Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

One-pot synthesis of well-defined polyether/polyester block co/terpolymers by a highly efficient catalyst-switch approach

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Experimental Section

Instrumentation

Size exclusion chromatography (SEC) with RI and UV detectors was carried out in THF at 35 °C and at a flow rate of 1 mL min^{-1} using two 7.8 mm × 300 mm (5 μm) Styragel columns (Styragel HR 2 and Styragel HR 4). A series of nine polystyrene (PS) standards (370 to 4220000) was used to calibrate the instrument and determine the polydispersity index (PDI = M_w/M_n) and apparent number-average molecular weight ($M_{n,SEC}$). Nuclear magnetic resonance (^{1}H NMR) spectroscopy was performed at room temperature in $CDCl_3$ (Aldrich) using a 400 MHz Bruker AVANCEDIII 400 spectrometer to: a) monitor the conversion of monomers during ROP, b). determine the real number-average molecular weight ($M_{n,NMR}$) from the integrals of the end group and the main chain signals, and c) characterize intermediate and final products.

Chemicals

All solvents were purchased from Fischer Scientific. Toluene was dried over calcium hydride (CaH_2) and distilled before use. DMSO was refluxed for 4h over CaH_2 and then distilled before use. THF was dried successively by sodium and n-BuLi. Styrene oxide (SO) (Sigma Aldrich, 97%) was distilled over NaH prior to use. 1,2 Butylene Oxide (BO) (Sigma Aldrich, 98%) and ε-CL (Alfa Aesar, 99%) was stirred with CaH_2 overnight and distilled under reduced pressure. 3-Phenyl-1-propanol (PPA, Sigma Aldrich, 98%) was dried over CaH_2 and distilled twice under vacuum. All other chemicals were purchased from Sigma-Aldrich. Phosphazene base (*t*-BuP_4, 0.8 M solution in hexane), Phosphazene base (*t*-BuP_2; 2 M solution in THF), diphenyl phosphate (DPP, 99%) and acetic acid were used as received. L-Lactide (LLA, 99%) was also purified twice by dissolving in THF and cryo-evaporating THF, and finally dissolved in pure THF.

Polymer Synthesis

Homopolymerization of styrene oxide with *t*-BuP_4 as catalyst

All polymerization were conducted on a Schlenk-line using a 100 mL glass reactor with a stopcock. Typical procedure is as follows. 0.0119 ml of PPA (0.087 mmol) was added to 0.6 mL of dry toluene at the flame-dried reactor via a syringe. Then 0.054 mL of *t*-BuP_4 solution (0.043 mmol) was added in an argon flow and the system was stirred until both the initiator and the catalyst were completely dissolved. After that, 1.0 mL of SO (8.78 mmol) was added to start the polymerization. Aliquots were withdrawn (0.1 mL each) in an argon flow after 20 h, and injected to a mixture of 1 mL of $CDCl_3$ and two drops of

acetic acid. This solution was used for ^{1}H NMR measurement to determine the monomer conversion. 0.1 mL of such $CDCl_3$ solution was diluted with 1 mL of THF for SEC analysis. 0.5 ml of the solution was quenched using acetic acid and poured into cold 2-propanol and the glassy white solid was used for the ^{1}H NMR analysis to determine the $M_{n,NMR}$ (Table 1). Conv.(SO) = 91%. $M_{n,NMR}$= 10.9 kg mol-1; SEC(RI): M_w/M_n=1.06.

^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm = 7.70-6.81 (aromatic protons), 4.78- 4.01 (-CH polymer backbone), 3.91-3.02 (CH_2O polymer backbone, Ph-$CH_2CH_2CH_2O$ of the initiator), 2.57 (Ph-CH_2), 2.30 (OH), 1.78 (Ph-CH_2CH_2).

PSO-*b*-polyester di/triblock co/terpolymer

Poly(styrene oxide)-*b*- poly(ε-caprolactone)-*b*-poly(L-lactide) in THF, solvent for the second monomer (Table 1, THF)

To the living PSO, 4 ml of dry THF was added followed by the addition of 0.09 ml of DPP solution (0.043 mmol DPP), upon which the dark red color disappeared immediately, a clear indication of the neutralization and deactivation of the active alkoxide PSO chain end. Then, 30 min later, 0.044 mL of *t*-BuP_2 (0.087 mmol) was added to the reaction mixture at room temperature and subsequently 3 mL of ε-CL (27 mmol) and the reaction mixture was stirred. Aliquots were withdrawn (0.1 mL each) at different time intervals in an argon flow. Each aliquot was injected to a solution of 1 mL of $CDCl_3$ and two drop of acetic acid. This mixture was used for ^{1}H NMR analysis to determine on one hand the ε-CL conversion during the copolymerization and on the other hand if the SO changes during the ε-CL polymerization. According to the measurements the SO

concentration stays unchangeable. From the mixture used for the ^{1}H NMR analysis, 0.15 mL was diluted with 1.5 mL of THF for SEC analysis. After 6h, 2.7 mL of THF solution of LLA (containing 0.54 g and 3.75 mmol LLA) was added quickly in an argon flow. Aliquots were withdrawn after 2 h for ^{1}H NMR and SEC analysis. The reaction was completely quenched after 2 h by addition of acetic acid, and the solution was poured into cold methanol to precipitate the terpolymer. The glassy solid was then collected, dried in vacuum and used for SEC and ^{1}H NMR analysis. Conv.(ε-CL) = 30%, conv.(LLA) > 97 %; $M_{n,theor}$(PCL) = 10.1 kg mol^{-1}, $M_{n,theor}$(PLLA) = 6.0 kg mol^{-1}, $M_{n,theor}$(PSO-b-PCL-b-PLLA) = 28.6 kg mol^{-1}. M_w/M_n(PSO-b-PCL) = 1.12, M_w/M_n(PSO-b-PCL-b-PLLA) = 1.15. ^{1}HNMR (600 MHz, $CDCl_3$) for the PCL and PLLA: δ/ppm =4.99-4.81 (PSO-CH_2*CH*(Phenyl)–OCO-PCL–), 4.34-3.71 (–OCO$CH_2CH_2CH_2CH_2$*CH*$_2$–), 2.43-2.17 (–OCO*CH*$_2CH_2CH_2CH_2CH_2$–),1.77-1.61 (–OCOCH_2*CH*$_2CH_2CH_2CH_2$–), 1.61-1.44 (–OCOCH (*CH*$_3$)–), 1.42-1.33 (–OCOCH_2CH_2*CH*$_2CH_2CH_2$–).

Poly(styrene oxide)-*b*-poly(ε-caprolactone)-*b*-poly(L-lactide) in dimethyl sulfoxide, solvent for the second monomer (Table 1, DMSO)

To the living PSO, 4 ml of dry DMSO was added and then 0.09 ml of DPP solution (0.043 mmol DPP) upon which the dark red color disappears immediately, a clear indication of the neutralization and deactivation of the active alkoxide PSO chain end. Then, 30 min later, 0.044 mL of *t*-BuP_2 (0.087 mmol) was added to the reaction mixture at room temperature and subsequently 3 mL of ε-CL (27 mmol), the reaction mixture was stirred. Aliquots were withdrawn (0.1 mL each) in different time intervals in an argon flow. Each aliquot was injected to a solution of 1 mL of $CDCl_3$ and two drop of acetic

acid. This mixture was used for ^{1}H NMR analysis for the determination of ε-CL conversion during the copolymerization and also to check the SO conversion (there was no evidence that there is any SO monomer consumption after the deactivation of the *t*-BuP_4 using DPP). From the mixture used for the ^{1}HNMR analysis, 0.15 mL was diluted with 1.5 mL of THF for SEC analysis. After 4 h, 2.7 mL of THF solution of LLA (containing 0.54, 3.75 mmol LLA) was added quickly in an argon flow. Aliquots were withdrawn after 30 min for ^{1}H NMR and SEC analysis. The reaction was completely quenched after 30 min by addition of acetic acid, and the solution was poured into cold methanol to precipitate the terpolymer. The glassy solid was then collected, dried in vacuum and used for SEC and ^{1}H NMR analysis. Conv.(ε-CL) = 65%, conv.(LLA)=35 %; $M_{n,theor}$(PCL) = 21.9 kg mol-1, $M_{n,theor}$(PLLA) = 1.9 kg mol-1, $M_{n,theor}$(PSO-b-PCL-b-PLLA) = 35 kg mol-1. M_w/M_n(PSO-*b*-PCL) = 1.21, M_w/M_n(PSO-*b*-PCL-*b*-PLLA) = 1.29.

Poly(styrene oxide)-*b*- poly(ε-caprolactone)-*b*-poly(L-lactide) in toluene, solvent for second monomer (Table 1, Toluene)

To the living PSO ($M_{n,nmr}$= 5.2 Kg/mol), 10 ml of dry toluene was added and then 0.09 ml of DPP solution (0.043 mmol DPP) upon which the dark red color disappears immediately, a clear indication of the neutralization and deactivation of the active alkoxide PSO chain end. Then, 30 min later, 0.044 mL of t-BuP_2 (0.087 mmol) was added to the reaction mixture at room temperature and subsequently 1 mL of ε-CL (9 mmol), the reaction mixture was stirred. Aliquots were withdrawn (0.1 mL each) at different time intervals in an argon flow. Each aliquot was injected to a solution of 1 mL of $CDCl_3$ and two drops of acetic acid. This mixture was used for ^{1}H NMR analysis for the

determination of ε-CL conversion during the copolymerization and also to check the SO conversion (there was no evidence that there is any SO monomer consumption after the deactivation of the *t*-BuP_4 with DPP). From the mixture used for the ^{1}HNMR analysis, 0.15 mL was diluted with 1.5 mL of THF for SEC analysis. After 5h, 2.7 mL of THF solution of LLA (containing 0.54 g and 3.75 mmol LLA) was added quickly in an argon flow. Aliquots were withdrawn after 30 min for ^{1}H NMR and SEC analysis. The reaction was completely quenched after 30 min by addition of acetic acid, and the solution was poured into cold methanol to precipitate the terpolymer. The glassy solid was then collected, dried in vacuum and used for SEC and ^{1}H NMR analysis. Conv.(ε-CL) = 90%, conv.(LLA)=35 %; $M_{n,theor}$(PCL) = 30.3 kg mol^{-1}, $M_{n,theor}$(PLLA) = 2.1 kg mol^{-1}, $M_{n,theor}$(PSO-*b*-PCL-*b*-PLLA) = 37.6 kg mol^{-1}. M_w/M_n(PSO-*b*-PCL) = bimodal distribution, M_w/M_n(PSO-*b*-PCL-*b*-PLLA) = bimodal distribution.

Sequential ROP of 1, 2-butylene oxide (BO) and ε-caprolactone (ε-CL) by using the new adapted catalyst switch approach

Typical procedure is as follows: 0.031 ml of PPA (0.23 mmol) was added at the flame-dried reactor via a syringe. Then 0.14 mL of *t*-BuP_4 solution (0.115 mmol) was added in an argon flow. After that, 1.0 mL of BO (11.5 mmol) was added to start the polymerization. Aliquots were withdrawn (0.1 mL each) in an argon flow after 20 h, and injected to a mixture of 1 mL of $CDCl_3$ and two drops of acetic acid. This solution was used for ^{1}H NMR measurement to determine the monomer conversion. 0.1 mL of such $CDCl_3$ solution was diluted with 1 mL of THF for SEC analysis. Conv. (BO) > 99%. $M_{n,theor}$ = 3.6 kg mol−1.$M_{n,SEC}$ = 6 kg mol^{-1}. M_w/M_n = 1.05.

To the living PBO ($M_{n,nmr}$= 3.4 Kg/mol), 5 ml of dry THF was added and then 0.23 ml of DPP solution (0.115 mmol DPP) upon which the yellow color disappears immediately, a clear indication of the neutralization and deactivation of the active alkoxide PBO chain end. Then, 30 min later, 0.12 mL of *t*-BuP_2 (0.23 mmol) was added to the reaction mixture at room temperature and subsequently 1 mL of ε-CL (9 mmol), the reaction mixture was stirred. Aliquots were withdrawn (0.1 mL each) at different time intervals in an argon flow. Each aliquot was injected to a solution of 1 mL of $CDCl_3$ and two drops of acetic acid. This mixture was used for ^{1}H NMR analysis to determine the ε-CL conversion during copolymerization. The reaction was quenched after 4h by addition of acetic acid, and the solution was poured into cold methanol to precipitate the copolymer. The white powder was then collected, dried in vacuum and used for SEC and ^{1}H NMR analysis. Conv.(ε-CL) = 30%, $M_{n,theor}$(PCL) = 1.2 kg mol^{-1}, , $M_{n,theor}$(PBO-b-PCL)= 4.8 kg mol^{-1}. M_w/M_n(PSO-b-PCL) = 1.09.

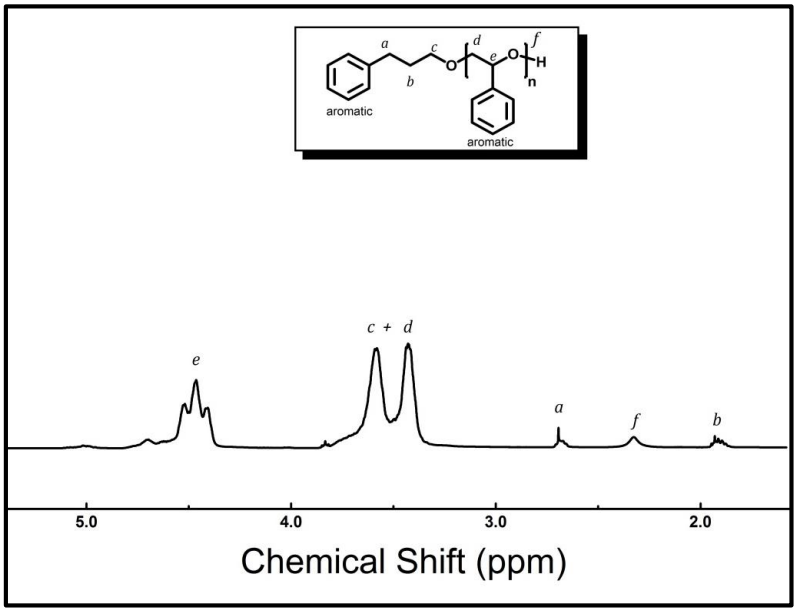

Figure S1. ^{1}H NMR spectrum of the PSO in $CDCl_3$

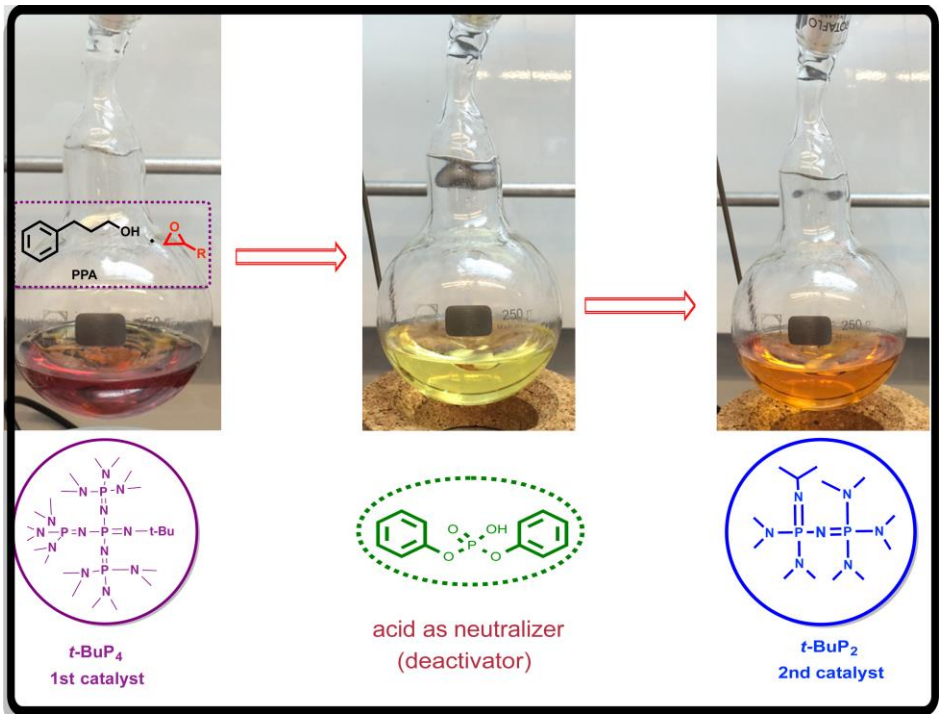

Figure S2. Left, living PSO with red color obtained by using t-BuP_4 as a catalyst; middle, deactivation of the strong base with DPP; Right, addition of t-BuP_2 as a base catalyst and sequential copolymerization of cyclic esters (ε-CL and L-lactide)

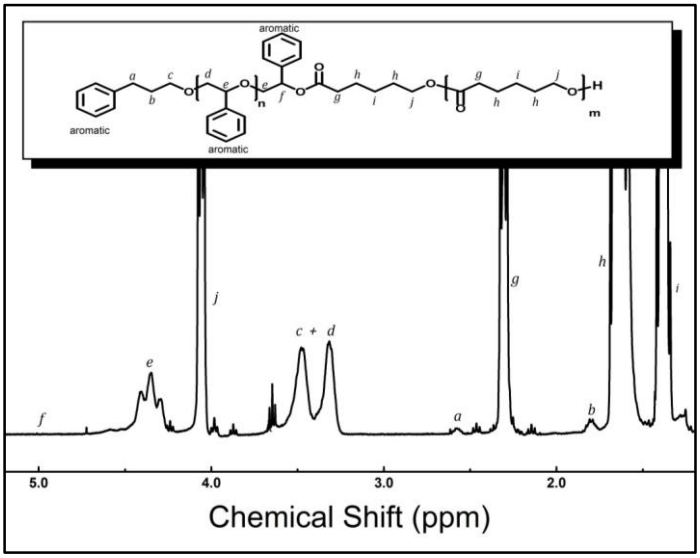

Figure S3. ^{1}H NMR spectra of poly (styrene oxide)-*b*-poly (*ε*-caprolactone) prepared by sequential addition *via* the new adapted organocatalyst switch approach

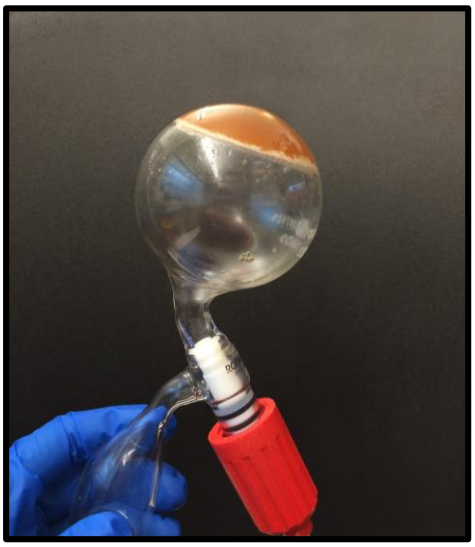

Figure S4. Gelation of poly (styrene oxide)-*b*-poly (*ε*-caprolactone) prepared by sequential addition *via* the new adapted organocatalyst switch approach using DMSO as solvent after 10 h upon addition of *ε*-CL monomer due to formation of intra/intermacromoleular esterification

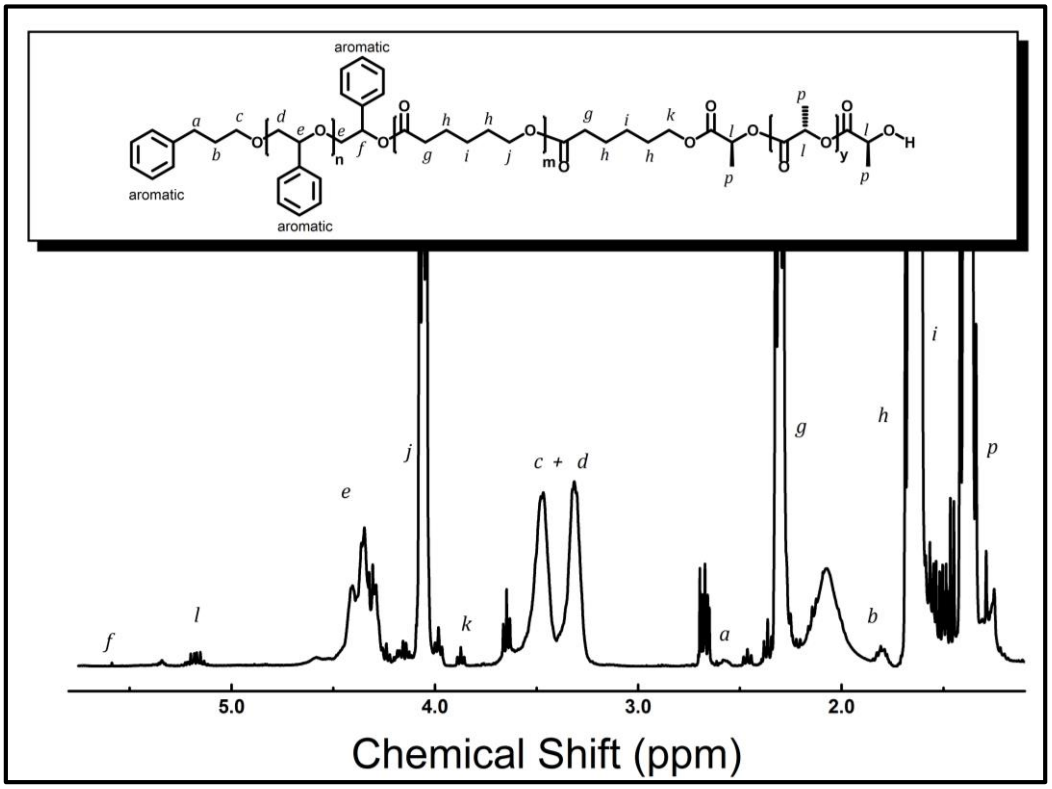

Figure S5. ^{1}H NMR spectra of the isolated poly(styrene oxide)-b-poly(ε-caprolactone)-b-poly(L-lactide) prepared by sequential addition via the new adapted organocatalyst switch approach in DMSO

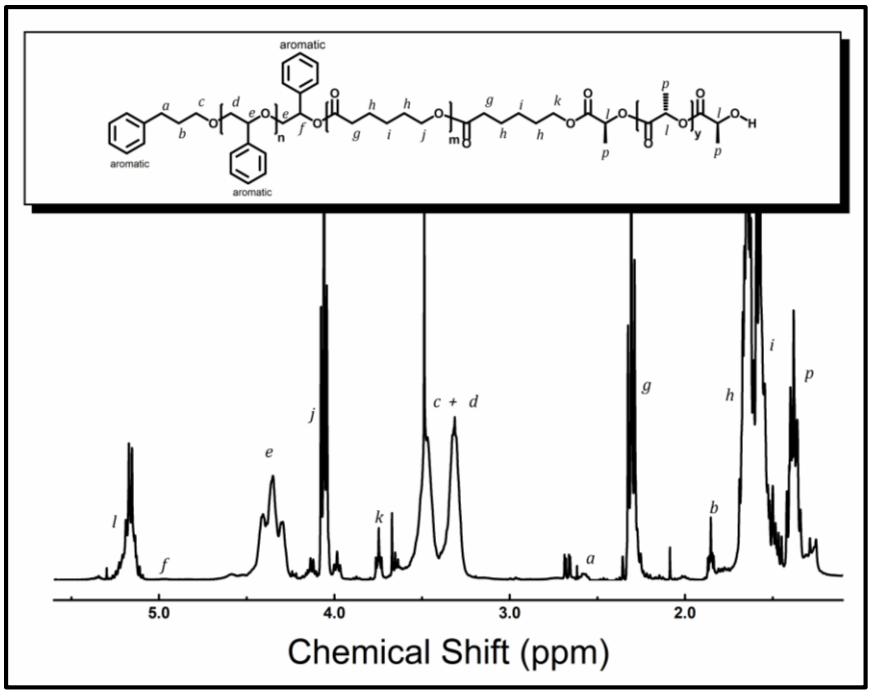

Figure S6. ^{1}H NMR spectra of the isolated poly(styrene oxide)-*b*-poly(*ε*-caprolactone)-*b*-poly(L-lactide) prepared by sequential addition *via* the new adapted organocatalyst switch approach in toluene

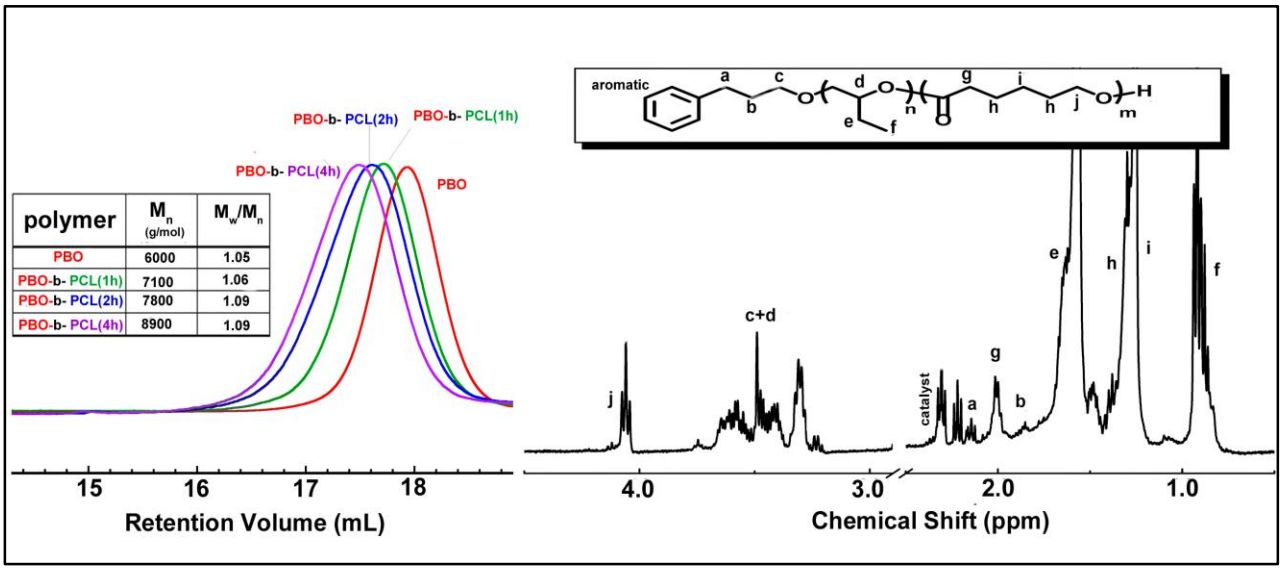

Figure S7. Left, SEC traces obtained from withdrawn aliquots during the *t*-BuP$_4$-catalyzed ROP of BO (red) and the sequential block copolymerization of ε-CL monomers in THF using the *t*-BuP$_2$ as a catalyst after the deactivation of *t*-BuP$_4$ with DPP. Right, ^{1}H NMR spectra of the isolated poly(butylene oxide)-b-poly(ε-caprolactone.

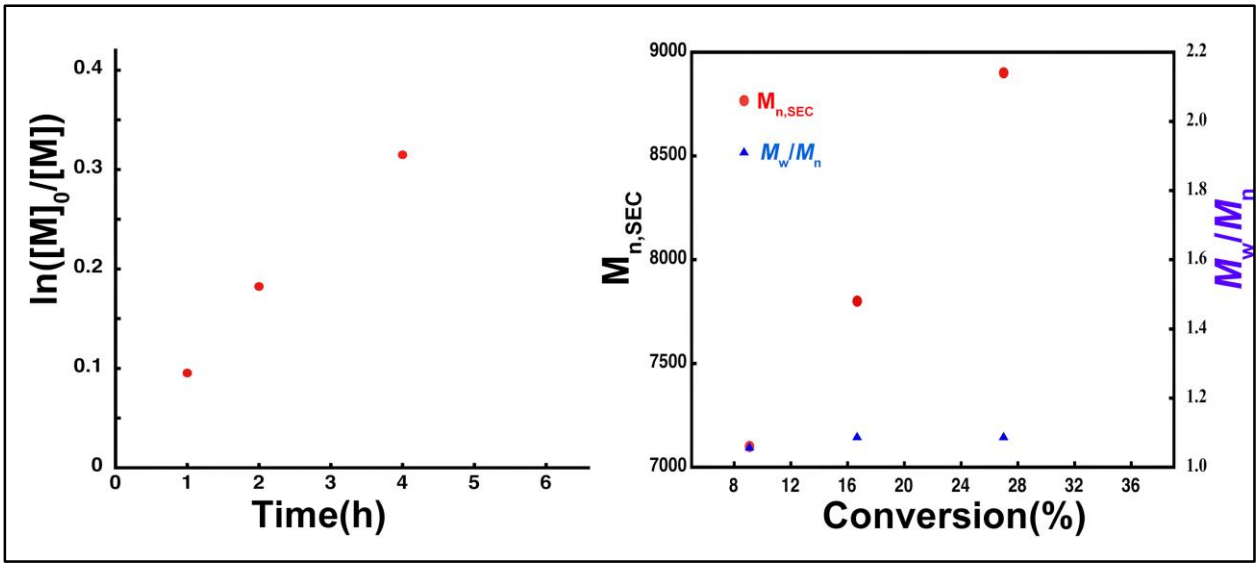

Figure S8. Left: Kinetic plots of the subsequent t-BuP_2-catalyzed ROP of ε-CL using the secondary alcohol macroinitiator (living poly Butylene oxide) via the new catalyst switch approach. Right: The dependence of the apparent molar mass and polydispersity of the growing PCL on monomer conversion during the above mentioned adapted catalyst switching approach

Table S1. Molecular characteristics as obtained from SEC analysis for the PSOs and the corresponding PSOs-*b*-PCLs and PSOs-*b*-PCL-*b*-PLLA prepared by *t*-BuP_2-catalyzed sequential ROP of ε-CL and LLA monomer, in THF

THF	$M_{n,SEC}$[a] (g/mol)	M_w/M_n[a]
PSO	5100	1.06
PSO-*b*-(PCL 1h)	6500	1.07
PSO-*b*-(PCL 2h)	7700	1.09
PSO-*b*-(PCL 4h)	9900	1.11
PSO-*b*-(PCL 6h)	11500	1.12
PSO-*b*-PCL-b-PLLA (2h)	13700	1.16

[a]as determined by SEC in THF at 35 °C calibrated using polystyrene standards

Table S2. Molecular characteristics as obtained from SEC analysis for the PSOs and the corresponding PSOs-*b*-PCLs and PSOs-*b*-PCL-*b*-PLLA prepared by *t*-BuP$_2$-catalyzed sequential ROP of ε-CL and LLA monomer, in DMSO

DMSO	$M_{n,SEC}$[a] (g/mol)	M_w/M_n[a]
PSO	6900	1.07
PSO-*b*-(PCL 2h)	13900	1.13
PSO-*b*-(PCL 4h)	15500	1.21
PSO-*b*-PCL-b-PLLA (30min)	16200	1.22

[a] as determined by SEC in THF at 35 °C calibrated using polystyrene standards

Table S3. Molecular characteristics as obtained from SEC analysis for the PSOs and the corresponding PSOs-*b*-PCLs and PSOs-*b*-PCL-*b*-PLLA prepared by *t*-BuP$_2$-catalyzed sequential ROP of ε-CL and LLA monomer, in toluene

Toluene	$M_{n,SEC}$[a] (g/mol)	M_w/M_n[a]
PSO	500	1.07
PSO-*b*-(PCL 1h)	1000	bimodal distribution
PSO-*b*-(PCL 5h)	1500	bimodal distribution
PSO-*b*-PCL-b-PLLA (30min)	2300	bimodal distribution

[a] as determined by SEC in THF at 35 °C calibrated using polystyrene standards