Electronic Supplementary Information

Metal-free Controlled Ring-Opening Polymerization of ε-Caprolactone in Bulk using Tris(pentafluorophenyl)borane as Catalyst

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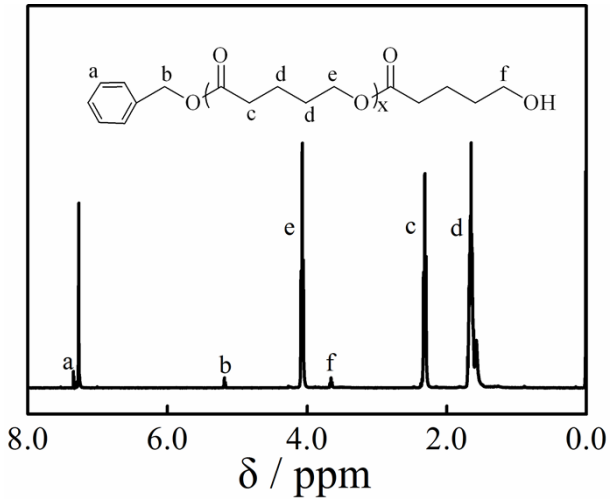

Figure S1. ^{1}H NMR spectrum of the obtained poly(*δ*-valerolactone) (PVL) initiated by benzyl alcohol (BnOH) in $CDCl_3$.

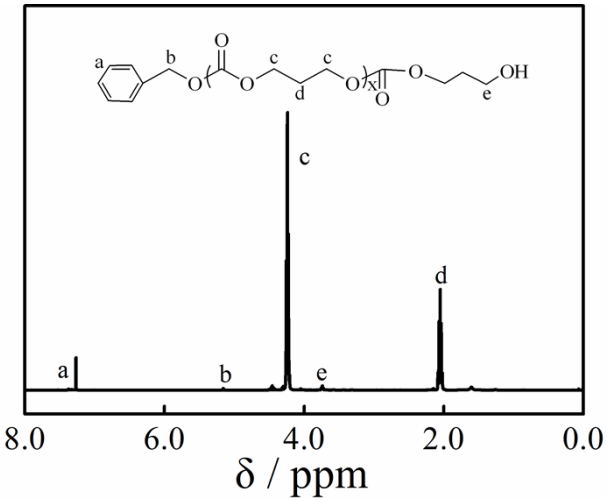

Figure S2. ^{1}H NMR spectrum of the obtained poly(trimethylene carbonate) (PTMC) copolymer initiated by benzyl alcohol (BnOH) in $CDCl_3$.

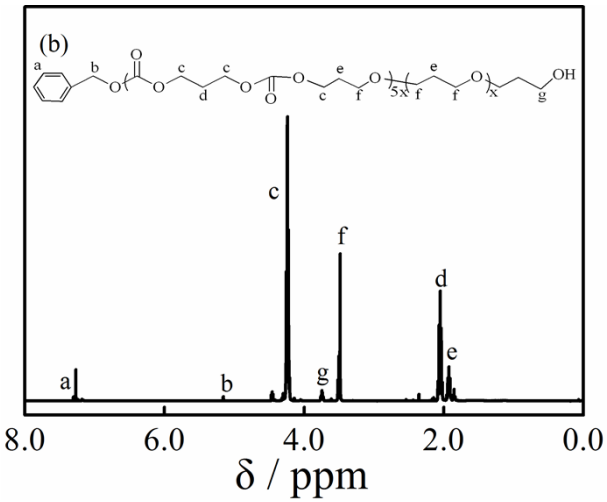

Figure S3. ^{1}H NMR spectrum of the obtained poly(trimethylene carbonate-*co*-trimethylene oxide) (P(TMC-*co*-TMO)) copolymer initiated by benzyl alcohol (BnOH) in $CDCl_3$.

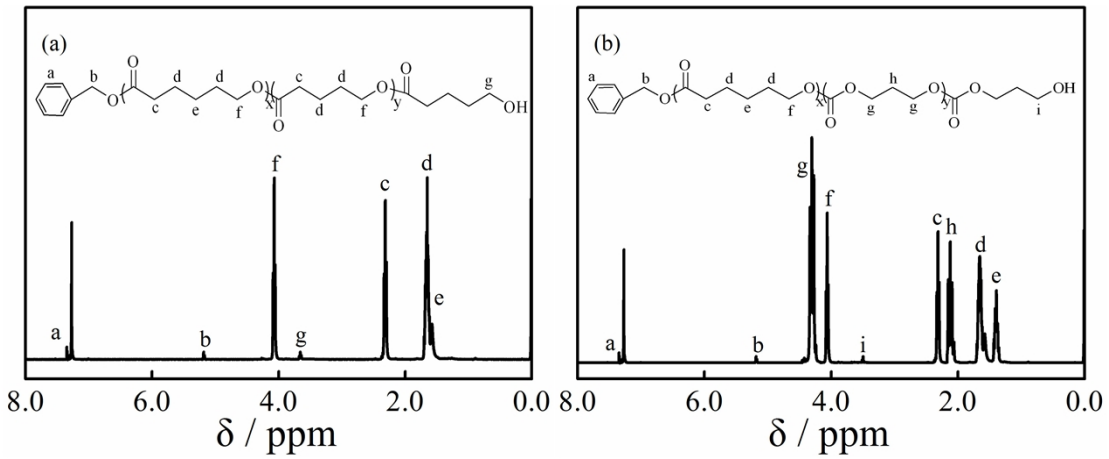

Figure S4. (a)^{1}H NMR spectrum of poly(*ε*-caprolactone)-*b*-poly(*δ*-valerolactone) (PCL-*b*-PVL) copolymer; (b) ^{1}H NMR spectrum of poly(*ε*-caprolactone)-*b*-poly(tirmethylene carbonate) (PCL-*b*-PTMC) in $CDCl_3$.

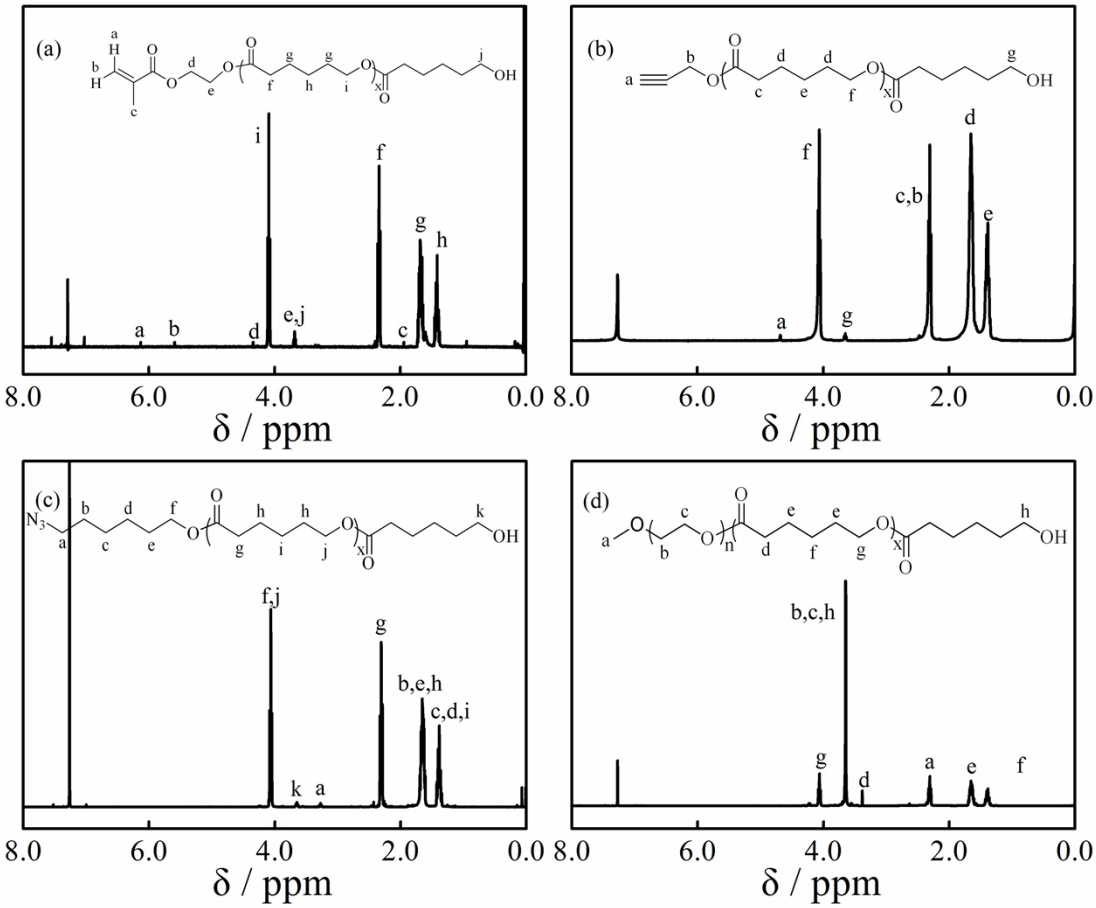

Figure S5. ^{1}H NMR spectra of the obtained functional poly(ε-caprolactone)s (PCL) initiated by (a) 2-hydroxyethyl methacrylate (HEMA), (b) propargyl alcohol (PGA), (c) 6-azido-1-hexanol (AHA) and (d) methoxy poly(ethylene glycol) (mPEG) in $CDCl_3$.

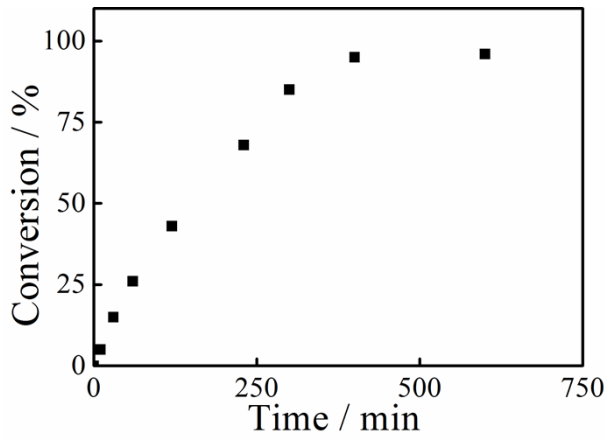

Figure S6. Monomer conversion vs time curve for CL polymerization ($[M]^0/[I]^0$=50).