Electronic Supplementary Material (ESI) for Dalton Transactions

Synthesis and structures of calcium and strontium 2,4-di-*tert*-butylphenolates and their reactivity towards the amine co-initiated ring-opening polymerisation of *rac*-lactide

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SUPPORTING INFORMATION

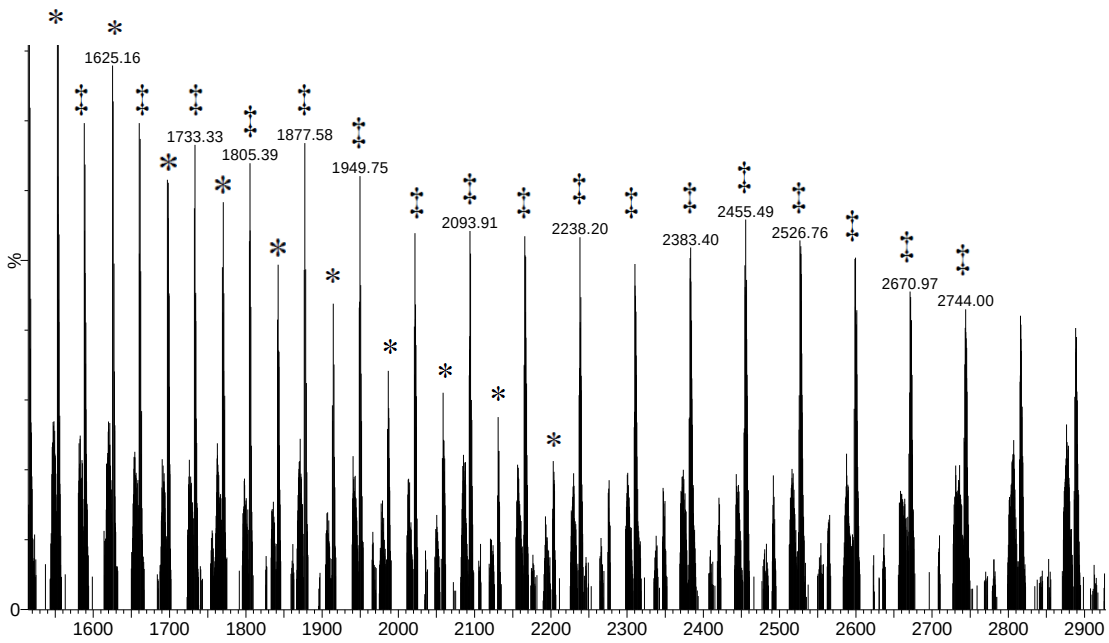

Figure S1. Representative MALDI-ToF mass spectrum of benzyl amine-capped (annotated peaks) poly(*rac*-LA) produced by $[Ca_2(DBP)_4(DME)_4(\mu\text{-DME})]$ (**2**) or $[Sr_2(DBP)(\mu\text{-DBP})_3(DME)_3]$ (**4**). Example shown is from the run with $[rac\text{-LA}]_0$:$[BnNH_2]_0$:$[\mathbf{4}]_0$ = 100:5:1. K^+ dopant. Peak envelopes labelled "*" are for cyclic PLA ($[PLA]_n$; e.g., *m/z* = 1625 corresponds to $\{K + [rac\text{-LA}]_{11}\}^+$). Peak envelopes labelled "‡" are for linear benzylamine-terminated PLA (H-$[LA]_n$-NHBn; e.g., *m/z* = 1733 corresponds to$\{K + H\text{-}[rac\text{-LA}]_{11}\text{-NHBn}\}^+$). Note that $\Delta(m/z)$ between peak envelopes = 72 g mol^{-1} due to transesterification.

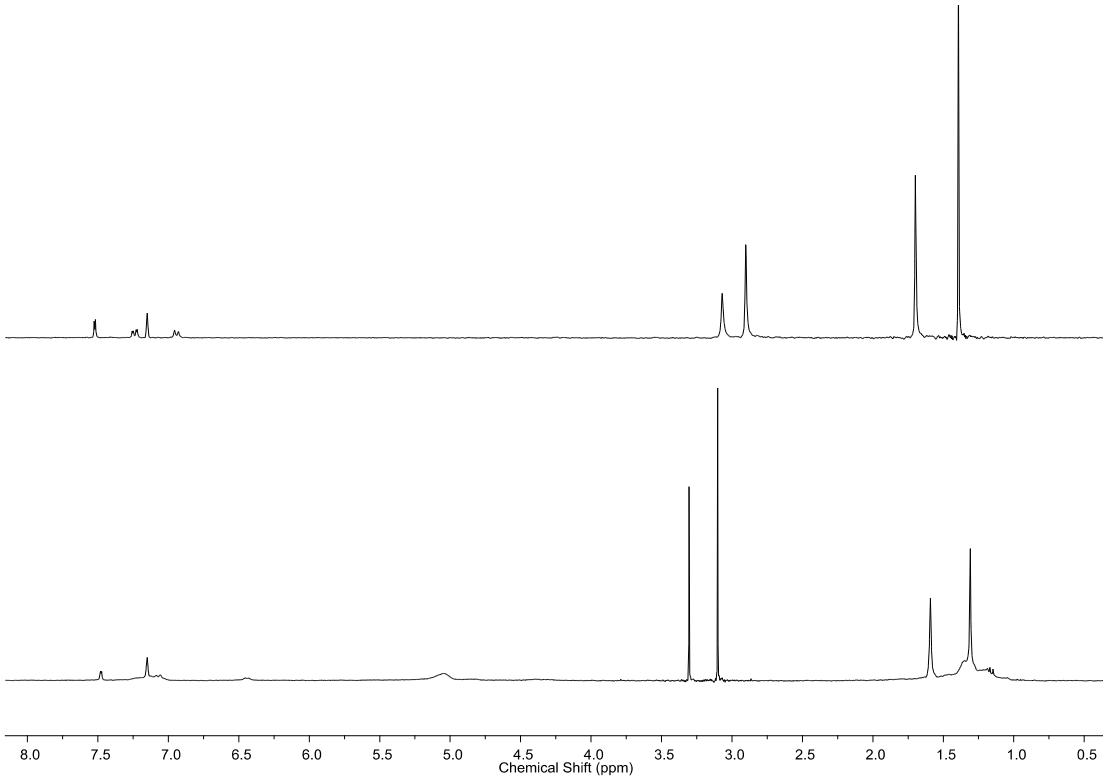

Figure S2. ^{1}H NMR (300.1 MHz, C_6D_6, 298 K) spectra of $[Ca_2(DBP)_4(DME)_4(\mu\text{-DME})]$ (**2**) (top), and for the NMR tube scale ROP reaction with $[rac\text{-LA}]_0$:$[BnNH_2]_0$:[**2**] = 20:4:1 (bottom). The signal at *ca*. 6.5 ppm in the bottom spectrum is for the NHC$\underline{H}_2$Ph methylene group of H-[PLA]-NHBn; the broad signals between 1.1 and 1.4 ppm and at *ca* 5.1 ppm are for the –[PLA]- main chain methyl and methylene groups. Residual protio-solvent, δ = 7.15 ppm.

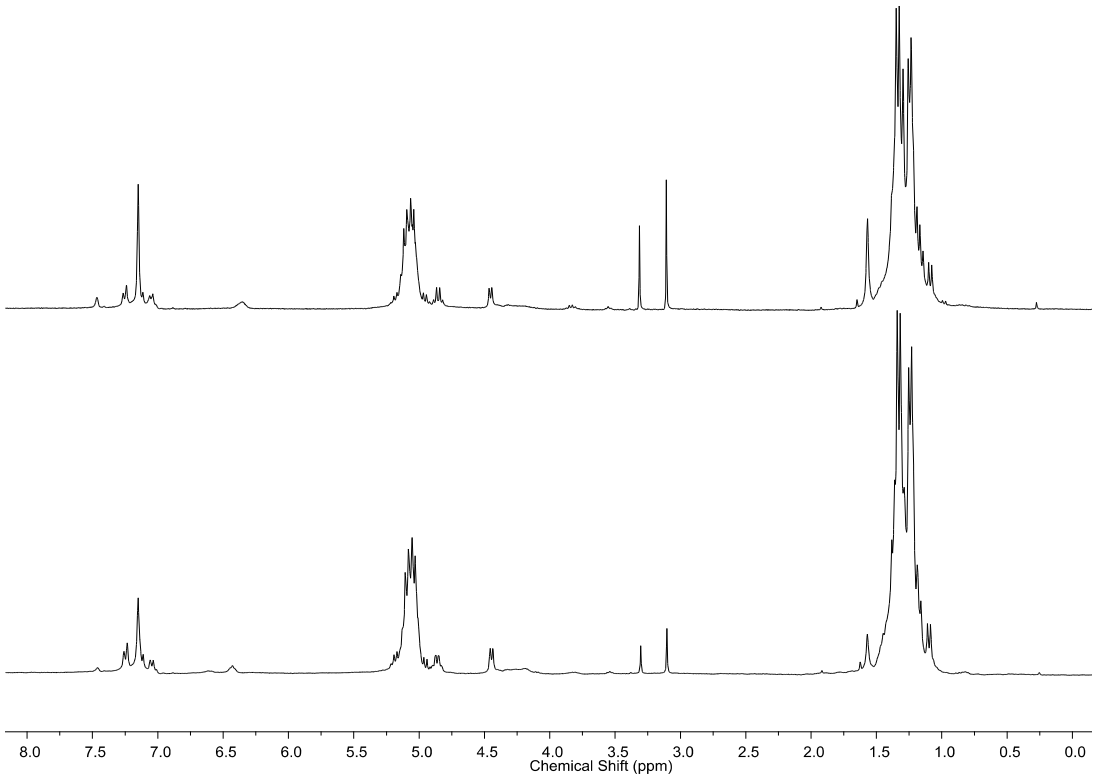

Figure S3. ^{1}H NMR (300.1 MHz, C_6D_6, 298 K) spectra from NMR tube scale reactions between the macromonomer H-[*rac*-LA]$_{10}$-NHBn and [Sr_2(DBP)(μ-DBP)$_3$(DME)$_3$] (**4**) (4:1, top), and *rac*-LA, macromonomer and **4** (20:4:1, bottom). Residual protio-solvent, δ = 7.15 ppm.

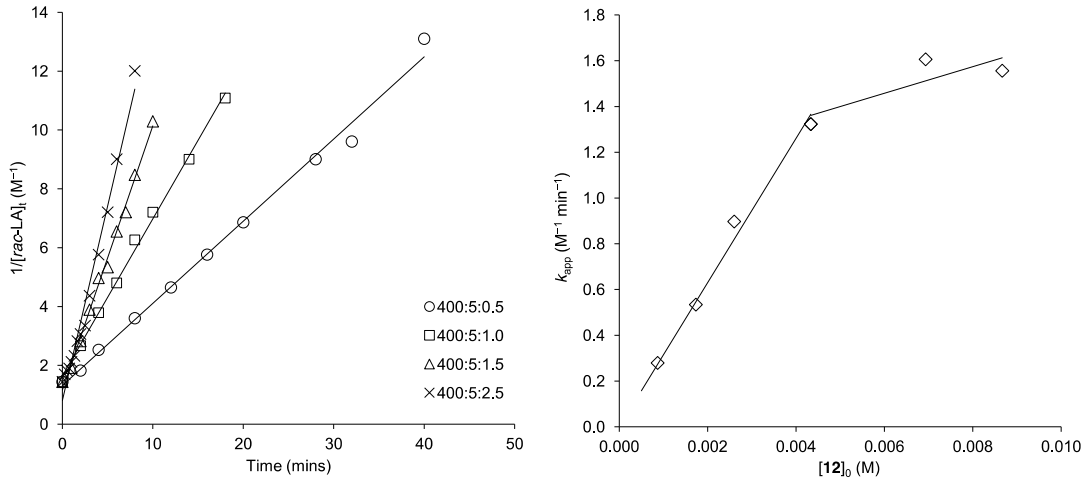

Figure S4. Left: second-order plots of 1/[*rac*-LA]$_t$ *vs*. Time with increasing concentrations of [**2**]$_0$. Rate constants, k_{app} = 0.279(8) (R^2 = 0.994), 0.534(13) (R^2 = 0.997), 0.897(22) (R^2 = 0.995) and 1.323(52) (R^2 = 0.982) M^{-1} min^{-1}. The vertical-axis intercepts of the plots are 1.3(17), 1.64(12), 1.17(12) and 0.81(18) M^{-1}, (expected value = 1/[*rac*-LA]$_0$ = 1.44 M^{-1}). Right: plots of k_{app} *vs*. [**2**]$_0$. [*rac*-LA]$_0$:[$BnNH_2$]$_0$ = 400:5. Molar equivs. [**2**]$_0$ = 0.5–1.5, 2.5, 4.0 or 5.0, $k_{p(Ca)}[BnNH_2]_0{}^c$ = 315(10) M^{-2} min^{-1} (R^2 = 0.987) based on $k_{app(Sr)}$ data in the range molar equivs. [**2**]$_0$ = 0.5 – 2.5.

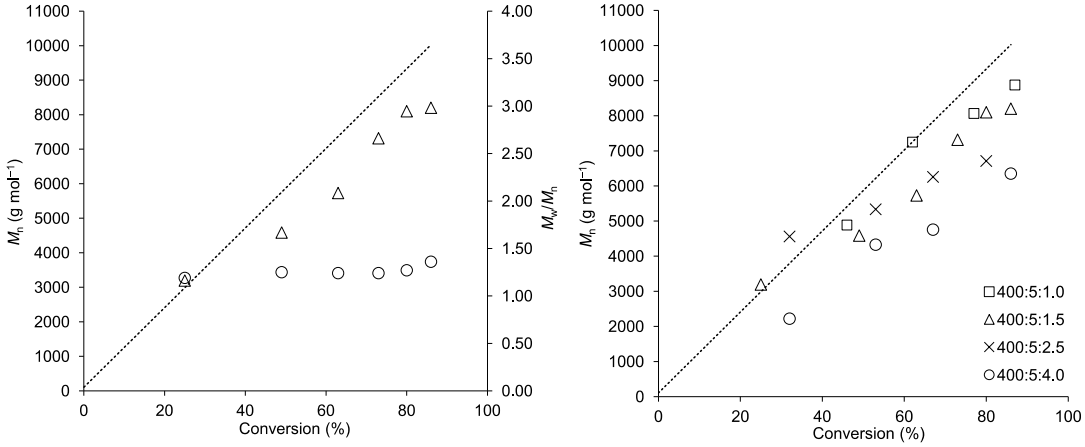

Figure S5. Left, M_n(GPC) *vs*. Conversion (triangles) and M_w/M_n *vs*. Conversion (circles) plots for the run [*rac*-LA]$_0$:[$BnNH_2$]$_0$:[**2**]$_0$ = 400:5:1.5. Right, M_n(GPC) *vs*. Conversion plots with [*rac*-LA]$_0$:[$BnNH_2$]$_0$ = 400:5 and [*rac*-LA]$_0$:[**2**]$_0$ = 400:1.0, 1.5, 2.5 or 4.0, PDIs = 1.4–1.5. The dashed lines represent M_n(calcd) based on [*rac*-LA]$_0$:[$BnNH_2$]$_0$ = 400:5.