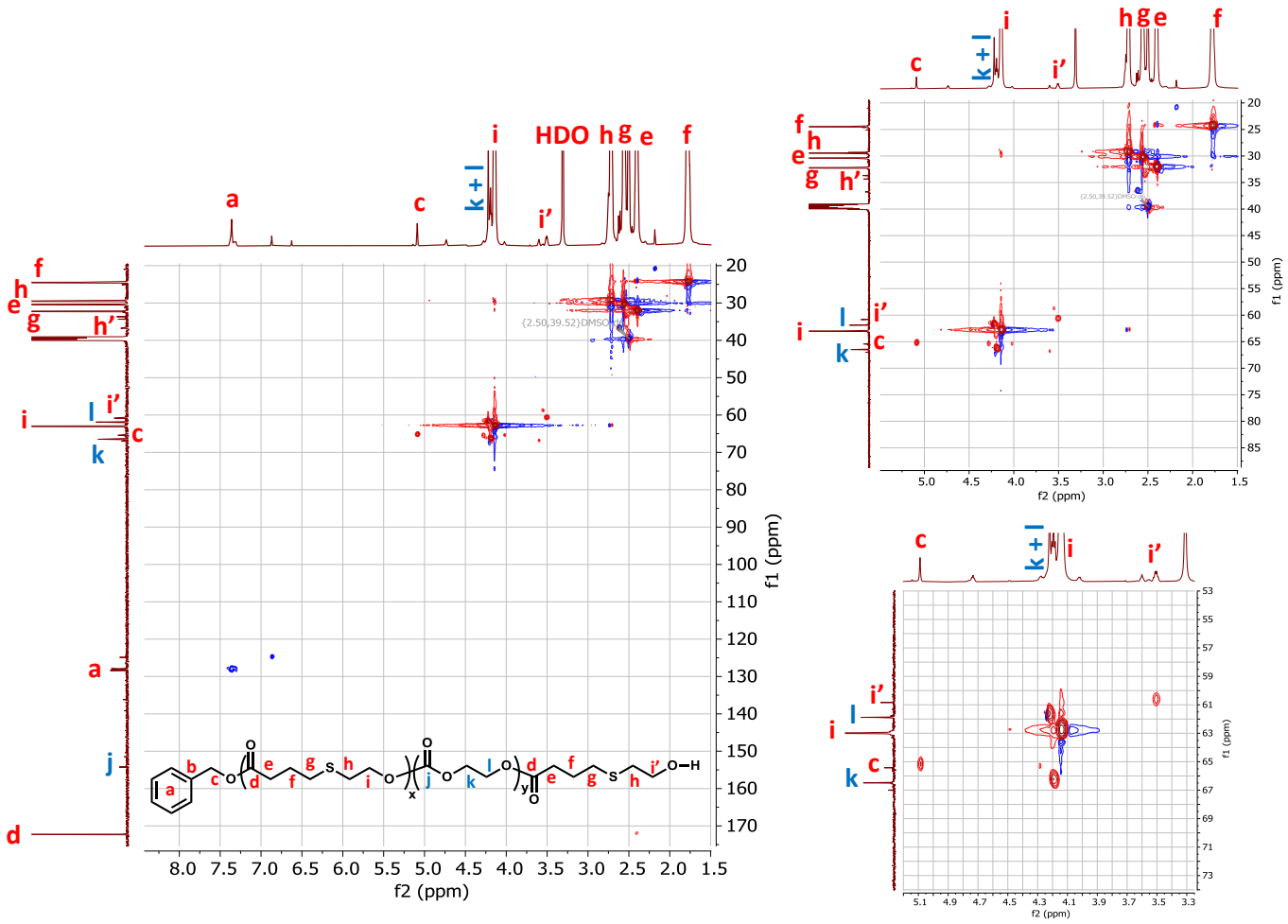


Figure S 9. ^{1}H-^{13}C HSQC NMR spectrum of PTE in DMSO-d_6 at room temperature (Table 1, run 8)

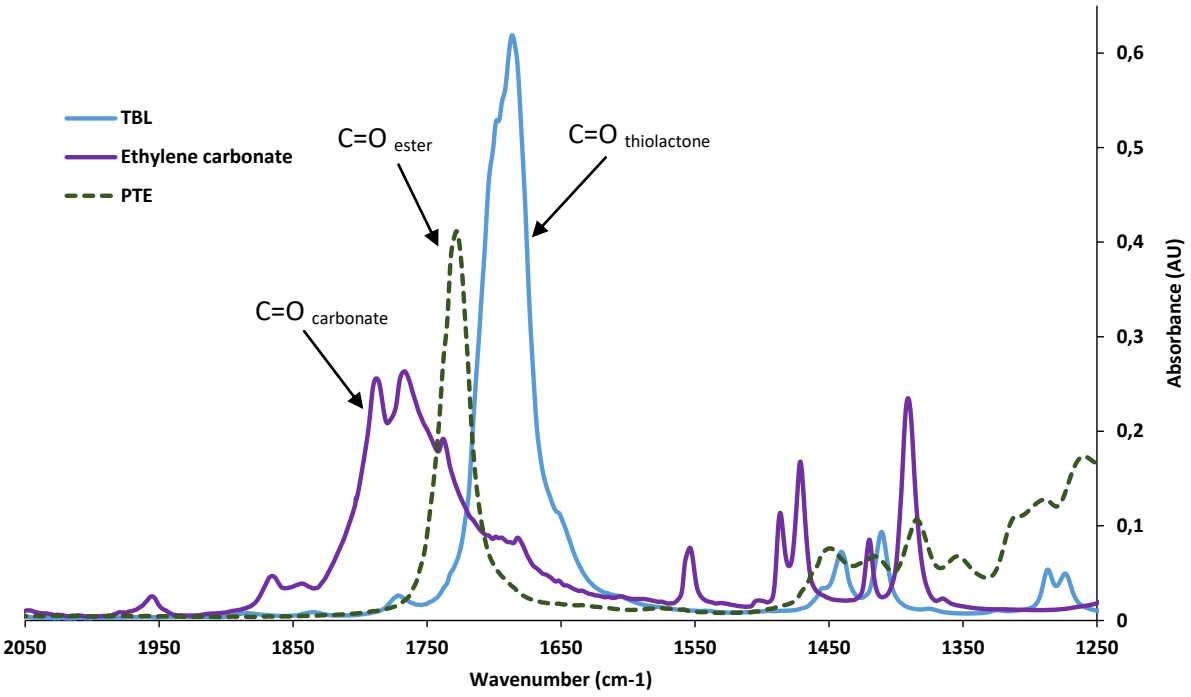
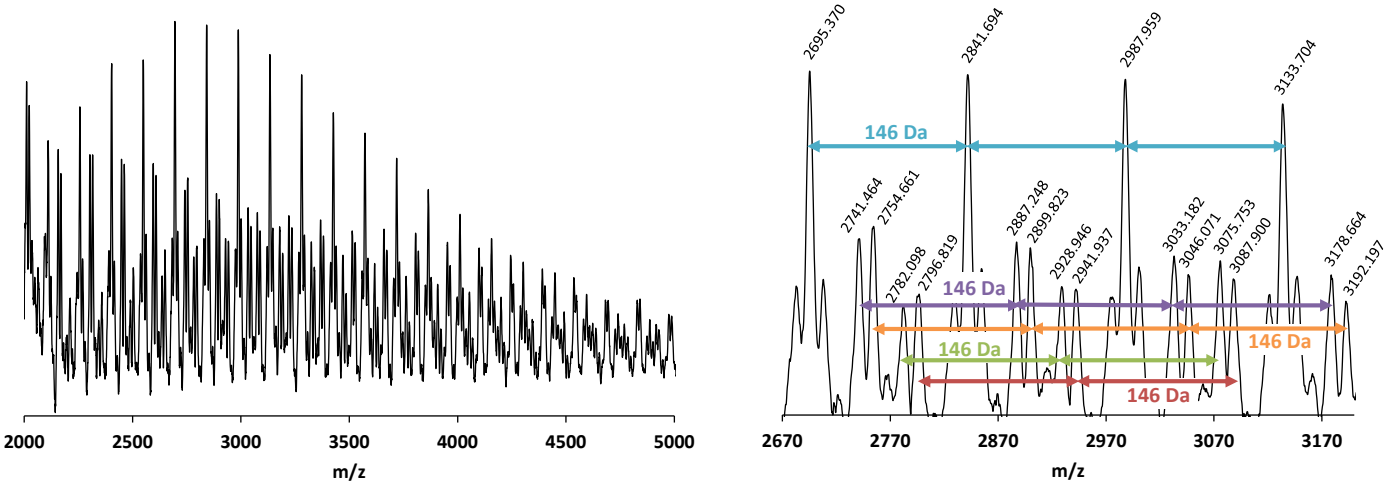


Figure S 10. ATR FT-IR analysis of TBL (blue curve), ethylene carbonate (purple curve) and PTE (green curve - Table 1, run 14)



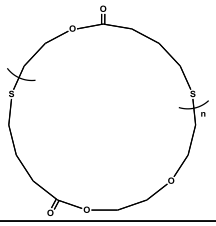
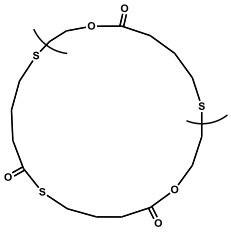
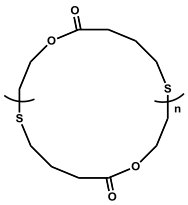
Structure	Cation	X_n	Calculated exact mass	MALDI-ToF m/z
	Na^+	17	2695.90	2695.37
	Na+	18	2753.60	2754.66
	Na^+	19	2943.79	2941.94

Figure S 11. MALDI-ToF mass spectrum (linear mode) of a PTE synthesized using benzyl alcohol - $^tBuP_4$ as initiating system in bulk at 100°C (Table 1, run 8)

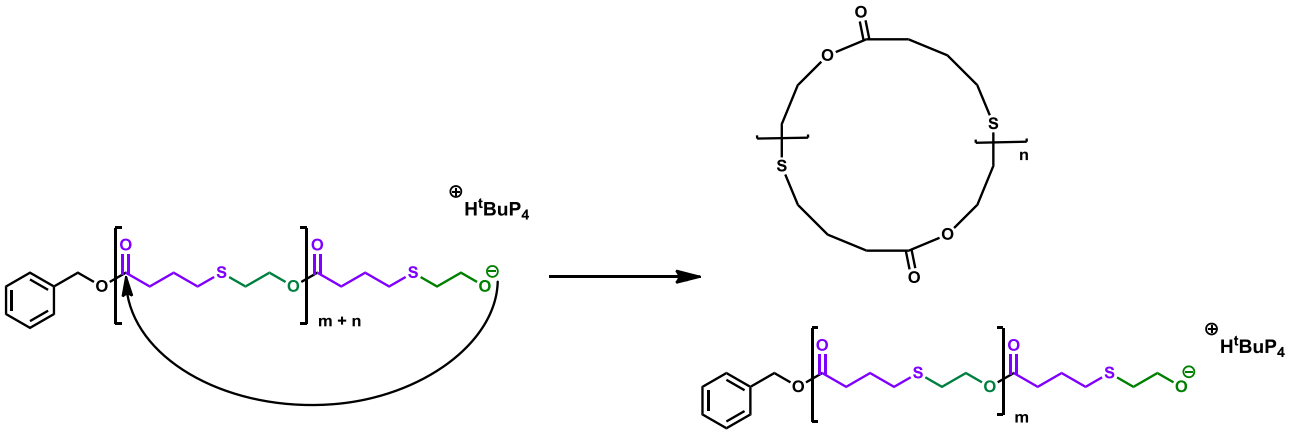


Figure S 12. Mechanism for the intramolecular transesterification of PTE explaining the formation of macrocycles.

PTE oxidation

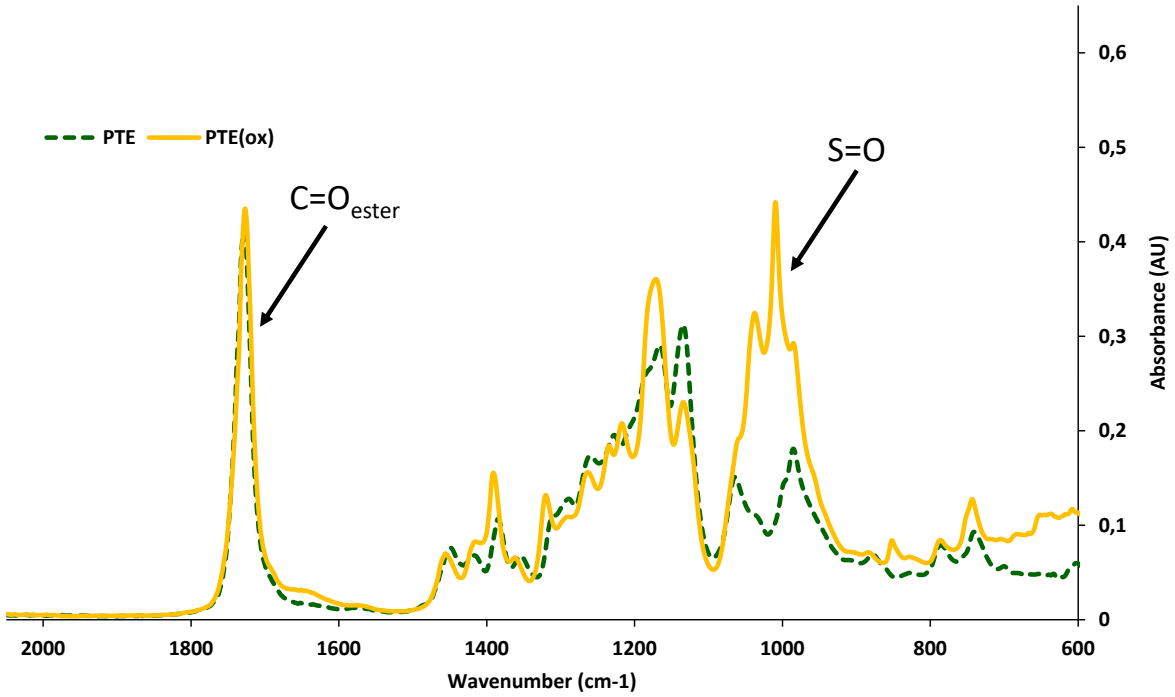


Figure S 13. ATR FT-IR spectrum of PTE before (green dot curve) and after (orange curve) oxidation (Table 1, run 14)

Thermal properties

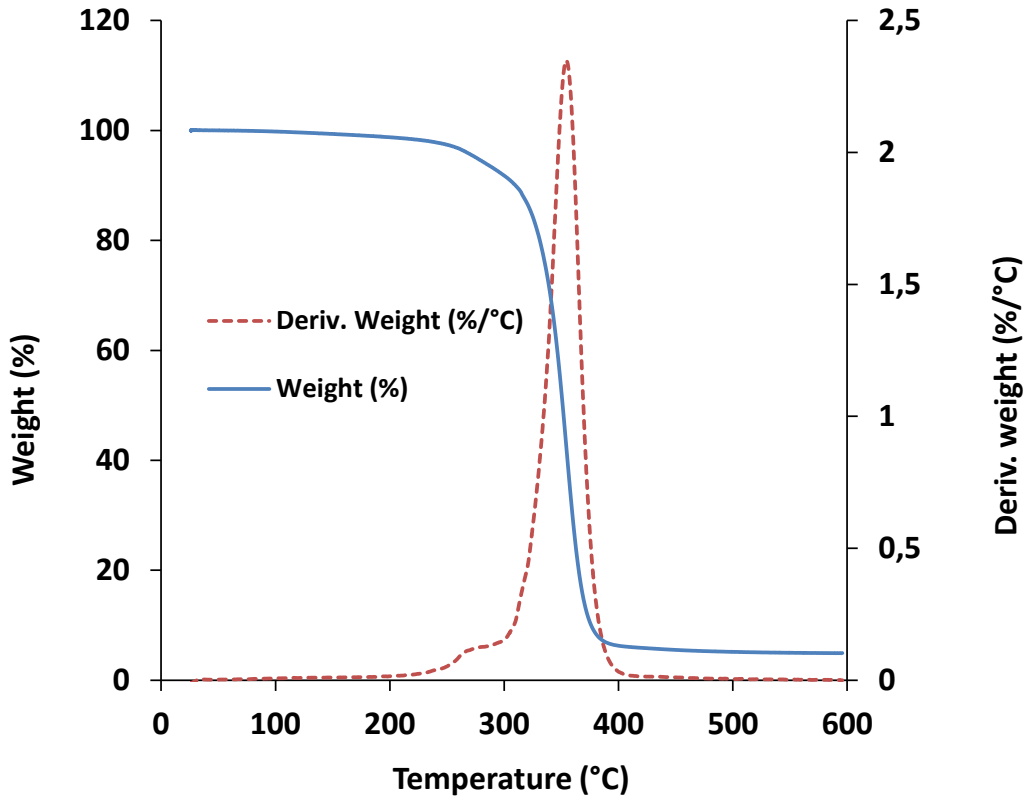


Figure S 14. TGA curve and its first derivative of a PTE (Table 1, run 8) measured under a stream of nitrogen between 25°C and 600 °C with a heating rate of 10 °C min^{-1}

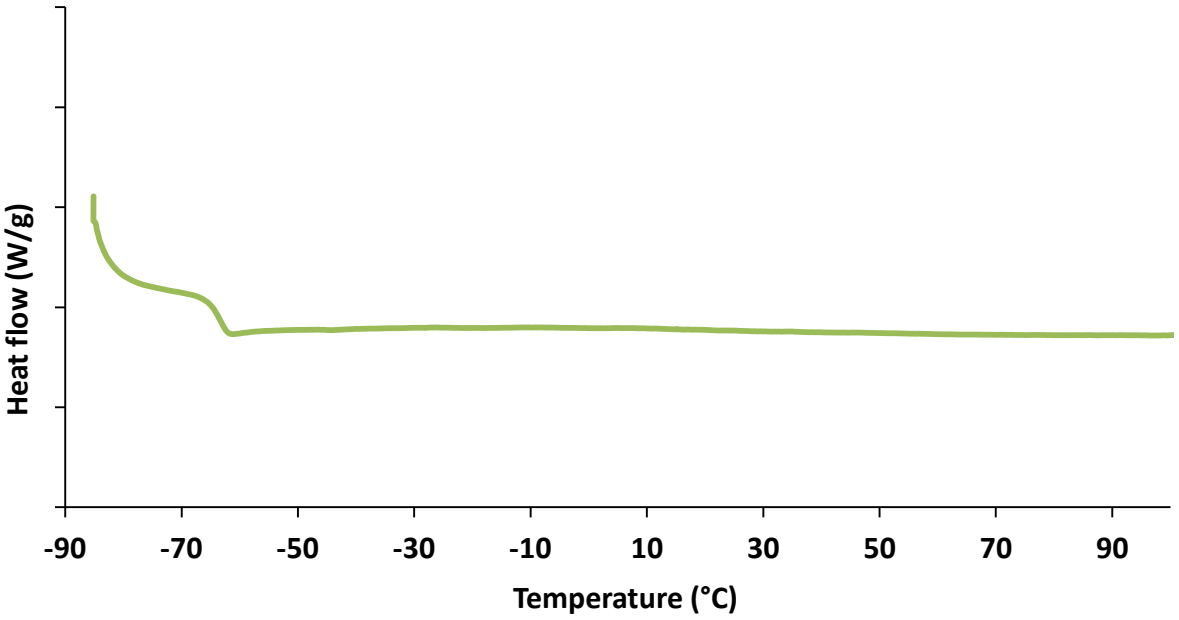


Figure S 15. DSC figures of PTE at 2 °C /min (Table 1, run 8)

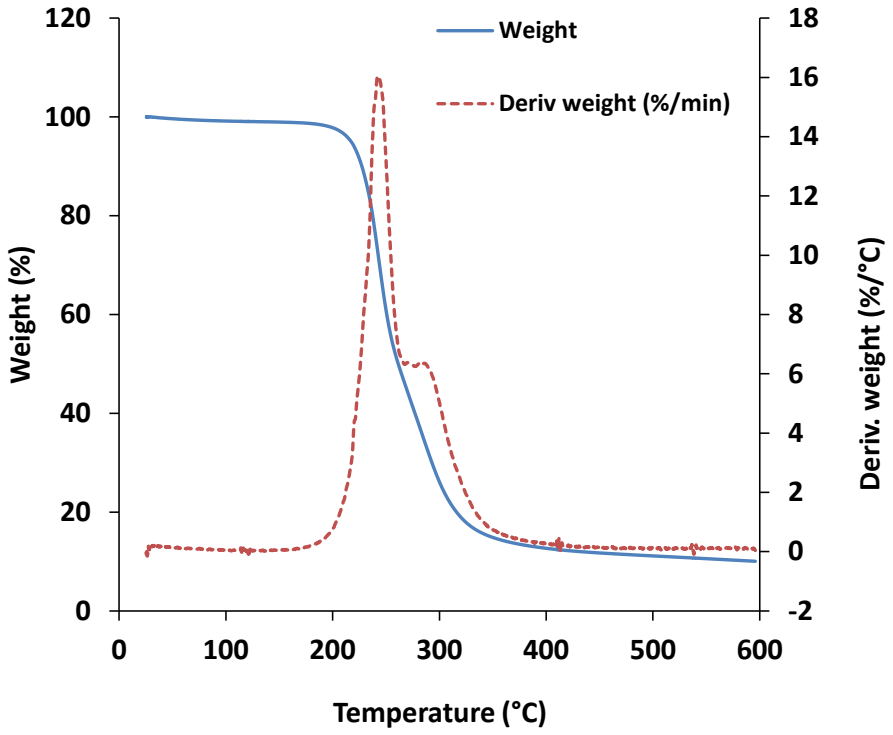


Figure S 16. TGA curve and its first derivative of a PTE after oxidation (Table 1, run 14) measured under a stream of nitrogen between 25°C and 600 °C with a heating rate of 10 °C min^{-1}

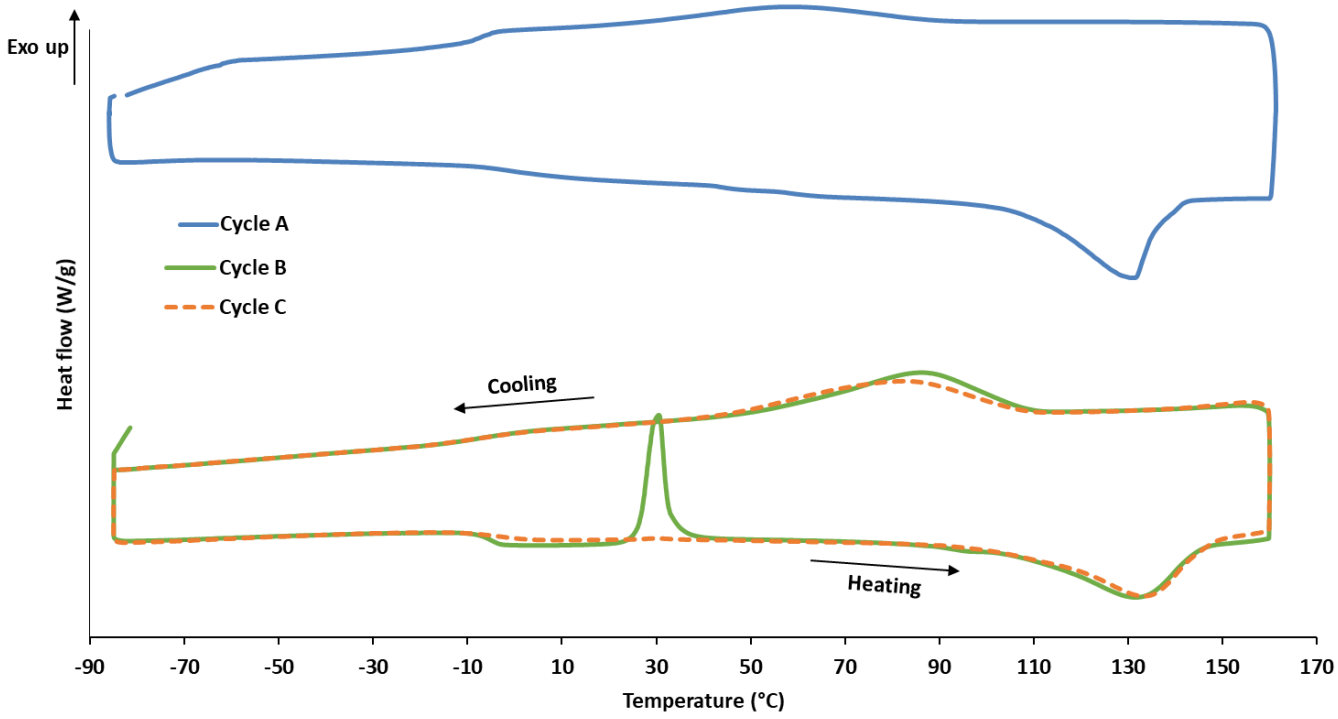


Figure S 17. DSC figures of a PTE after oxidation (Table 1, run 14). Cycle A is at 10°C/min from -85°C to 155°C. Cycle B is at 2 °C /min from -85°C to 155°C (T_c = 89°C ; T_f = 133 °C ; the T_c located at 37°C is reflecting the crystallization of the previous heating cycle made at 10 °C/min where no fusion occurred). Cycle C follows cycle A at 2°C/min from -85°C to 155°C.

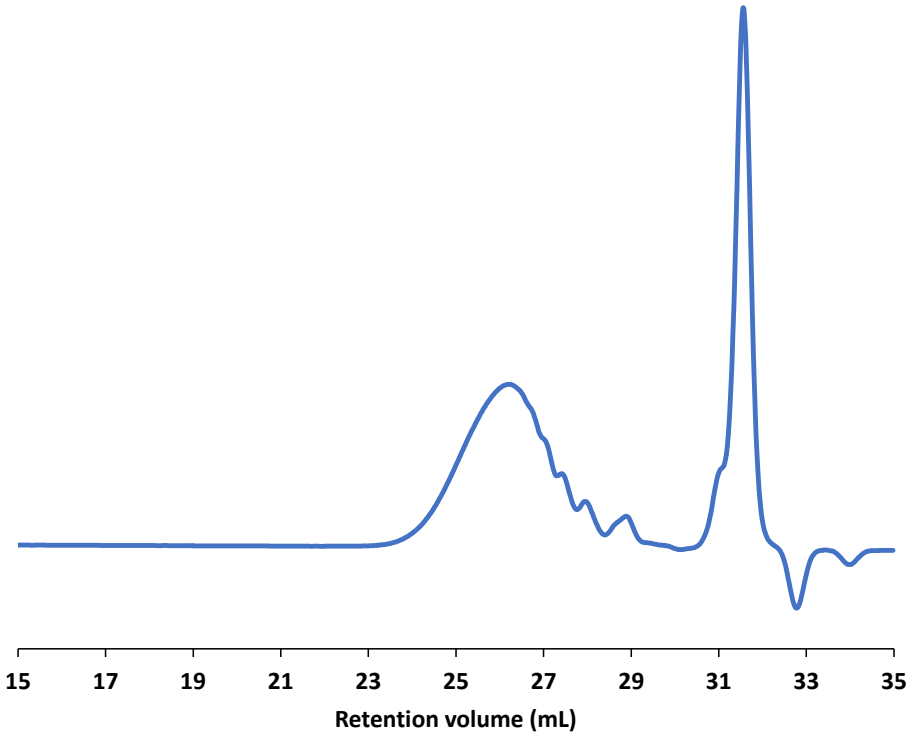


Figure S 18. SEC trace of PTE synthesized in THF using benzyl alcohol-*t*BuP$_4$ as initiating system (Table 1, run 6)

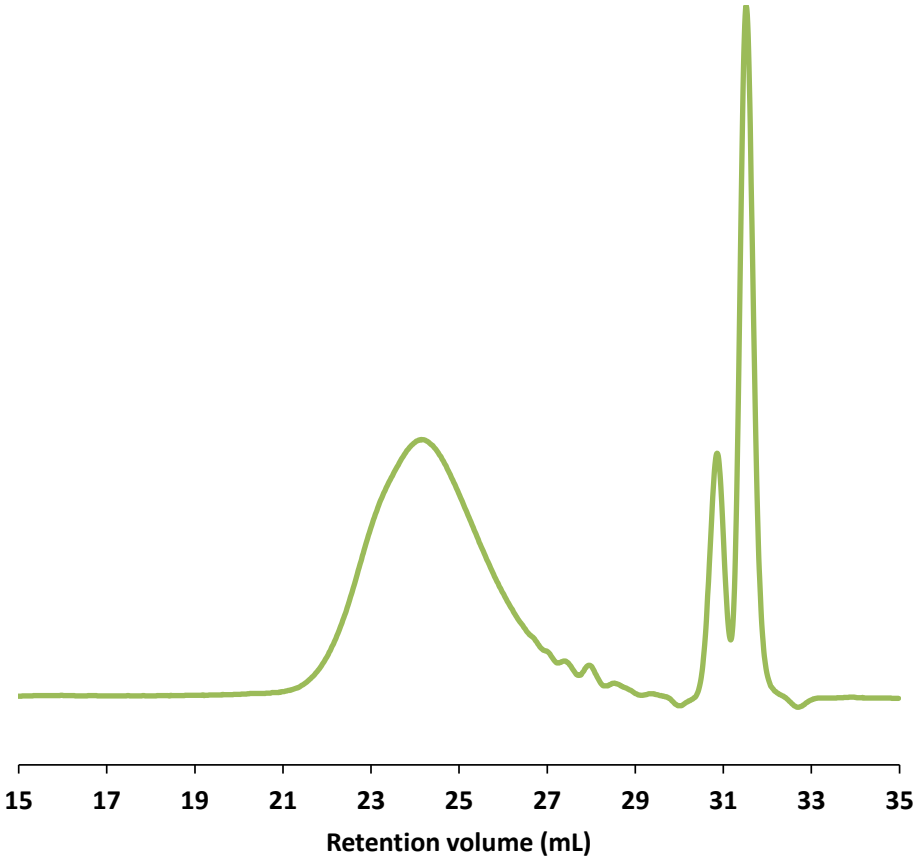


Figure S 19. SEC trace of PTE synthesized in bulk using benzyl alcohol-tBuP4 as initiating system (Table 1, run 8)

Table S 1. Solubility of alternated copolymers in organic solvent (10 mg/mL, room temperature, visual inspection)

Chemical nature	Solubility														
	H_2O	**MeOH**	**EtOH**	**DMF**	**Acetone**	**THF**	**Toluene**	**$CHCl_3$**	**Cyclohexane**	**CH_2Cl_2**	**ACN**	**DMSO**	**Ethyl acetate**	**Diethyl ether**	**N-pentane**
PTE (Table 1, run 7)	-	-	-	+	+	+	+/-	+	-	+	+/-	+	+	+	-
PTE_{ox} (Table 1, run 14)[c]	+	-	-	-	-	-	-	-	-	-	-	+	-	-	-

[c] After oxidation in THF and 2 eq of H_2O_2 per repeating unit at room temperature and dialysis in 1 kDa membrane in water.