SUPPORTING INFORMATION

for

Cyclodextrin-Centered Polyesters: Controlled Ring-Opening Polymerization of Cyclic Esters from β-Cyclodextrin-Diol

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Figure S1. 1H NMR spectrum (500 MHz, CDCl₃, 23 °C) of perbenzylated β-cyclodextrin (β-CD(OBn)₂₁).

Figure S2. 1H NMR spectrum (500 MHz, CDCl₃, 23 °C) of β-cyclodextrin-diol (β-CD(OH)₂).

Figure S3. 13C NMR spectrum (100 MHz, CDCl₃, 23 °C) of β-cyclodextrin-diol (β-CD(OH)₂).

Figure S4. MALDI-ToF mass spectrum of β-cyclodextrin-diol (β-CD(OH)₂)Na⁺ (calculated mass for C₁₇₅H₁₈₄Na₁O₃₅ = 2870.3088 g·mol⁻¹).

Figure S5. Detail of the methine region of the homodecoupled 1H NMR spectrum (500 MHz, CDCl₃, 23 °C) of a β-CD(OBn)₁₉(OPLA)₂ sample prepared upon ROP of rac-LA from the [(BDIᵢPr)Zn(N(SiMe₃)₂)]/β-CD(OH)₂ system (Table 1, entry 1).

Figure S6. 13C NMR spectrum (100 MHz, CDCl₃, 23 °C) of a β-CD(OBn)₁₉(OPLA)₂ sample prepared upon iROP of rac-LA from the [(BDIᵢPr)Zn(N(SiMe₃)₂)]/β-CD(OH)₂ system (Table 1, entry 4).

Figure S7. 1H NMR spectrum (500 MHz, CDCl₃, 23 °C) of a β-CD(OBn)₁₉(OPHB)₂ sample prepared upon iROP of rac-BL from the [(BDIᵢPr)Zn(N(SiMe₃)₂)]/β-CD(OH)₂ system (Table 1, entry 17).

Figure S8. 1H NMR spectrum (400 MHz, THF- d₈, 23 °C) of a precipitated β-CD(OBn)₁₉(OPHB)₂ sample prepared upon iROP of rac-BL from the [(BDIᵢPr)Zn(N(SiMe₃)₂)]/β-CD(OH)₂ system (Table 1, entry 15).
Figure S9. $^{13}$C{$^1$H} NMR spectrum (100 MHz, CDCl$_3$, 23 °C) of a β-CD(OBn)$_{19}$(OPHB)$_2$ sample prepared upon iROP of rac-LA from the [(BDI$^{iPr}$)Zn(N(SiMe$_3$)$_2$)]/β-CD(OH)$_2$ system (Table 1, entry 17).

Figure S10. Size Exclusion Chromatography profile in THF of a β-CD(Obn)$_{19}$(OPHB)$_2$ sample prepared upon iROP of rac-BL from the [(BDI$^{iPr}$)Zn(N(SiMe$_3$)$_2$)]/β-CD(OH)$_2$ system (Table 1, entry 17).

Figure S11. $^1$H NMR spectrum (400 MHz, THF-$d_8$, 23 °C) of a β-CD(Obn)$_{19}$(OPTMC)$_2$ sample prepared upon iROP of tmc from the [(BDI$^{iPr}$)Zn(N(SiMe$_3$)$_2$)]/β-CD(OH)$_2$ system (Table 1, entry 23). * and ** stand for residual signals of THF-$d_8$ and water, respectively.

Figure S12. FTIR spectrum of a β-CD(Obn)$_{19}$(OPLA)$_2$ sample prepared upon iROP of rac-LA from the [(BDI$^{iPr}$)Zn(N(SiMe$_3$)$_2$)]/β-CD(OH)$_2$ system (Table 1, entry 4).

Figure S13. FTIR spectrum of β-cyclodextrin-diol (β-CD(OH)$_2$).

Figure S14. DSC trace of β-cyclodextrin-diol (β-CD(OH)$_2$).

Figure S15. DSC trace of a TEMPO-OPLLA-H sample prepared upon ROP of L-LA from a [(BDI$^{iPr}$)Zn(N(SiMe$_3$)$_2$)]/TEMPO-OH system ($\overline{M_n}$ = 29 800 g.mol$^{-1}$, $\overline{M_w}/\overline{M_n}$ = 1.14).

Figure S16. DSC trace of a β-CD(Obn)$_{19}$(OPLA)$_2$ sample prepared upon iROP of L-LA from the [(BDI$^{iPr}$)Zn(N(SiMe$_3$)$_2$)]/β-CD(OH)$_2$ system (Table 1, entry 11).
Figure S1. Detail of the $^1$H NMR spectrum (500 MHz, CDCl$_3$, 23 °C) of perbenzylated β-cyclodextrin ($\beta$-CD(OBn)$_{21}$).
Figure S2. $^1$H NMR spectrum (500 MHz, CDCl$_3$, 23 °C) of β-cyclodextrin-diol (β-CD(OH)$_2$).
Figure S3. $^{13}$C($^1$H) NMR spectrum (100 MHz, CDCl$_3$, 23 °C) of β-cyclodextrin-diol (β-CD(OH)$_2$).
Figure S4. MALDI-ToF mass spectrum of β-cyclodextrin-diol (β-CD(OH)$_2$Na$^+$ (calculated mass for C$_{175}$H$_{184}$Na$_1$O$_{35}$ = 2870.3088 g.mol$^{-1}$).
Figure S5. Detail of the methine region of the homodecoupled $^1$H NMR spectrum (500 MHz, CDCl$_3$, 23 °C) of a β-CD(Obn)$_{19}$(OPLA)$_2$ sample prepared upon ROP of rac-LA from the [(BDI$_{Pr}$)Zn(N(SiMe$_3$)$_2$)]/β-CD(OH)$_2$ system (Table 1, entry 1).
Figure S6. $^{13}$C$^{1}$H NMR spectrum (100 MHz, CDCl$_3$, 23 °C) of a β-CD(OBn)$_{19}$(OPLA)$_2$ sample prepared upon iROP of rac-LA from the [(BDI$^{iv}$)Zn(N(SiMe$_3$)$_2$)]/β-CD(OH)$_2$ system (Table 1, entry 4).
Figure S7. $^1$H NMR spectrum (500 MHz, CDCl$_3$, 23 °C) of a β-CD(OBn)$_{19}$(OPHB)$_2$ sample prepared upon iROP of rac-BL from the [(BDI$_{18}^{iPr}$)Zn(N(SiMe$_3$)$_2$)]/β-CD(OH)$_2$ system (Table 1, entry 17).
Figure S8. $^1$H NMR spectrum (400 MHz, THF-$d_8$, 23 °C) of a precipitated β-CD(OBn)$_{19}$(OPHB)$_2$ sample prepared upon iROP of rac-BL from the [(BDI)$_{iPr}$Zn(N(SiMe$_3$_2)$_2$)/β-CD(OH)$_2$ system (Table 1, entry 15).
Figure S9. $^{13}$C($^1$H) NMR spectrum (100 MHz, CDCl₃, 23 °C) of a $\beta$-CD(OBn)$_{19}$(OPHB)$_2$ sample prepared upon iROP of rac-BL from the [(BDI$^{Pr}_i$)Zn(N(SiMe$_3$)$_2$)]/$\beta$-CD(OH)$_2$ system (Table 1, entry 17).
Figure S10. Size Exclusion Chromatography profile in THF of a β-CD(OBn)_{19}(OPHB)_{2} sample prepared upon iROP of rac-BL from the [(BDI^{iPr})Zn(N(SiMe_{3})_{2})]/β-CD(OH)_{2} system (Table 1, entry 17).
Figure S10. $^1$H NMR spectrum (400 MHz, THF-$d_8$, 23 °C) of a $\beta$-CD(OBn)$_{19}$(OPTMC)$_2$ sample prepared upon iROP of TMC from the [BDi($^{iPr}$)Zn(N(SiMe$_3$)$_2$)]/β-CD(OH)$_2$ system (Table 1, entry 23). Markers * and ** stand for residual signals of THF-$d_8$ and water, respectively (the intensity of these residual signals stem from the poor solubility of these polymers, even in THF).
Figure S12. FTIR spectrum of a β-CD(Obn)_{19}(OPLA)_{2} sample prepared upon iROP of rac-LA from the [(BDI^{Pr})Zn(N(SiMe_{3})_{2})]/β-CD(OH)_{2} system (Table 1, entry 4).
Figure S13. FTIR spectrum of β-cyclodextrin-diol (β-CD(OH)₂).
Figure S14. DSC trace of β-cyclodextrin-diol (β-CD(OH)$_2$).
Figure S15. DSC trace of a TEMPO-OPLLA sample ($M_n = 29\ 800\ \text{g.mol}^{-1},\ \overline{M}_w/\overline{M}_n = 1.14$). 

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Figure S16. DSC trace of a $\beta$-CD($\text{OBn})_{19}$($\text{OPLA})_{2}$ sample prepared upon iROP of L-LA from the $[(\text{BDI})_{\text{Pr}}\text{Zn(N(SiMe}_{3})_{2})]/\beta$-CD(OH)$_{2}$ system (Table 1, entry 11).