Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting information

Ring-opening polymerization of ω-pentadecalactone catalyzed by phosphazene superbases

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Experimental

Materials

Toluene (AnalaR NORMAPUR® ACS, VWR international chemicals) was dried over calcium hydride (CaH_2, 95%, Sigma-Aldrich) and polystyrilithium and distilled before used. ω-pentadecalactone (PDL, >98%) from Tokyo Chemical Industry (TCI) was distilled twice over CaH_2 under dynamic vacuum and stored under argon (Ar) in glovebox (MBraun, Germany). Phosphazene superbases (PSBs) (t-BuP_2: 2 M solution in THF; t-BuP_4: 0.8 M solution in hexane; t-octylP_4:1.0 M solution in hexane), acetic acid (99.7%) were purchased from Sigma-Aldrich. Poly(ethylene glycol) monomethyl ether (MPEG, Sigma-Adrich) with an average M_w of 2000 g mol^{-1} was purified by dissolving in 1,4-dioxane (anhydrous, 99.8%, Sigma-Aldrich) and cryo-evaporating 1,4-dioxane, followed by drying on the vacuum line overnight. Benzyl alcohol (BnOH, 99.8%) and 3-phenyl-1-propanol (PPA, 98%) from Sigma-Aldrich were distilled under vacuum. N,N'-dimethyl ethanolamine (DMEA, 99.5%) was dried by anhydrous sodium sulfide under Ar overnight and filtered twice. All alcohols and PSBs were stored in glovebox under Ar. Trans-2-[3-(4-tertbutylphenyl)-2-methyl-2-propylidene] malonitrile (DCTB, 99.0%), dithranol (≥98.0%), and sodium-trifluoroacetate (Na-TFA, 98%) were used as received.1-(3,5-

bis(trifluoromethyl)phenyl)-3-cyclohexylthiourea (TU-1, Scheme S3) was prepared according to literature.[1,2] Sodium methoxide (NaOMe) was prepared by reacting sodium metal (≥98.0%, Sigma-Aldrich) with methanol under Ar atmosphere. 1,3-bis(4-trifluoromethyl)phenyl thiourea (TU-2, Scheme S3) (>97.0%) was purchased from TCI. Triethylborane (1.0 M in THF) and tris(perfluorophenyl)borane (95%) were purchased from Sigma-Aldrich and used as received.

Instrumentation

Nuclear magnetic resonance (NMR) measurements were carried out at 55 °C using a Bruker AVANCEDIII spectrometer operating at 600 MHz; $CDCl_3$ (Aldrich) was used as solvent. ^1H NMR spectra were used to calculate the number-average molecular weight (M_n, NMR) of the polyester by using the integrals of the characteristic signals from the end group and polyester main body. High-temperature gel permeation chromatography (HT-GPC) measurements were performed with a Viscoteck HT-GPC module 350 instrument with two PLgel 10 mm MIXED-B columns. 1,2,4 –trichlorobenzene (TCB) was used as eluent at a flow rate of 0.8 mL min^{-1} at 150 °C. The instrument was calibrated with PS standards. Matrix assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI−TOF−MS) measurements were performed on a Bruker Ultraflex III MALDI−TOF mass spectrometer (Bruker Daltonik, Bremen, Germany). Samples were dissolved in $CHCl_3$ (10 mg mL^{-1}) and mixed with a solution of sodium trifluoroacetate in THF (3 mg mL^{-1}) in a volume ratio of 10:3. This solution was then mixed with a matrix solution, DCTB or dithranol in THF (20 mg mL^{-1}), in a volume ratio of 1:1. Then, 0.1 μL of the final solution was spotted on the target plate. The linear positive ion mode was used to acquire the mass spectra of the samples. The calibration was done externally with poly(methyl methacrylate) standards. Differential scanning calorimetry (DSC) measurements were performed with a Mettler Toledo DSC1/TC100 under nitrogen (N_2) atmosphere. The samples were first heated from room temperature to 150 °C in order to erase the thermal history, then cooled to −100 °C and finally heated again to 150 °C at a heating/cooling rate of 10 °C min^{-1}. The second heating curve was used to determine the melting temperature (T_m).

Synthetic procedure

Typical polymerization procedure (Table 1, entry 12): in a glove box under Ar atmosphere, 1.08 g PDL (4.5 mmol), 4.6 µL BnOH (45 µmol), 56 µL (45 µmol) *t*-BuP$_4$ solution and 4.6 mL dry toluene were charged into a round bottom flask. The flask was quickly sealed by a stopcock, removed from the glove box and stirred for 2 h in a preheated oil bath at 80 ˚C. The reaction was quenched by adding CH_3COOH/MeOH (10 vol%) and cooled to room temperature. For all polymerization reactions, 0.1 mL of crude product was withdrawn and dissolved in $CDCl_3$ to check the conversion of monomer by ^1H NMR spectroscopy. The rest of the reaction mixture was precipitated in 200 mL of methanol, filtered by glass filter and dried in *vacuo* at 45 ˚C for 12 h.

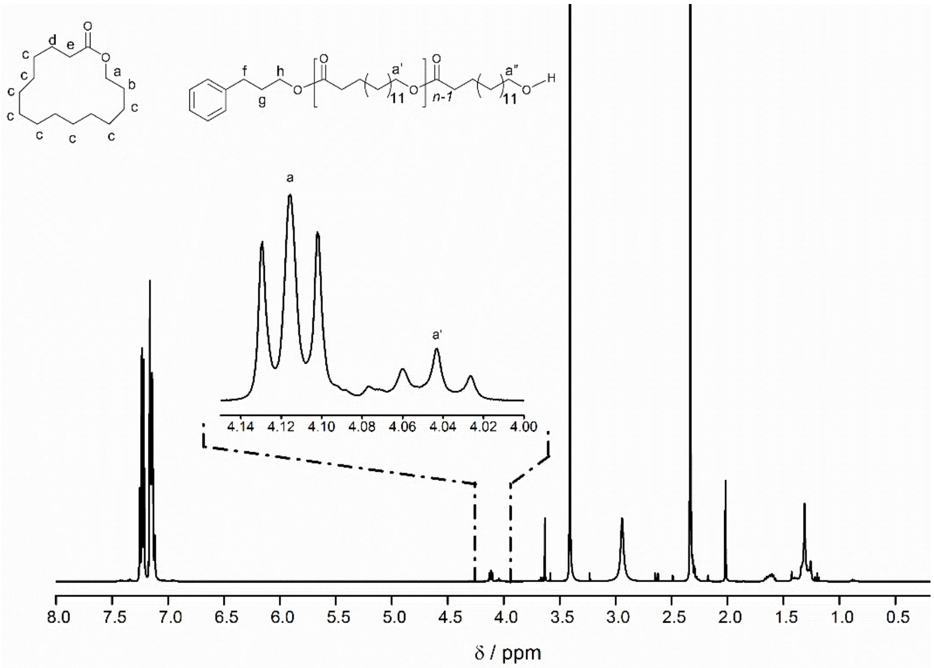


Figure S1. Monitoring the conversion of PDL to PPDL with the time, by 400 MHz ^1H NMR spectroscopy ($CDCl_3$, 55 ˚C)

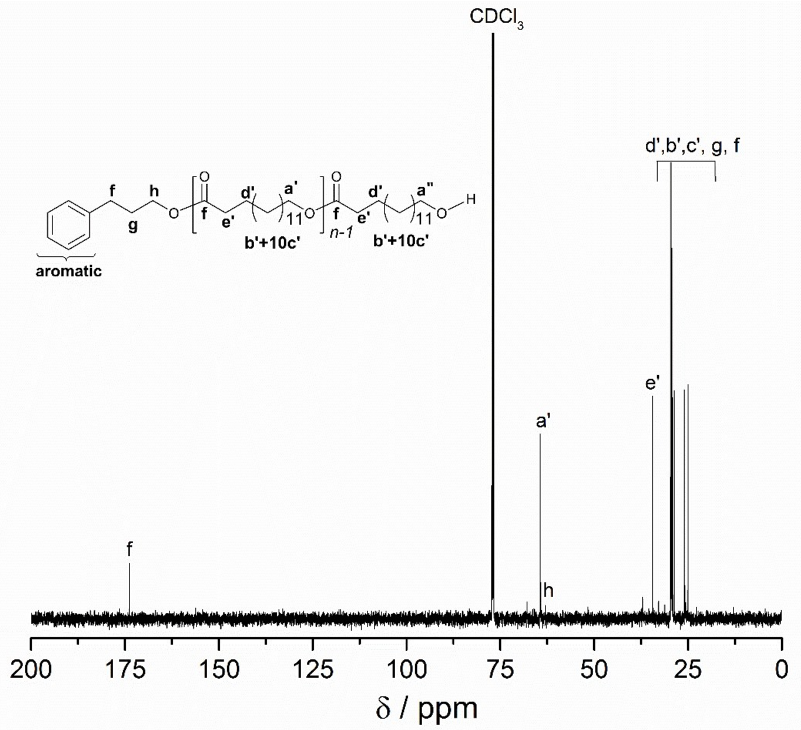


Figure S2. ^{13}C NMR spectrum of PPDL prepared by ROP of PDL catalyzed by *t*-BuP$_4$ at 0.4 M (CDCl$_3$, 55 ˚C).

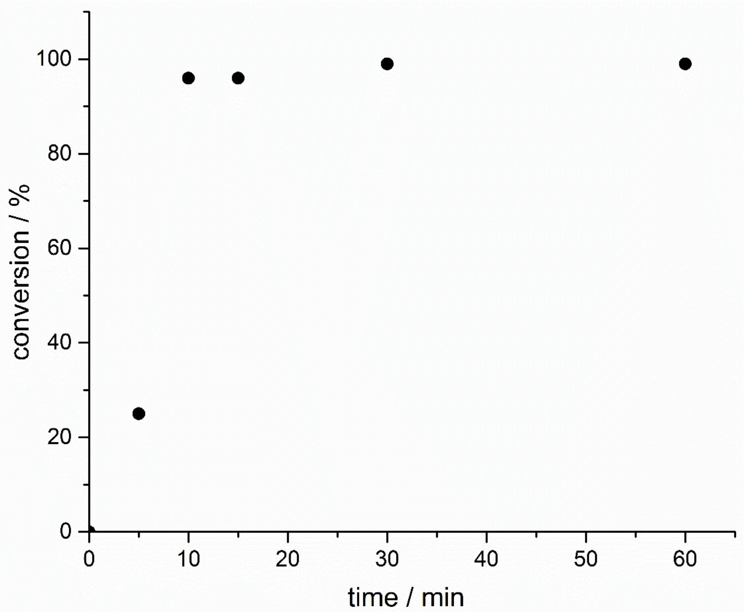


Figure S3. Time *vs* conversion plot of ROP of PDL catalyzed by *t*-BuP$_4$ with [PDL]$_o$ 0.7 M.

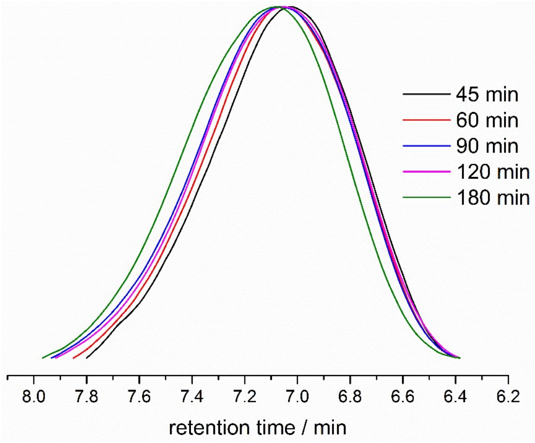
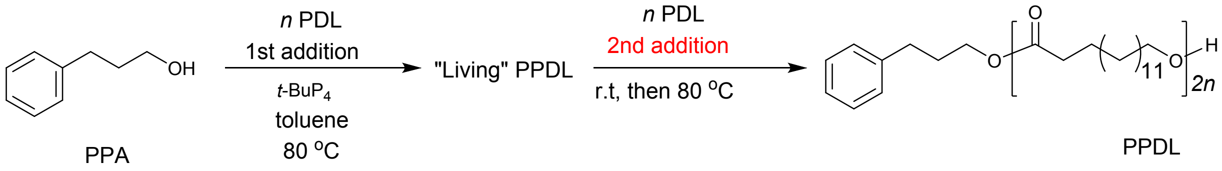


Figure S4. HT-GPC traces of PPDL from kinetic experiments of the PDL ROP catalyzed by *t*-BuP$_4$ (TCB, 150 °C).



Scheme S1. One-pot sequential block homopolymerization of PDL catalyzed by *t*-BuP$_4$.

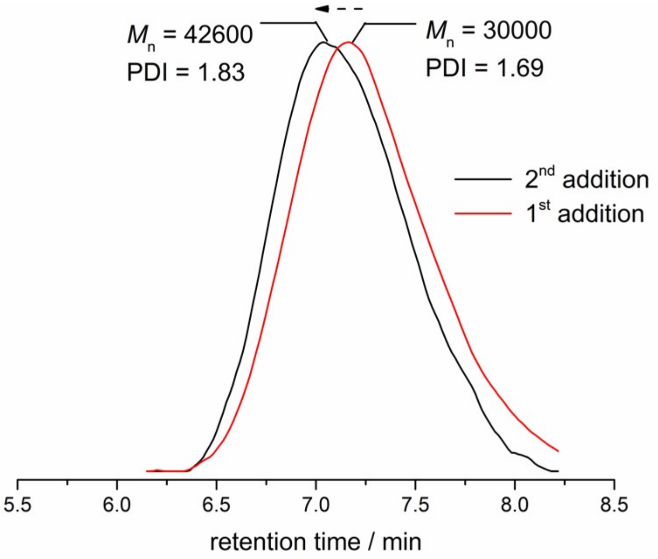


Figure S5. Sequential block homopolymerization of PDL: HT-GPC traces of PPDL after the first and second addition of PDL catalyzed by *t*-BuP$_4$ (TCB, 150 °C).

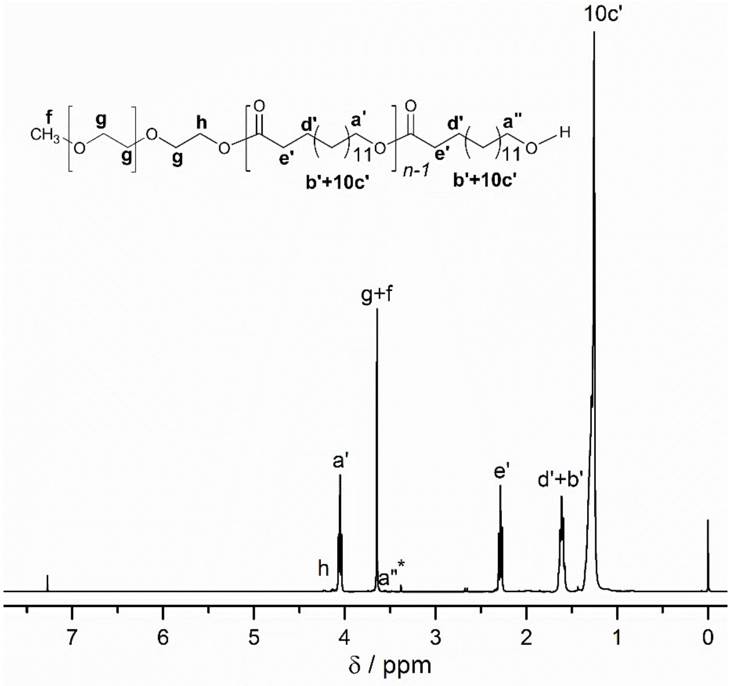
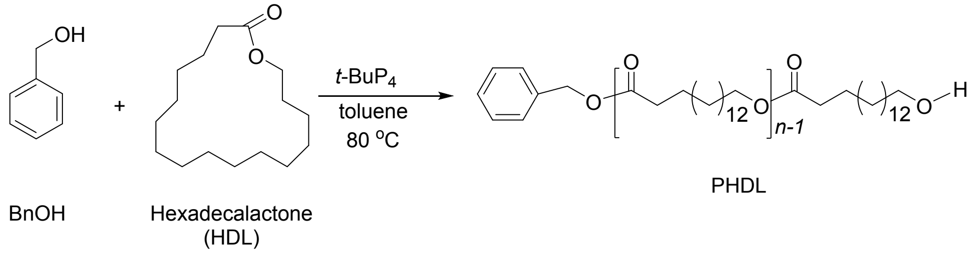


Figure S6. 600 MHz ^{1}H NMR spectrum of PPDL-*b*-MPEG [MPEG:poly(ethylene glycol) monomethyl ether) prepared by sequential block RO copolymerization of PDL and MPEG, catalyzed by *t*-BuP$_4$ (CDCl$_3$, 55 °C).

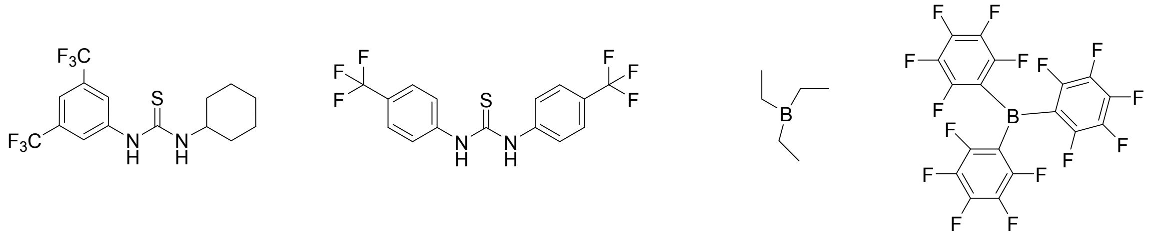


Scheme S2. ROP of hexadecalactone (HDL) catalyzed by *t*-BuP$_4$.

Table S1. ROP of HDL catalyzed by *t*-BuP$_4$.[a]

I	Cat.	$[HDL]_0/[I]_0/[P_4]$	$[HDL]_0$ (M)	T (°C)	time (h)	conv[b] (%)	TOF[c] (h^{-1})	$M_{n,calcd}$[d] (Kg mol^{-1})	$M_{n,NMR}$[e] (Kg mol^{-1})	$Đ_M$[f]
BnOH	*t*-BuP$_4$	100/1/0.4	0.4	80	2	91	45.5	21.8	51.8	1.56

[a]Polymerization was performed in toluene under Ar. [b]Conversion of HDL was determined by 400 MHz ^{1}H NMR spectrum of the polymerization product from the integral of α-methylene protons of HDL and PHDL in CDCl$_3$. [c] Turnover frequency was determined from the conversion and reaction time. [d]Number-average molecular weight calculated from [HDL]/[OH] × conv × 254.41 (mol. Weight of HDL). [e]Determined by 600 MHz ^{1}H NMR spectrum of methylene protons from initiator and α-methylene protons of PHDL. [f]Determined by HT-GPC in 1,2,4-trichlorobenzene (TCB) at 150 °C with polystyrene standards.



TU-1 TU-2 B-1 B-2

Scheme S3. Different thiourea and borane derivatives tested as PDL activators for the ROP.

Table S2. Polymerization of PDL initiated by NaOMe or BnOH with different PDL activators (M_{act}).[a]

run	I	$M_{act.}$	$[PDL]_0/[I]_0/[P_4]/[M_{act}.]$	[PDL] (M)	T (°C)	time (days)	conv (%)	$M_{n,calcd}$ (Kg mol^{-1})	$M_{n,NMR}$ (Kg mol^{-1})	$Đ_M$
1	NaOMe	TU-1	50/1/-/4.8	1.9	80	3	–	–	–	–
2	BnOH	TU-1	100/1/1/3	1	80	4	–	–	–	–
3	BnOH	TU-2	100/1/0.6/2.7	1.5	80	7	–	–	–	–
4	BnOH	B-1	100/1/0.4/2	0.7	80	4	–	–	–	–
5	BnOH	B-2	50/1/0.6/1.5	1	80	5	–	–	–	–

[a] Polymerization was performed in toluene under Ar.

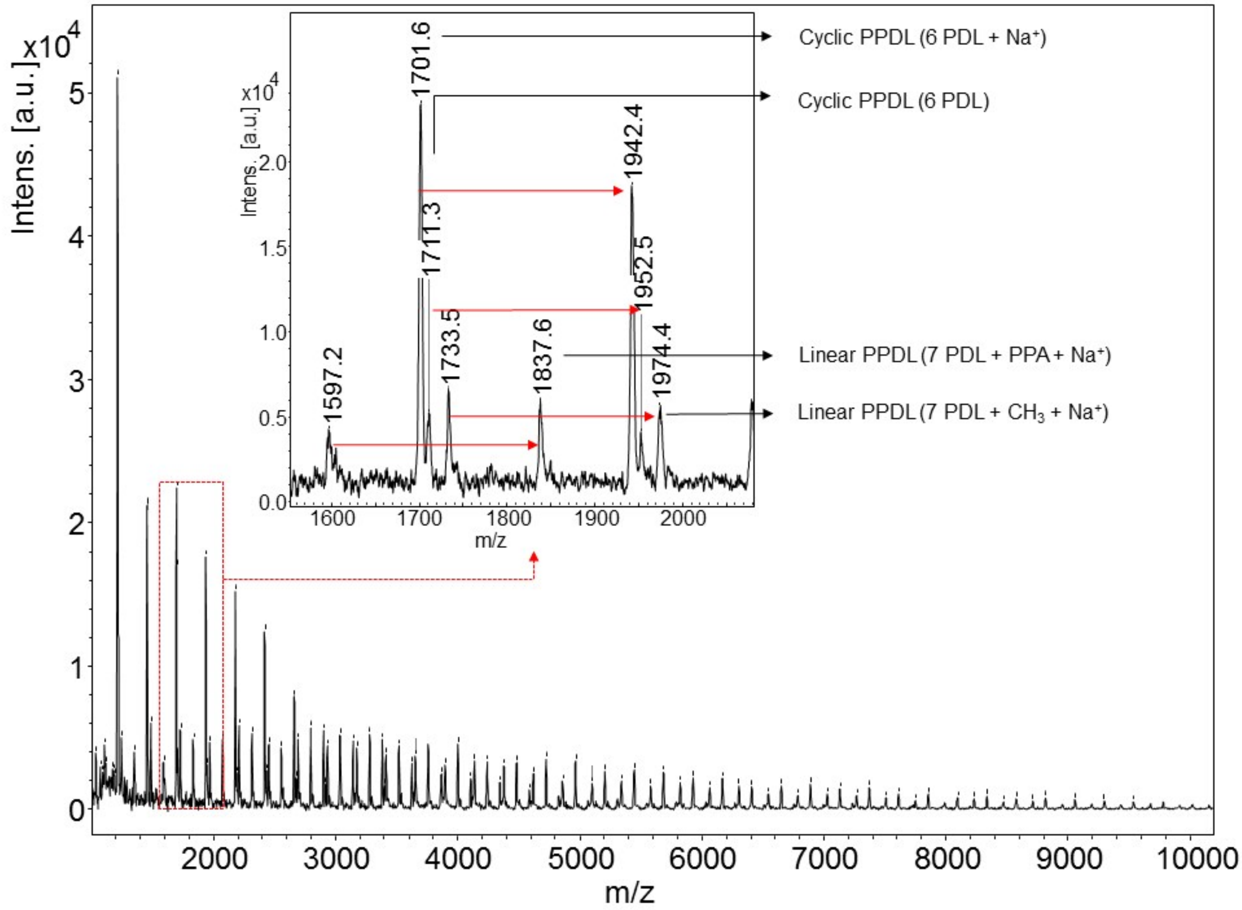


Figure S7. MALDI-TOF-MS spectrum of PPDL precipitated in MeOH.

References

1. A. Lu, Z. Wang, Z. Zhou, J. Chen and Q. Wang, *Journal of Agricultural and Food Chemistry*, 2015, **63**, 1378-1384.
2. P. Thanigaimalai, K.-C. Lee, V. K. Sharma, C. Joo, W.-J. Cho, E. Roh, Y. Kim and S.-H. Jung, *Bioorganic & Medicinal Chemistry Letters*, 2011, **21**, 6824-6828.