## **Supporting Information**

### 2,4-Dinitrobenzenesulfonic Acid as an Efficient Brønsted Acid-

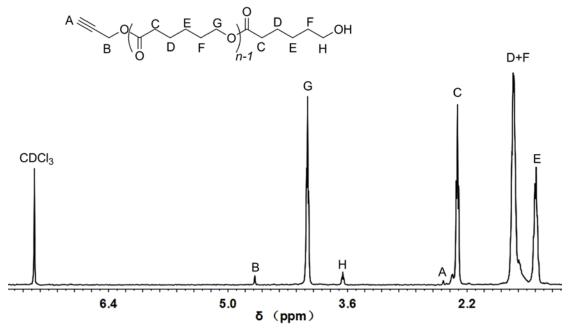
# Catalyzed Controlled/Living Ring-Opening Polymerization of $\varepsilon$ caprolactone

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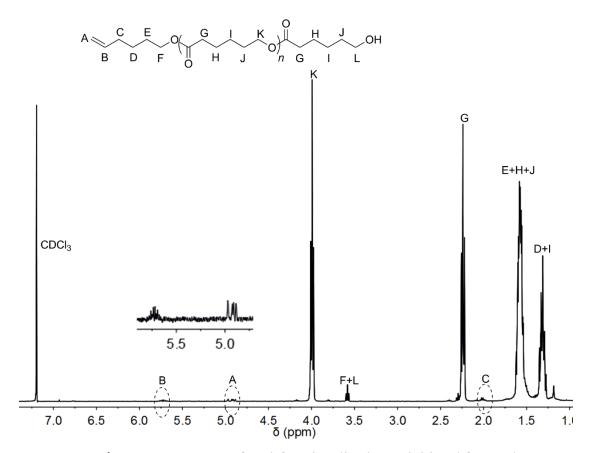
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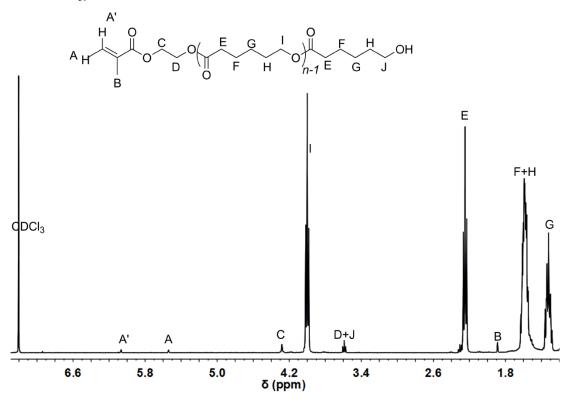
Syntheses of End-Functionalized and *a*,ω-Dihydroxy Telechelic Poly(ε-caprolactone)



**FIGURE S1** <sup>1</sup>H NMR spectrum of End-functionalized PCL initiated from propargyl alcohol in CDCl<sub>3</sub>.



**FIGURE S2**  $^{1}$ H NMR spectrum of End-functionalized PCL initiated from 5-hexen-1-ol in CDCl<sub>3.</sub>



**FIGURE S3** <sup>1</sup>H NMR spectrum of End-functionalized PCL initiated from 2-hydroxyethyl methacrylate in CDCl<sub>3</sub>.

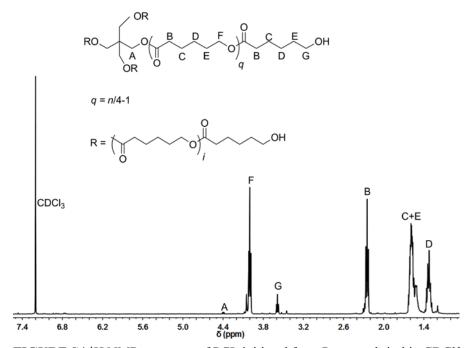
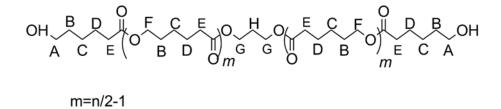


FIGURE S4 <sup>1</sup>H NMR spectrum of PCL initiated from Pentaerythritol in CDCl3.



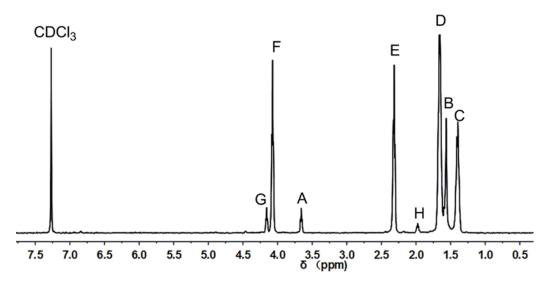


FIGURE S5  $^1H$  NMR spectrum of  $a,\omega$ -Dihydroxy Telechelic PCL initiated from 1,3-Propanediol in CDCl<sub>3</sub>.

### Diblock Copolymers of ε-Caprolactone and δ-Valerolactone, Trimethylene Carbonate.

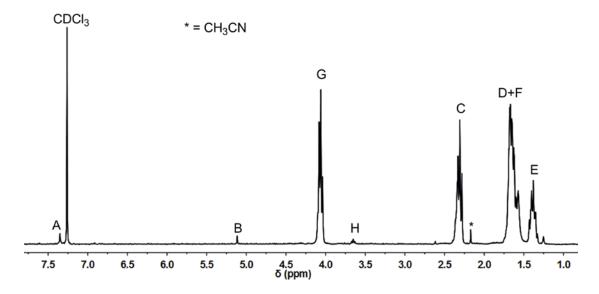


FIGURE S6 <sup>1</sup>H NMR spectrum of PCL-b-PVL initiated from BnOH in CDCl3

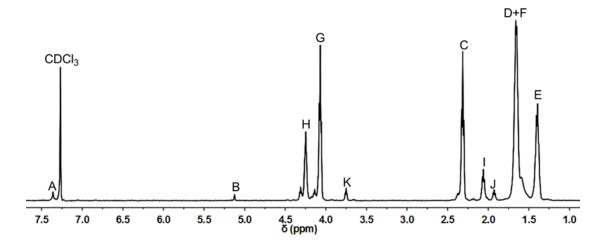


FIGURE S7 <sup>1</sup>H NMR spectrum of PCL-b-PTMC initiated from BnOH in CDCl<sub>3</sub>.

### The calculation details of $\varepsilon$ -CL conversion

The calculated conversions of  $\varepsilon$ -CL were obtained from <sup>1</sup>H NMR spectra of reaction mixtures, and the details were as follows: the integral area of the signal of methylene protons at 4.25 ppm of  $\varepsilon$ -CL monomer was appointed to 1, and then the integral area of the signal at 4.06 ppm (–CH<sub>2</sub>CH<sub>2</sub>O–)<sub>n</sub> was appointed to n. based on the formula, conv. = n/(n+I) \* 100%.