

Supporting Information

Phosphazene-Catalyzed Ring-Opening Polymerization of ϵ -Caprolactone: Influence of Solvent and Initiator

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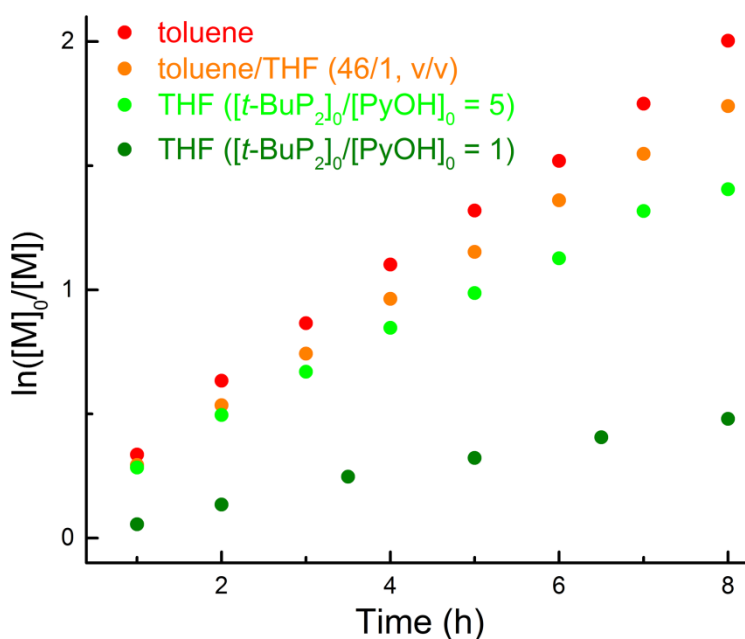


Figure S1. Kinetic plots for *t*-BuP₂-catalyzed ROP of ϵ -caprolactone using 1-pyrenebutanol (PyOH) as initiator in toluene or toluene/THF (46/1, v/v) where $[t\text{-BuP}_2]_0/[\text{PyOH}]_0 = 1$ (entries 1 and 2 in Table 1), and in THF where $[t\text{-BuP}_2]_0/[\text{PyOH}]_0 = 1$ or 5 (entries 3 and 4 in Table 1).

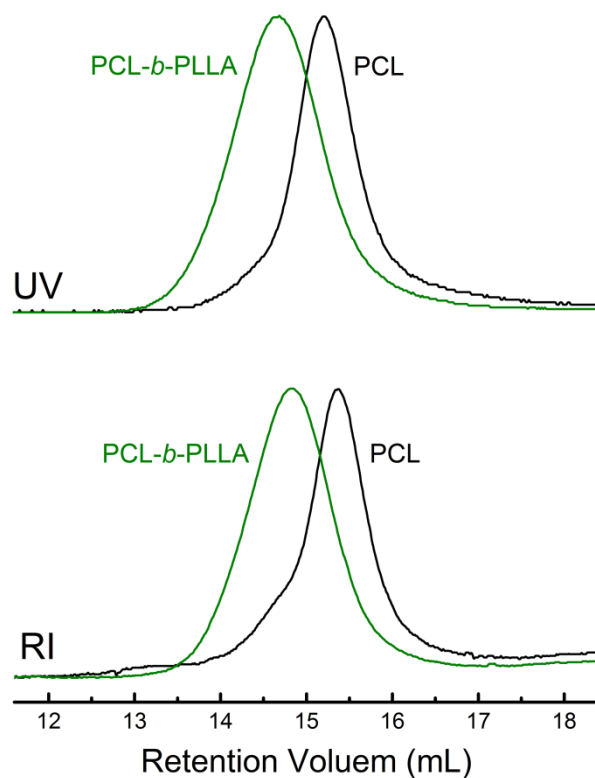


Figure S2. SEC traces (RI and UV signals) of a representative poly(ϵ -caprolactone) and the corresponding poly(ϵ -caprolactone)-*b*-poly(L-lactide) obtained from the *t*-BuP₂-catalyzed sequential ring-opening polymerization of ϵ -caprolactone (8 h) and L-lactide (10 min) (also see entry 1 in Table 1 and 2).

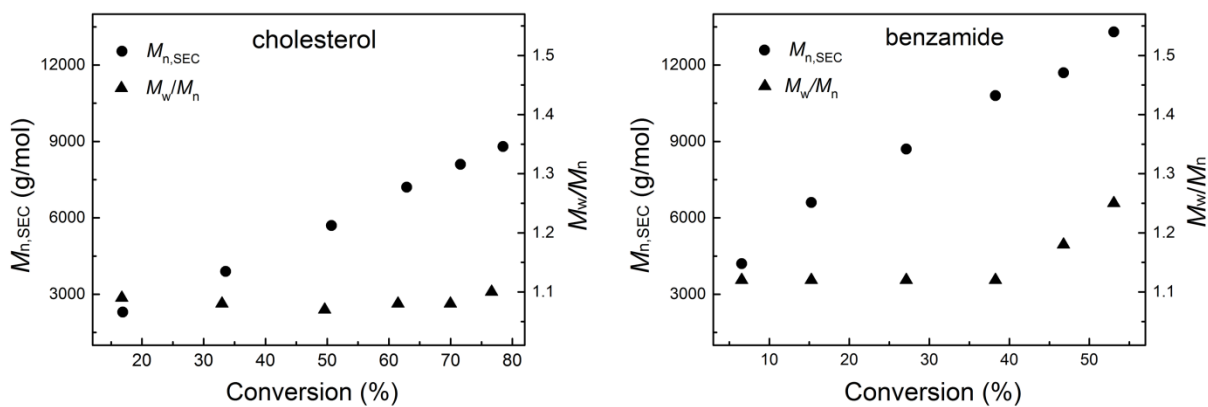


Figure S3. Dependence of apparent molecular weight ($M_{n,SEC}$) and dispersity (M_w/M_n) of poly(ϵ -caprolactone) on monomer conversion during the *t*-BuP₂-catalysed ring-opening polymerization of ϵ -caprolactone using cholesterol or benzamide as initiator (entries 10 and 13 in Table 1).

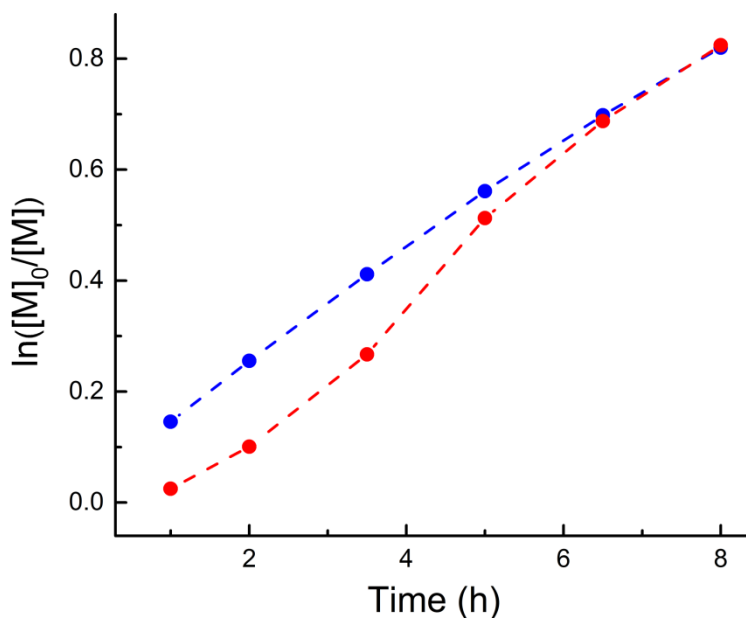


Figure S4. Kinetic plots of *t*-BuP₂-catalysed ring-opening polymerization of ϵ -caprolactone using a poly(ethylene glycol) monomethyl ether (blue) and a poly(propylene glycol) monobutyl ether (red) as initiators (entries 11 and 12 in Table1).

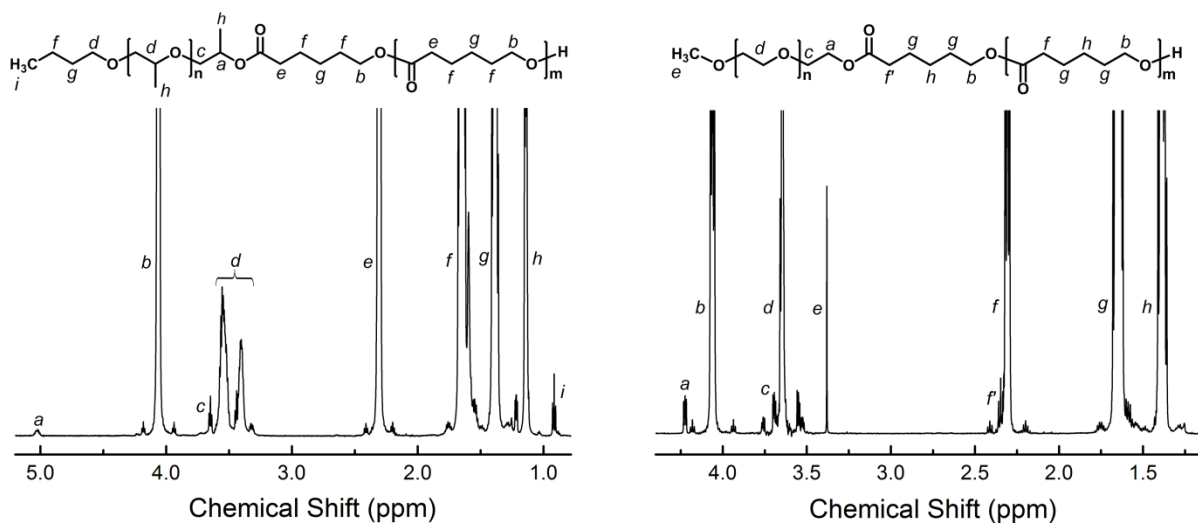


Figure S5. ¹H NMR spectra of the isolated products of poly(propylene glycol)-*b*-poly(ϵ -caprolactone) (left) and poly(ethylene glycol)-*b*-poly(ϵ -caprolactone) (right) prepared by *t*-BuP₂-catalysed ring-opening polymerization of ϵ -caprolactone from the corresponding macro-initiators (entries 11 and 12 in Table1).