Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Traceless switch organocatalysis enables multiblock ring-opening copolymerizations of lactones, carbonate, and lactide: by one plus one and in one-pot

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Contents

Experimental section

One-pot synthesis of poly(*ε*-caprolactone)-*b*-poly(L-lactide)-*b*- poly(trimethylene carbonate) and poly(*δ*-valerolactone)-*b*-poly(L-lactide)-*b*-poly(trimethylene carbonate) tribock terpolymers.

Following the Procedure of synthesis of PVL-*b*-PLLA, TMC (183.6 mg, 1.8 mmol) was placed to the mixture of PVL-*b*-PLA to start the third polymerization. After 6 h, the whole third polymerization was quenched by addition of triethylamine and benzoic acid. Before this step, an aliquot of the reaction mixture was obtained and an excess of triethylamine and benzoic acid was added for determining the monomer conversion from ^{1}H NMR measurements. The triblock terpolymer (PVL-*b*-PLLA-*b*-PTMC) was isolated by reprecipitation in cold methanol, and then was filtered and dried under vacuum. Conv.: 95 %. $M_{n,\ NMR}$ = 14200 g mol^{-1}; M_w/M_n = 1.30. ^{1}H NMR ($CDCl_3$, 300 MHZ): δ (ppm) 1.57 (q, 3H × m (–C*H*$_3$)$_m$), 1.68 (m, 2H × n, (–CH$_2$C*H*$_2$CH$_2$O–)$_n$; m, 2H × n, (–COCH$_2$C*H*$_2$CH$_2$–)$_n$), 2.01–2.05 (m, 2H × j − 1, (–OCH$_2$C*H*$_2$–)$_{j-1}$; q, 2H, –C*H*$_2$CH$_2$OH), 2.34 (t, 2H × n, (–OCOC*H*$_2$CH$_2$–)$_n$), 3.74 (t, 2H, –C*H*$_2$OH), 4.08 (t, 2H × n, (–CH$_2$C*H*$_2$O-)$_n$), 4.18–4.34 (m, 4H × j − 1, (–OC*H*$_2$CH$_2$C*H*$_2$O–)$_{j-1}$; m, 2H, –OC*H*$_2$CH$_2$CH$_2$OH), 5.11–5.23 (q, 1H × m, (–C*H*(CH$_3$)O–)$_m$; s, 2H, ArC*H*$_2$O), 7.24–7.41 (m, 5H, aromatic).

A similar condition was used for one-pot block copolymerization of CL and LA with TMC to precisely synthesize triblock terpolymer of PCL-*b*-PLLA-*b*-PTMC. Conv.: 94 %. $M_{n,\ NMR}$ = 15700 g mol^{-1}; M_w/M_n = 1.37. ^{1}H NMR ($CDCl_3$, 300 MHZ): δ (ppm) 1.40 (m, 2H × n, (–CH$_2$CH$_2$C*H*$_2$CH$_2$CH$_2$–)$_n$), 1.54 (q, 3H × m (–C*H*$_3$)$_m$), 1.65 (m, 2H × 2n, (–C*H*$_2$CH$_2$C*H*$_2$CH$_2$O–)$_n$), 1.95–2.12 (m, 2H × j − 1, (–OCH$_2$C*H*$_2$–)$_{j-1}$; q, 2H, –C*H*$_2$CH$_2$OH), 2.31 (t, 2H × n, (–OCOC*H*$_2$CH$_2$–)$_n$), 3.75 (t, 2H, –C*H*$_2$OH), 4.06 (t, 2H × n, (–CH$_2$C*H*$_2$O–)$_n$), 4.18–4.36 (m, 4H × j − 1, (–OC*H*$_2$CH$_2$C*H*$_2$O–)$_{j-1}$; m, 2H, –OC*H*$_2$CH$_2$CH$_2$OH), 5.10–5.26 (q, 1H × m, (–C*H*(CH$_3$)O–)$_m$; s, 2H, ArC*H*$_2$O), 7.21–7.43 (m, 5H, aromatic).

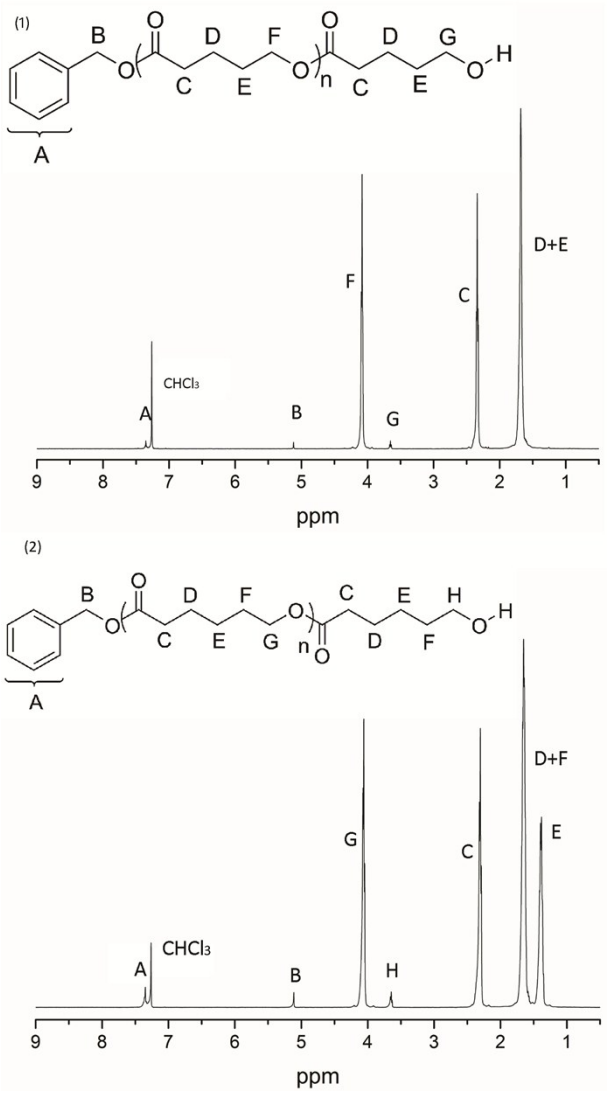

Figure S1: The ^{1}H NMR spectra ($CDCl_3$, 300 MHz) of (1) poly(*δ*-valerolactone) (PVL, Table 1, run1)and (2) poly(*ε*-caprolactone) (PCL, Table 1, run 5) initiated from benzyl alcohol (BnOH).

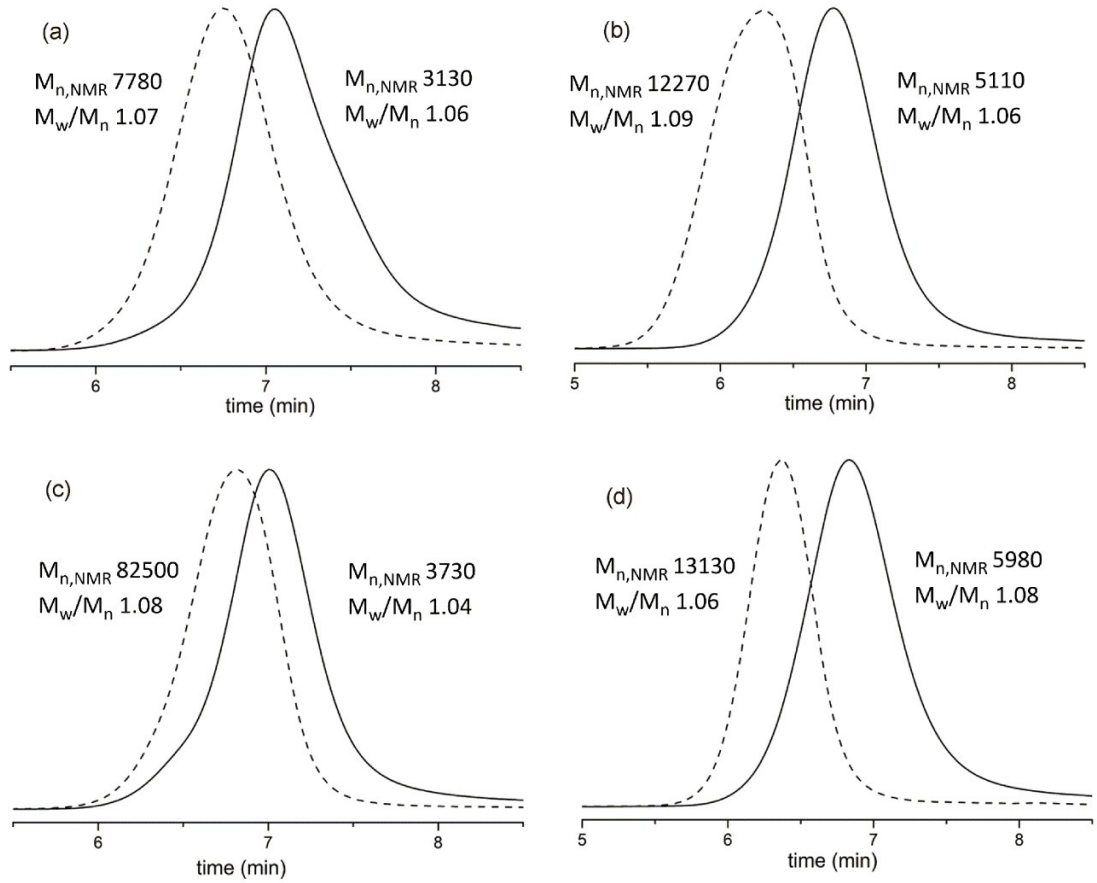

Figure S2: SEC traces of the first sequence of PVL (**a**, solid line; PVL, Table 1, run 1; and **b**, solid line; PVL, Table 1, run 11), and PCL (**c**, solid line; PCL, Table 1, run 3; and **d**, solid line; PCL, Table 1, run 12), the PVL-*b*-PLA diblock copolymer (**a**, dashed line; PVL-PLA, Table 1, run 14; and **b**, dashed line; PVL-PLA, Table 1, run 15), and the PCL-*b*-PLA diblock copolymer (**c**, dashed line; PCL-PLA, Table 1, run 17; and **d**, dashed line; PCL-PLA, Table 1, run 18) (eluent, THF; flow rate, 1.0 mL min^{-1}).

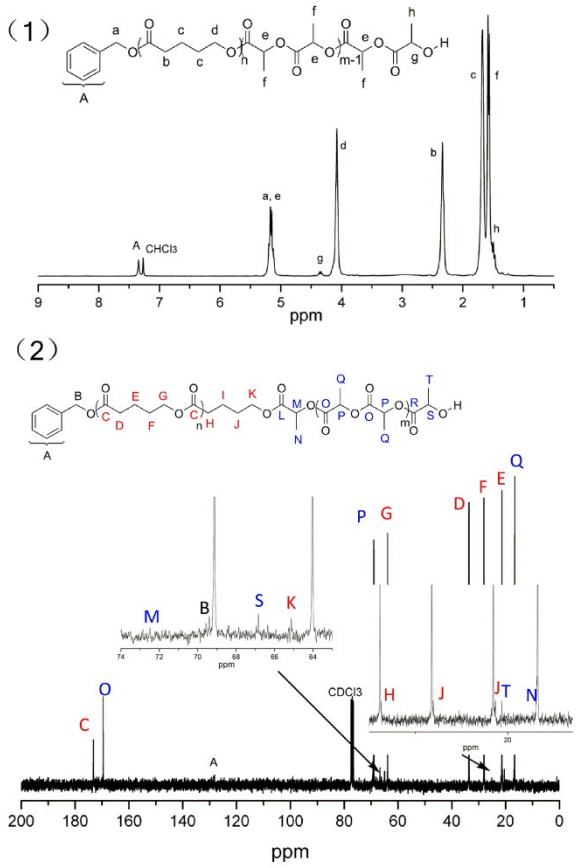

Figure S3: The ^{1}H NMR (1) and ^{13}C NMR (2) spectra ($CDCl_3$) of PVL-*b*-PLLA (PVL-PLA, Table 1, run 15) initiated from benzyl alcohol (BnOH).

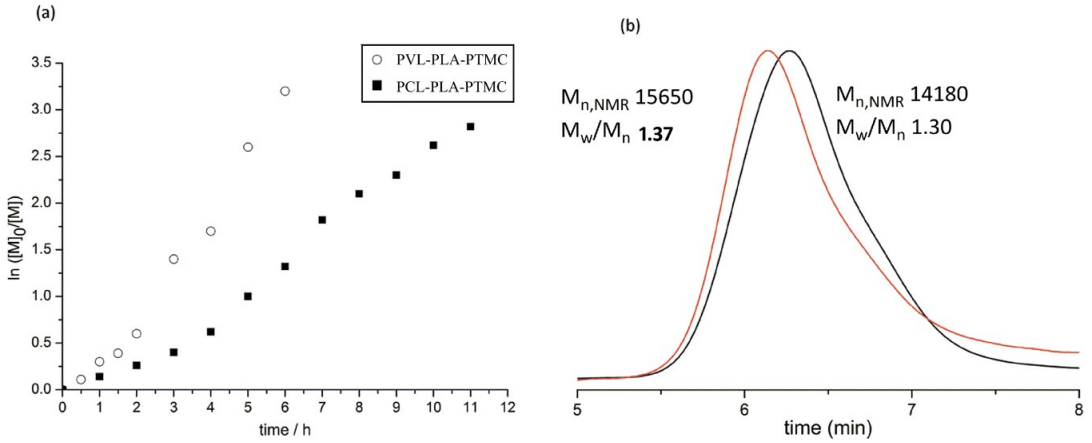

Figure S4: (a) The kinetics plots of TMC (○, PVL-PLA-PTMC in Table 1, run 19; ■, PCL-PLA-PTMC in Table 1, run 20) in their third feed ROPs, and **(b)** The SEC traces of the triblock terpolymers (black, PVL-PLA-PTMC; red, PCL-PLA-PTMC) (eluent, THF; flow rate, 1.0 mL min^{-1}).

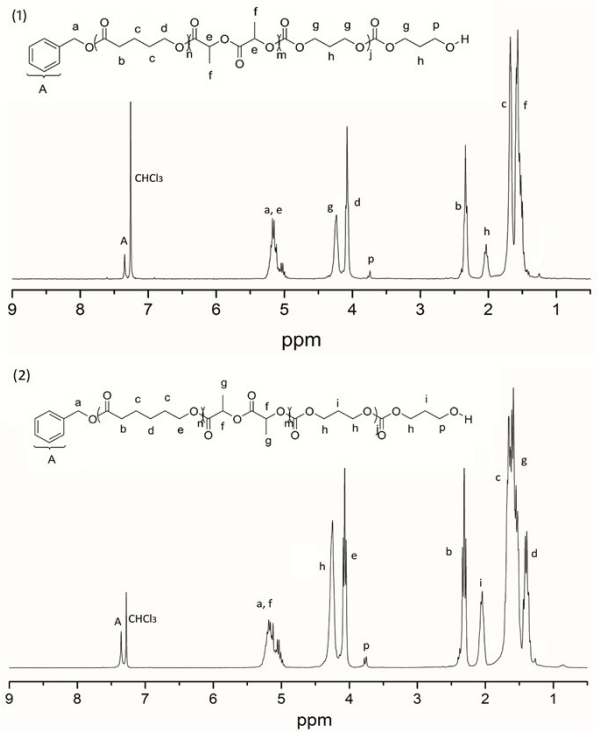

Figure S5: The ^{1}H NMR spectra ($CDCl_3$, 300 MHz) of (1) PVL-*b*-PLLA-*b*-PTMC triblock terpolymer (Table 1, run 19) and (2) PCL-*b*-PLLA-*b*-PTMC triblock terpolymer (Table 1, run 20) initiated from benzyl alcohol (BnOH).

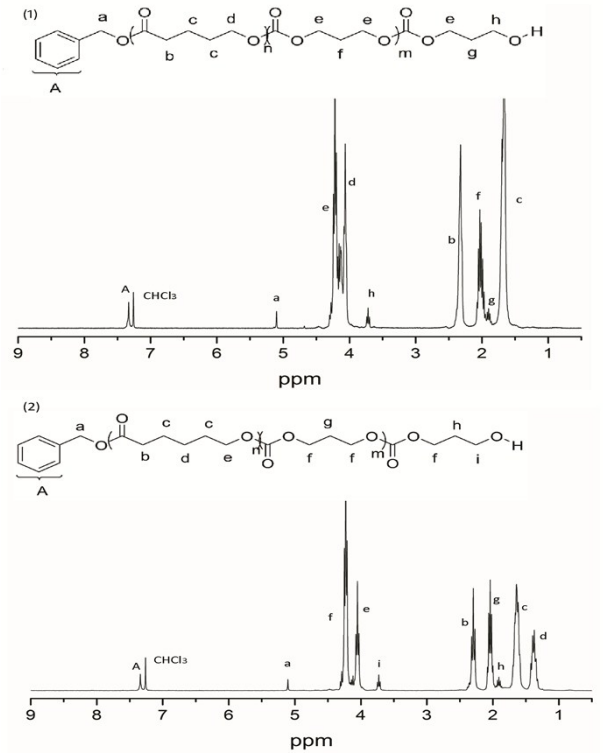

Figure S6: The ^{1}H NMR spectra ($CDCl_3$, 300 MHz) of (1) PVL-*b*-PTMC diblock copolymer (Table 2, run 21) and (2) PCL-*b*-PTMC diblock copolymer (Table 2, run 22) initiated from benzyl alcohol (BnOH).

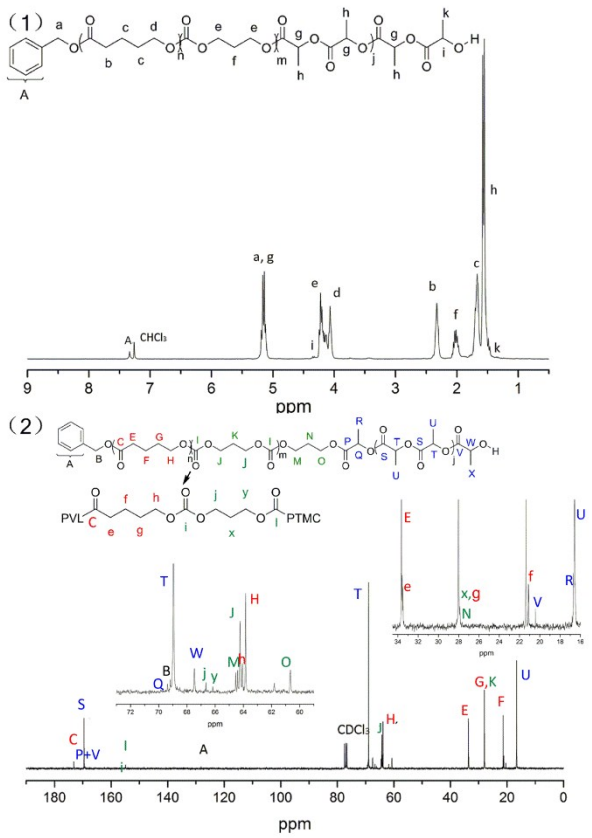

Figure S7: The ^{1}H NMR (1) and ^{13}C NMR (2) spectra ($CDCl_3$) of PVL-*b*-PTMC-*b*-PLLA (PVL-PTMC-PLA, Table 2, run 25) initiated from benzyl alcohol (BnOH).

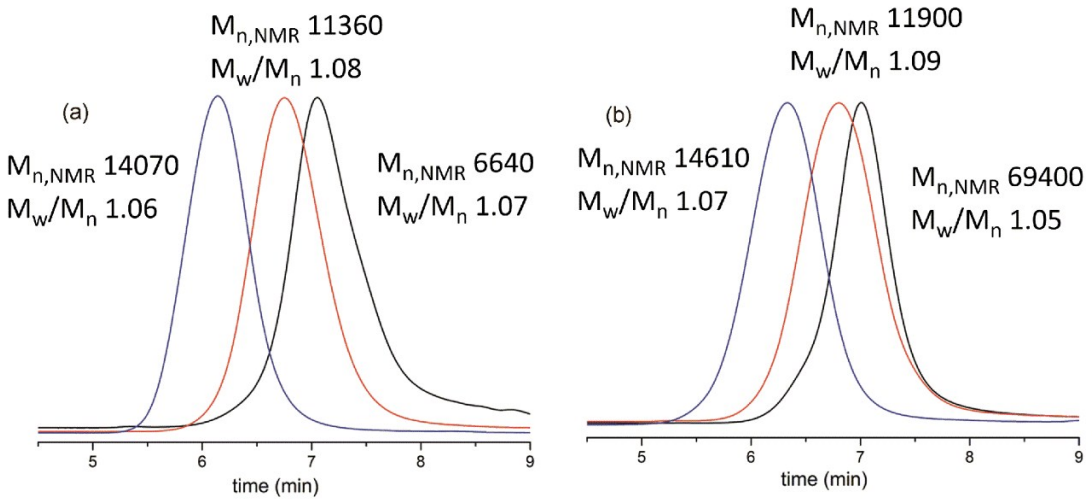

Figure S8: SEC traces of **(a)** the diblock copolymer of PVL-*b*-PTMC (black, PVL-PTMC, Table 2, run 21), the triblock terpolymer PVL-*b*-PTMC-*b*-PLA (red, PVL-PTMC-PLA, Table 2, run 23) and the triblock terpolymer PVL-*b*-PTMC-*b*-PLA (blue, PVL-PTMC-PLA, Table 2, run 25); and **(b)** the diblock copolymer of PCL-*b*-PTMC (black, PCL-PTMC, Table 2, run 22), the triblock terpolymer PCL-*b*-PTMC-*b*-PLA (red, PCL-PTMC-PLA,

Table 2, run 24) and the triblock terpolymer PCL-*b*-PTMC-*b*-PLA (blue, PCL-PTMC-PLA, Table 2, run 26) (eluent, THF; flow rate, 1.0 mL min^{-1}).