Figure S1. Kinetic plots for \( t\)-BuP\(_2\)-catalyzed ROP of \( \varepsilon \)-caprolactone using 1-pyrenebutanol (PyOH) as initiator in toluene or toluene/THF (46/1, v/v) where \([t\text{-BuP}_2]_0/[\text{PyOH}]_0 = 1\) (entries 1 and 2 in Table 1), and in THF where \([t\text{-BuP}_2]_0/[\text{PyOH}]_0 = 1\) or 5 (entries 3 and 4 in Table 1).
Figure S2. SEC traces (RI and UV signals) of a representative poly(ε-caprolactone) and the corresponding poly(ε-caprolactone)-b-poly(1-lactide) obtained from the t-BuP₂-catalyzed sequential ring-opening polymerization of ε-caprolactone (8 h) and 1-lactide (10 min) (also see entry 1 in Table 1 and 2).

Figure S3. Dependence of apparent molecular weight (\(M_{n,SEC}\)) and dispersity (\(M_w/M_n\)) of poly(ε-caprolactone) on monomer conversion during the t-BuP₂-catalysed ring-opening polymerization of ε-caprolactone using cholesterol or benzamide as initiator (entries 10 and 13 in Table 1).
Figure S4. Kinetic plots of $t$-BuP$_2$-catalysed ring-opening polymerization of $\varepsilon$-caprolactone using a poly(ethylene glycol) monomethyl ether (blue) and a poly(propylene glycol) monobutyl ether (red) as initiators (entries 11 and 12 in Table1).

Figure S5. $^1$H NMR spectra of the isolated products of poly(propylene glycol)-$b$-poly($\varepsilon$-caprolactone) (left) and poly(ethylene glycol)-$b$-poly($\varepsilon$-caprolactone) (right) prepared by $t$-BuP$_2$-catalysed ring-opening polymerization of $\varepsilon$-caprolactone from the corresponding macro-initiators (entries 11 and 12 in Table1).