Supporting Information

Polymerization of 5-Alkyl δ-Lactones Catalyzed by Diphenyl Phosphate and Their Sequential Organocatalytic Polymerization with Monosubstituted Epoxides

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Figure S1. Dependence of apparent molecular weight $(M_{n,SEC})$ and dispersity (M_w/M_n) of PNL (left) and PHL (right) on monomer conversion during the DPP-catalyzed ROP of NL and DL, respectively, corresponding to PNL11 and PHL11 in Table 1.



Figure S2. Upper: SEC traces of the products from DPP-catalyzed ROP of NL upon the first and second monomer feed (PNL11 and PNL12 in Table 1). Lower: ¹H NMR spectrum obtained from the isolated PNL (PNL12 in Table 1).



Figure S3. Upper: SEC traces of the products from DPP-catalyzed ROP of HL upon the first and second monomer feed (PHL11 and PHL12 in Table 1). Lower: ¹H NMR spectrum obtained from the isolated PHL (PHL12 in Table 1).



Figure S4. Upper: Evolution of SEC traces during the transformation of PEHGE to PEHGE-*b*-PNL (PEHGE2 and PEHGE2PNL in Table 1) using the "catalyst switch" strategy. Lower: ¹H NMR spectrum obtained from the isolated PEHGE-*b*-PNL.



Figure S5. Upper: Evolution of SEC traces during the transformation of PBO to PBO-*b*-PHL (PBO3 and PBO3PHL in Table 1) using the "catalyst switch" strategy. Lower: ¹H NMR spectrum obtained from the isolated PBO-*b*-PHL.



Figure S6. Kinetic plots of HL in its sequential ROP with BO (left) and EHGE (right) using the "catalyst switch" strategy, respectively corresponding to PBO3PHL and PEHGE3PHL in Table 1. Line connections are given here to help demonstrate the nonlinearity of the plot.



Figure S7. ¹H NMR spectrum of the isolated PEHGE-*b*-PHL (PEHGE3PHL in Table 1).