'Immortal’ ring-opening polymerisation of ω-
pentadecalactone by Mg(BHT)$_2$(THF)$_2$

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Supplementary Information

Materials All reagents were purchased from Sigma Aldrich, except 2,6-Di-tert-4-methylphenol was purchased from Alfa Aesar and ε-caprolactone was purchased from Acros. All solvents were supplied by Fischer and dried using an Innovative Technology Inc. Pure Solv MD-4-EN solvent purification system. Benzyl alcohol and ε-caprolactone were dried over calcium hydride for 24 h before vacuum distillation. ω-Pentadecalactone was dissolved in 75 wt.% toluene and dried for 18 h on molecular sieves. All other reagents were used as received.

Instrumental methods Proton ($^1$H) NMR spectra were recorded using a Bruker DPX-300 spectrometer at 300 MHz. Carbon ($^{13}$C) NMR spectra were recorded using a Bruker DPX-400 spectrometer or Bruker AV-II-700 spectrometer. All chemical shifts were recorded in parts per million (ppm) relative to a reference peak of chloroform solvent at $\delta = 7.26$ ppm and 77.16 ppm for $^1$H and $^{13}$C NMR spectra respectively. Molecular weights were determined through gel permeation chromatography (GPC) using an Agilent 390-MDS on PLgel Mixed-D type columns in series with refractive index (RI) detection. Weights were calculated using a calibration curve determined from poly(styrene) standards with chloroform with 2.5 %vol NEt$_3$ as eluent at 40 °C, flowing at 1.0 mL.min$^{-1}$ and sample concentration 3 mg mL$^{-1}$.

Synthesis of Mg(BHT)$_2$(THF)$_2$: Di-n-butylmagnesium (1 M in heptane, 30 mL, 30 mmol) was added dropwise to a solution of 2,6-di-tert-butyl-4-methylphenol (13.22 g, 60 mmol) in dry toluene (60 mL) with stirring at room temperature. The exotherm raised the temperature of the flask but it did not peak above 60 °C. The solution was stirred for a further 2 h before the
solvent was removed under vacuum. The resultant white solid was dissolved in dry pentane (25 mL) before dry tetrahydrofuran (5 mL) was added dropwise with stirring. The reaction was stirred for a further 2 h before removing solvent under vacuum. The product was vacuum dried overnight and stored in an inert atmosphere glovebox. Yield = 69% (12.70 g, 20.9 mmol)

Characterising data was in accordance with that reported previously. $^1$H NMR (300MHz, 298K, CDCl$_3$): $\delta$ = 7.01 (s, BHT Ar), 3.59 (t, $^3J_{H,H}$ = 6.4, THF CH$_2$CH$_2$O), 2.30 (s, BHT CH$_3$Ar), 1.48 (s, BHT (CH$_3$)$_3$Car), 1.20 (m, THF CH$_2$CH$_2$O). $^{13}$C NMR (400MHz, C$_6$D$_6$): $\delta$ = 160.8 (BHT ArCO), 137.5, 137.2, 129.1, 128.8, 128.6, 128.2, 127.9, 127.7 (BHT Ar), 24.9 (THF CH$_2$CH$_2$O), 21.6 (THF CH$_2$CH$_2$O) ppm. $^{13}$C NMR (400MHz, 298K, CDCl$_3$): $\delta$ = 159.0, 154.4, 139.5, 139.3, 130.0, 127.2, 123.1 (BHT Ar C), 72.6 (THF CH$_2$CH$_2$O), 37.5 (BHT ArCH$_3$), 34.0 (BHT ArC(CH$_3$)$_3$), 27.0 (THF CH$_2$CH$_2$O), 23.7 (BHT ArC(CH$_3$)$_3$) ppm.

**Figure S1.** $^1$H NMR spectrum of Mg(BHT)$_2$(THF)$_2$ (300 MHz, C$_6$D$_6$).

**General procedure of $\omega$-pentadecalactone polymerization** In an inert atmosphere glovebox Mg(BHT)$_2$(THF)$_2$ (10 mg, 16.5 µmol), benzyl alcohol (1.7 µL, 16.5 µmol) and $\omega$-pentadecalactone stock solution (75 wt.% toluene, 824.0 µmol) were charged into an ampoule. The ampoule was sealed and heated to 80 °C for a defined time period. The reaction was quenched with the
addition of acidified (5% HCl) methanol. Chloroform was added to dissolve any solids and the polymer was precipitated in excess methanol. $^1$H NMR (300MHz, 298K, CDCl$_3$): $\delta = 7.35$ (s, Ar), 5.20 (s, C=OOC$_2$H$_2$Ar), 5.11 (s, C=OOC$_2$H$_2$Ar), 4.05 (t, $^3$$J_{H-H} = 6.8$ Hz, CH$_2$OC=O), 2.28 (t, $^3$$J_{H-H} = 7.5$ Hz, CH$_2$C=OO), 1.61 and 1.25 (all remaining hydrogens) ppm. $^{13}$C NMR (400MHz, 298K, CDCl$_3$): $\delta = 174.12$ (CH$_2$C=OO), 128.59, 128.21 (aromatic CH), 66.10 (Bn COC=O), 64.45 (PDL COC=O), 34.47 (CH$_2$C=OO), 30-28, 26-24 (all other carbons) ppm. GPC (CHCl$_3$, 2.5 vol% NEt$_3$; PS standards): $M_n = 16,500$ g mol$^{-1}$ ($M_n$ th. = 12,100 g mol$^{-1}$); $D_M = 2.91$. Yield in inert conditions: 76%. Yield in non-inert conditions: 72%.

**General procedure of ε-caprolactone polymerization** In an inert atmosphere glovebox Mg(BHT)$_2$(THF)$_2$ (21.3 mg, 35 µmol), benzyl alcohol (3.63 µL, 35 µmol), ε-caprolactone (0.4 g, 3.5 mmol) and dry toluene (1.4 mL) were charged into an ampoule. The ampoule was sealed and heated at 80 °C for a defined time period. The reaction was quenched with the addition of acidified (5% HCl) methanol. Chloroform was added to dissolve any solids and the polymer was precipitated in excess methanol. $^1$H NMR (300MHz, 298K, CDCl$_3$): $\delta = 7.29$ (s, Ar), 5.20 (s, C=OOC$_2$H$_2$Ar), 5.06 (s, C=OOC$_2$H$_2$Ar), 4.01 (t, $^3$$J_{H-H} = 6.7$ Hz, CH$_2$OC=O), 2.25 (t, $^3$$J_{H-H} = 6.4$ Hz, CH$_2$C= OO), 1.60 and 1.33 (all remaining hydrogens) ppm. $^{13}$C NMR (400MHz, 298K, CDCl$_3$): $\delta = 173.51$ (CH$_2$C= OO), 128.55, 128.18 (aromatic CH), 66.13 (Bn COC=O), 64.12 (εCL COC=O), 34.11 (CH$_2$C=OO), 28.35, 25.53 and 24.57 (all other carbons) ppm. GPC (CHCl$_3$, 2.5 vol% NEt$_3$; PS standards): $M_n = 23,800$ g mol$^{-1}$ ($M_n$ th. = 11,500 g mol$^{-1}$); $D_M = 1.75$.

**General procedure of ω-pentadecalactone polymerization in ‘air’ conditions** In an inert atmosphere glovebox, an ampoule was charged with Mg(BHT)$_2$(THF)$_2$ (50 mg, 82.5 µmol) and removed from the glovebox without sealing. A solution of benzyl alcohol (10.2 µL, 82.5 µmol), ω-pentadecalactone (1 g, 4.2 mmol) and toluene (3 g) was prepared directly from stock bottles and added to the ampoule. The ampoule was then sealed and heated at 80 °C for a defined time period. The reaction was quenched with the addition of acidified (5% HCl) methanol. Chloroform was added to dissolve any solids and the polymer was precipitated in excess methanol.
Figure S2. $^1$H NMR spectrum of PPDL (300 MHz, CDCl$_3$).

Figure S3. ln([M$_o$]/[M$_t$]) versus time plot for PDL homopolymerizations in toluene at 80 °C with [PDL]:[BnOH] of [100]:[1].
Figure S4. GPC chromatograms for PPDL polymerized using Mg(BHT)$_2$(THF)$_2$.

Figure S5. $^1$H NMR spectrum of PCL (300 MHz, CDCl$_3$).

References: