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Supporting Information

Poly(β-hydroxyalkanoate) / polymethacrylate self-assembled architectures by ringopening polymerization (ROP) / reversible addition-fragmentation chain-transfer

(RAFT) polymerization and polymerization-induced self-assembly (PISA)

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Figure S2: J-MOD spectrum (125 MHz, CDCl₃, 25 °C) of the PHB₈₃-TTC prepared by ROP of racemic β -butyrolactone catalyzed by Y{ONNO^{Me2}} with CTA-OH as initiator (Table 1, entry 1).



Figure S3: Typical ¹H NMR (400 MHz, $(CD_3)_2SO$, 25 °C) of the crude reaction mixture for the preparation of a PHB-*b*-PHEMA copolymer (entry 5, Table 2). The HEMA comonomer conversion was calculated according the following equation:

 $Conv_{HEMA}$ (%) = 100 × [1 – (Ia + Ib) / Ic)]



Figure S4: ¹H NMR spectra (500 MHz, (CDCl₃, 25 °C) of the PHB resulting from the ROP of *rac*- β -BL promoted by BEMP (top) and of the PHB-TTC (obtained from esterification of the PHB with TTC-OH) using DMAP and DCC (bottom).



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Figure S10: SEC chromatogram in THF superimposed with the isoabsorbance plot of the PHB₄₈-TTC prepared by ROP of *racemic* β -butyrolactone catalyzed by Y{ONNO^{Me2}} in the presence of TTC-OH (Table 1, entry 1).



Figure S11: SEC chromatogram in THF superimposed with the isoabsorbance plot of the PHB₅₇-TTC prepared by ROP of *racemic* β -butyrolactone catalyzed by Y{ONNO^{Me2}} in the presence of TTC-OH (Table 1, entry 2).



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