Electronic Supplementary Information (ESI)

A unique cooperative catalytic system carrying metallic iron and 2-hydroxyethyl 2-bromoisobutyrate for the controlled/living ring-opening polymerization of *ε*-caprolactone

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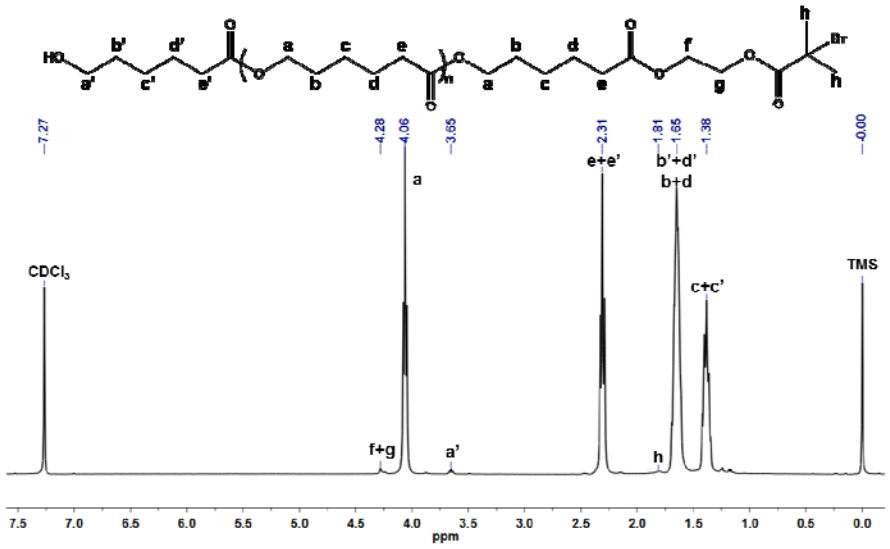

Figure S1. ^{1}H NMR spectrum of poly(ε-caprolactone) (PCL) catalyzed by Fe/2-hydroxyethyl 2-bromoisobutyrate (HEBiB).

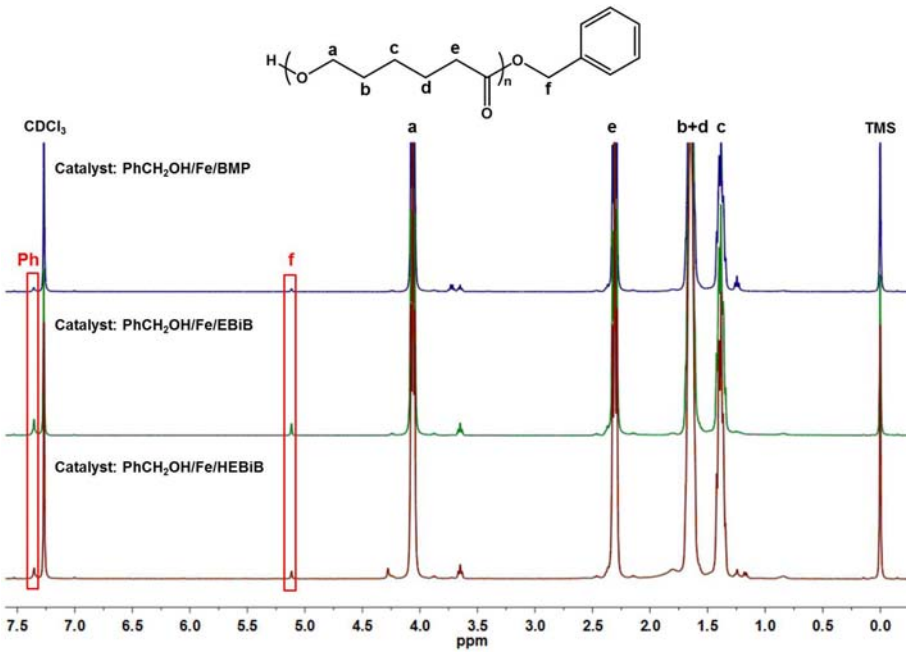

Figure S2. ^{1}H NMR spectra of poly(ε-caprolactone) (PCL) initiated by benzyl alcohol ($PhCH_2OH$) and catalyzed by iron powder along with different haloalkanes like 2-bromo-2-methylpropane (BMP), ethyl-2-bromoisobutyrate (EBiB) and 2-hydroxyethyl 2-bromoisobutyrate (HEBiB).

Table S1. Polymerization of ε-caprolactone (CL) by stepwise addition of the reactants.

Entry	M_n[d] (g/mol)	M_{theo}[e] (g/mol)	PDI[d]	Yield[f] (%)
1[a]	23040	22830	1.24	100
2[b]	19990	22830	1.27	100
3[c]	18280	22830	1.33	100

Reaction condition: solvent: toluene; reaction temperature: 110 ºC; HEBiB: 2-hydroxyethyl 2-bromoisobutyrate. [a] $[Fe]_0$:$[HEBiB]_0$ = 1:1 was added first and heated for 24 h, then 100 equiv of CL was added and heated for another 24 h. [b]$[CL]_0$:$[Fe]_0$:$[HEBiB]_0$ = 1:1:1 was added first and heated for 24 h, then 99 equiv of CL was added and heated for another 24 h. [c=] $[CL]_0$:$[Fe]_0$:$[HEBiB]_0$ = 50:1:1 was added first and heated for 24 h, then 50 equiv of CL was added and heated for another 24 h. [d] Determined by GPC analysis in THF, calibrated to a polystyrene standard. [e] M_{thoe} = yield (%) × ratio $[CL]_0/[HEBiB]_0$ × 2 × M (CL). [f] Yield: weight of polymer obtained/weight of monomer used.