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

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SUPPORTING INFORMATION

Figure S1. Representative MALDI-ToF mass spectrum of benzyl amine-capped (annotated peaks) poly(\textit{rac}-LA) produced by \([\text{Ca}_2(\text{DBP})_4(\text{DME})_4(\mu-\text{DME})]\) (2) or \([\text{Sr}_2(\text{DBP})(\mu-\text{DBP})_3(\text{DME})_3]\) (4). Example shown is from the run with \([\text{rac-LA}]_0:[\text{BnNH}_2]_0:[4]_0 = 100:5:1. K^+ dopant. Peak envelopes labelled "*" are for cyclic PLA (\([\text{PLA}]_n\); e.g., \(m/z = 1625\) corresponds to \(\{\text{K} + [\text{rac-LA}]_{11}\}^+\)). Peak envelopes labelled "‡" are for linear benzylamine-terminated PLA (\(H-[\text{LA}]_0\text{-NHBn}; \text{e.g., } m/z = 1733\) corresponds to\(\{\text{K} + H-[\text{rac-LA}]_{11}\text{-NHBn}\}^+\)). Note that \(\Delta(m/z)\) between peak envelopes = 72 g mol\(^{-1}\) due to transesterification.
Figure S2. $^1$H NMR (300.1 MHz, C$_6$D$_6$, 298 K) spectra of [Ca$_2$(DBP)$_4$(DME)$_4$(μ-DME)] (2) (top), and for the NMR tube scale ROP reaction with [rac-LA]$_0$:[BnNH$_2$]$_0$:[2] = 20:4:1 (bottom). The signal at ca. 6.5 ppm in the bottom spectrum is for the NHCH$_3$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, $\text{C}_6\text{D}_6$, 298 K) spectra from NMR tube scale reactions between the macromonomer $\text{H-}[\text{rac-LA}]_{10}$-$\text{NHBn}$ and [Sr$_3$(DBP)(μ-DBP)$_3$(DME)$_3$] (4) (4:1, top), and rac-LA, macromonomer and 4 (20:4:1, bottom). Residual protio-solvent, $\delta = 7.15$ ppm.
Figure S4. Left: second-order plots of $1/[\text{rac-LA}]_0$ vs. Time with increasing concentrations of $[2]_0$. Rate constants, $k_{\text{app}} = 0.279(8)$ ($R^2 = 0.994$), 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 = $1/[\text{rac-LA}]_0 = 1.44$ M$^{-1}$). Right: plots of $k_{\text{app}}$ vs. $[2]_0$. $[\text{rac-LA}]_0:[\text{BnNH}_2]_0 = 400:5$. Molar equivs. $[2]_0 = 0.5–1.5, 2.5, 4.0$ or 5.0, $k_{p\text{Ca}i}[\text{BnNH}_2]_0 = 315(10)$ M$^{-2}$ min$^{-1}$ ($R^2 = 0.987$) based on $k_{\text{app}(S)}$ data in the range molar equivs. $[2]_0 = 0.5–2.5$.

Figure S5. Left, $M_n$(GPC) vs. Conversion (triangles) and $M_n/M_n$ vs. Conversion (circles) plots for the run $[\text{rac-LA}]_0:[\text{BnNH}_2]_0:[2]_0 = 400:5:1.5$. Right, $M_n$(GPC) vs. Conversion plots with $[\text{rac-LA}]_0:[\text{BnNH}_2]_0 = 400:5$ and $[\text{rac-LA}]_0:[2]_0 = 400:1.0, 1.5, 2.5$ or 4.0, PDIs = 1.4–1.5. The dashed lines represent $M_n$(calcd) based on $[\text{rac-LA}]_0:[\text{BnNH}_2]_0 = 400:5$. 

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