

## SUPPORTING INFORMATION

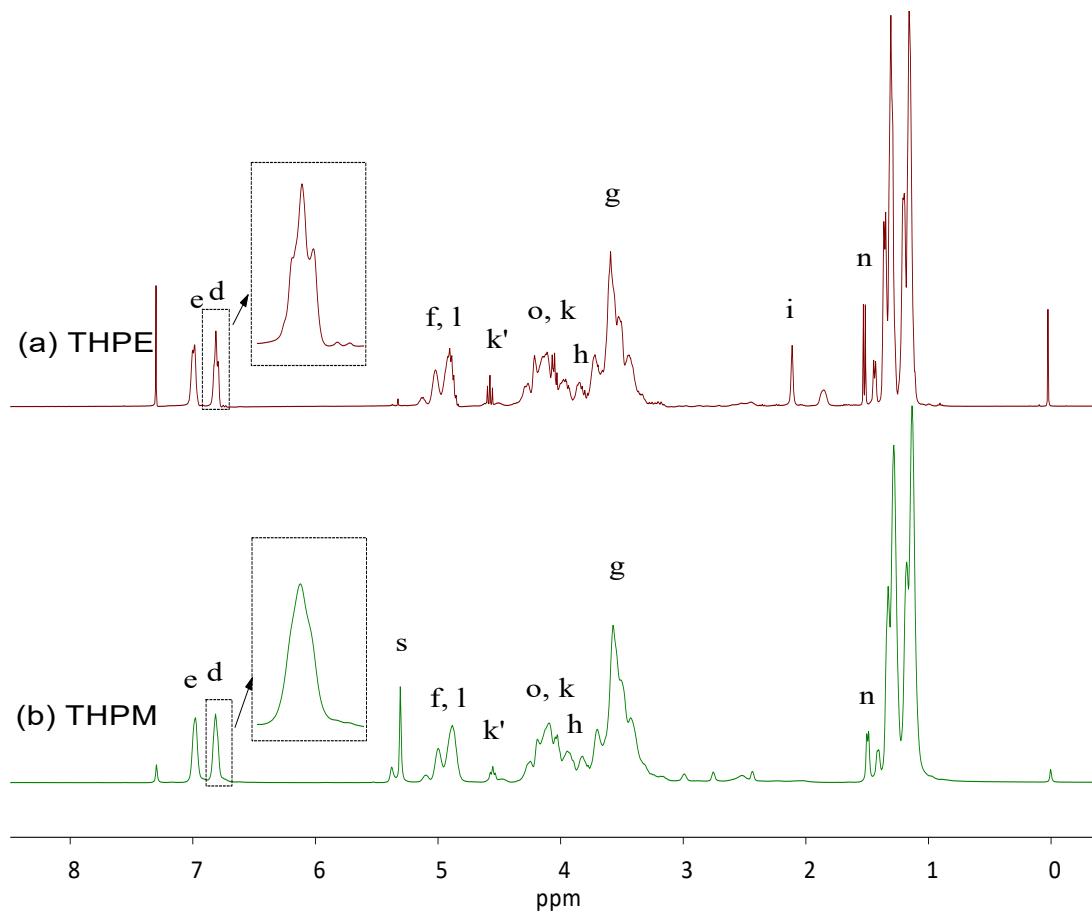
### Construction and Arm Evolution of Trifunctional Phenolic Initiator-Mediated Polycarbonate Polyols Produced by Using Double Metal Cyanide Catalyst

Xiao Zhang,<sup>a</sup> Jincheng Dong,<sup>a</sup> Yun Su,<sup>a</sup> Eun Gyeong Lee,<sup>b</sup> Zhongyu Duan,<sup>a</sup> Il Kim\*,<sup>b</sup> and Binyuan Liu\*,<sup>a</sup>

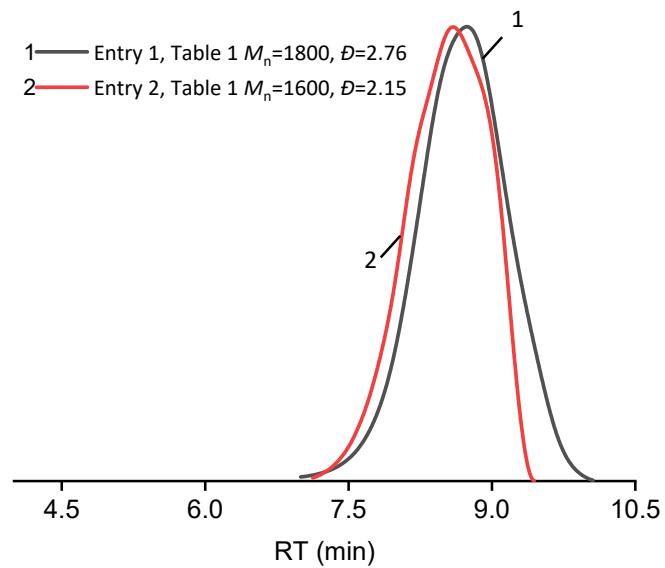
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<sup>a</sup> Hebei Key Laboratory of Functional Polymer, School of Chemical Engineering and Technology, Hebei University of Technology, Tianjin 300130, China. E-mail: byliu@hebut.edu.cn.

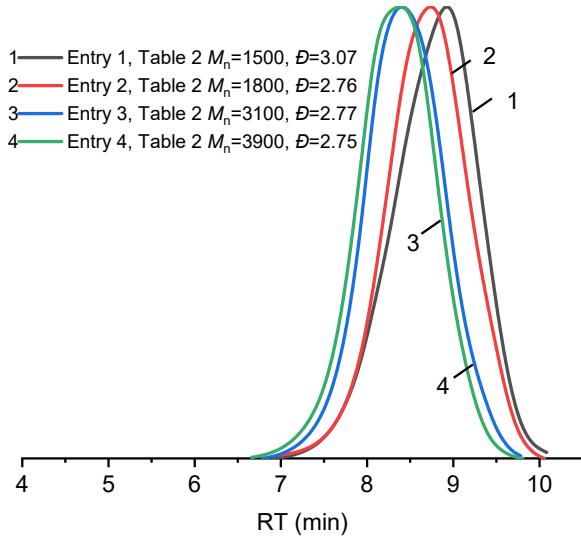
<sup>b</sup> School of Chemical Engineering, Pusan National University, Busan 46241, Korea. E-mail: ilkim@pusan.ac.kr.



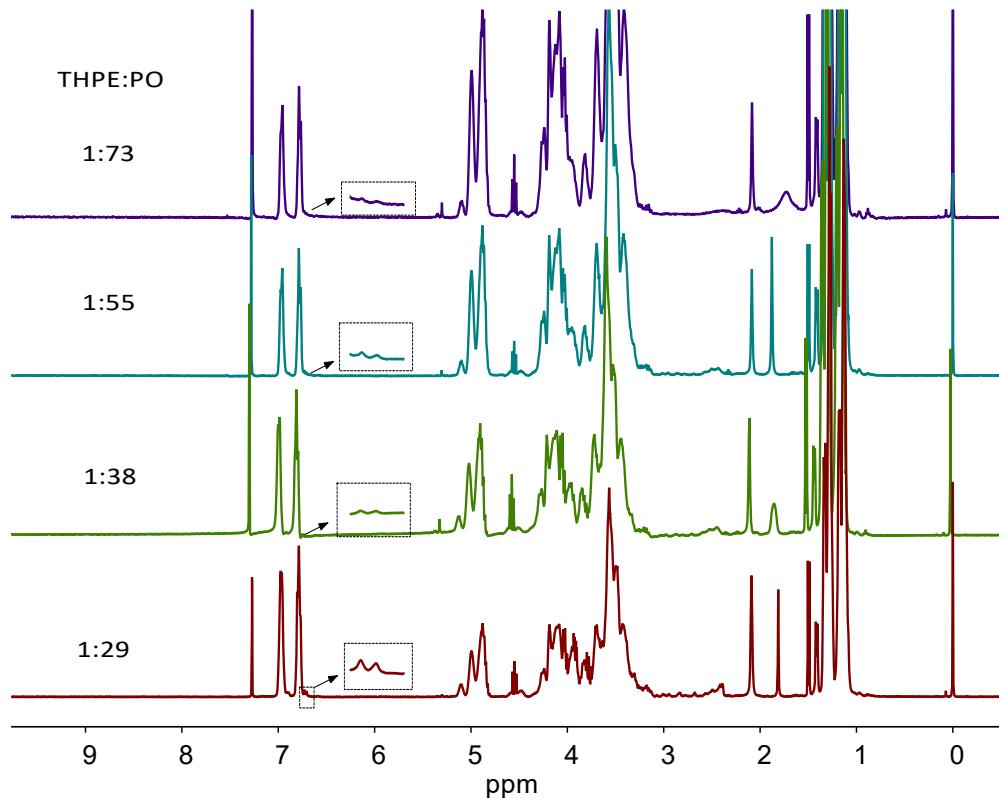
**Figure S1.** <sup>1</sup>H NMR spectra of poly(carbonate-ether) polyols prepared using THPE and THPM as initiators (Entries 1 and 2, Table 1).



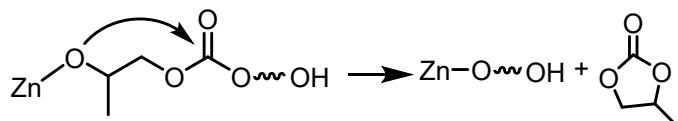
**Figure S2.** GPC plots of poly(carbonate-ether) polyols prepared using THPE and THPM as starters (Entries 1 and 2, Table 1).



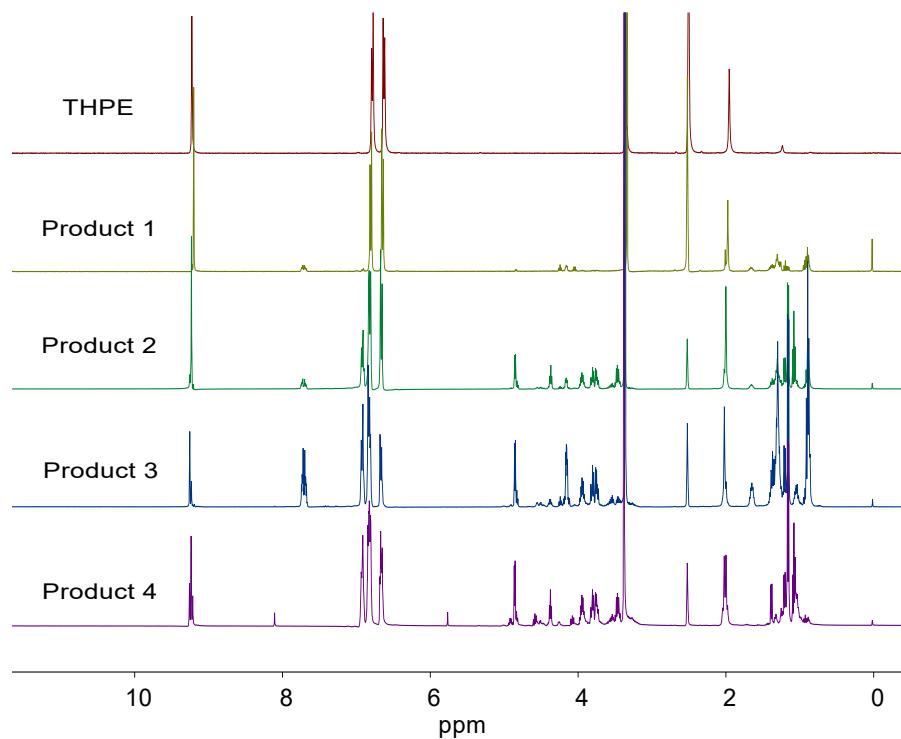
**Figure S3.** GPC curves of products obtained by using different dosages of THPE (Entries 1–4, Table 2).



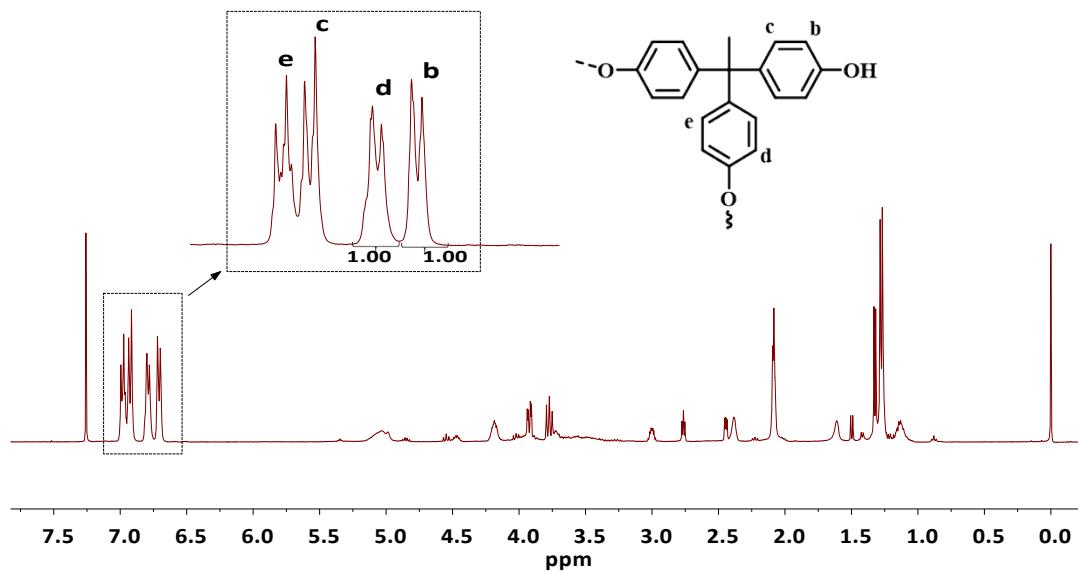
**Figure S4.** <sup>1</sup>H NMR spectra of products obtained by using different dosages of THPE (Entries 1–4, Table 2).



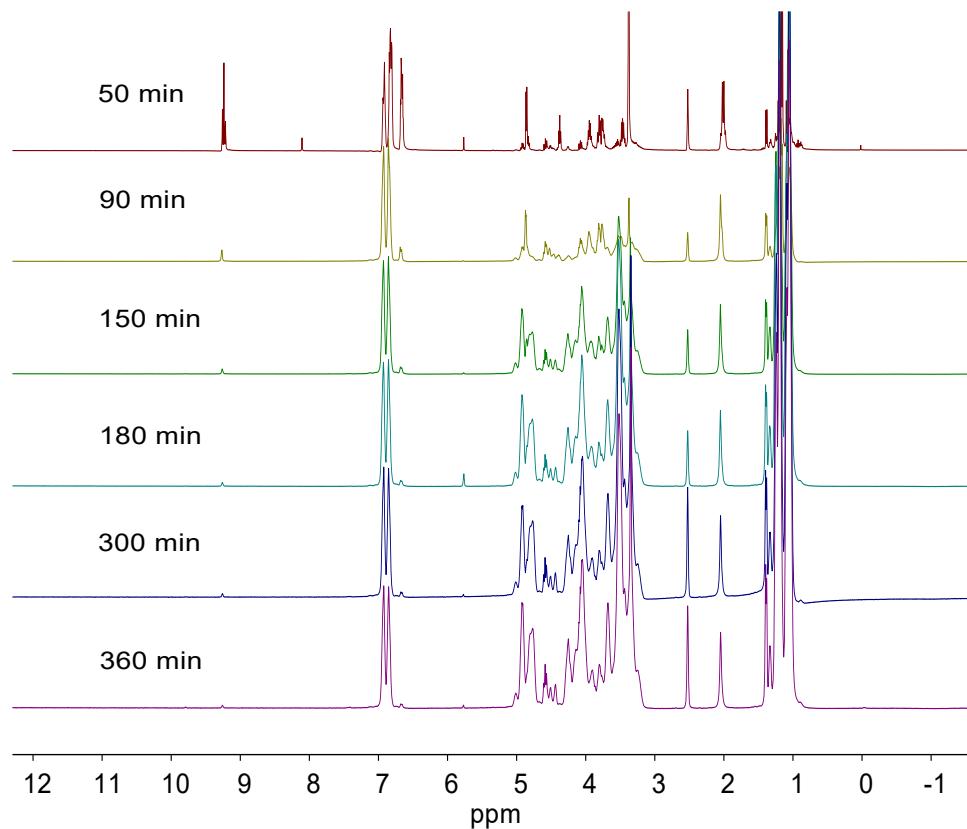
**Figure S5.** Plausible mechanism of backbite.



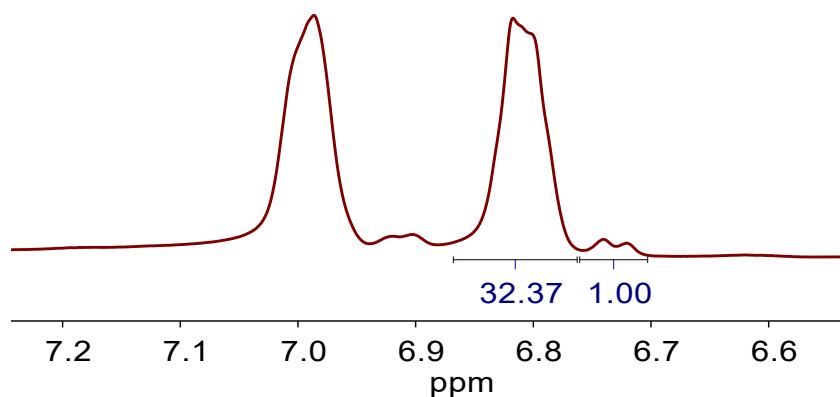
**Figure S6.** <sup>1</sup>H NMR (DMSO) spectra of the three different species (Products 1–3) separated from the CH<sub>2</sub>Cl<sub>2</sub> insoluble sample and <sup>1</sup>H NMR spectrum of the CH<sub>2</sub>Cl<sub>2</sub> soluble sample (Product 4). Copolymerizations were carried out at 95 °C, 4 MPa with PO (50 mL, 41.5 g, 0.72 mol), 13 mg DMC, n<sub>THPE</sub>:n<sub>PO</sub>=1:38 (5.8 g THPE).



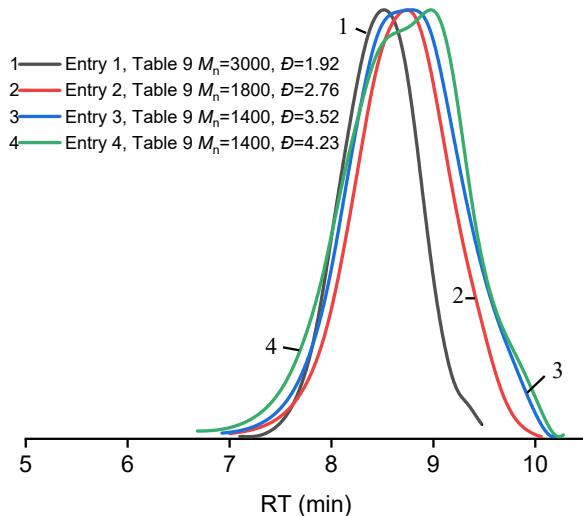
**Figure S7.**  $^1\text{H}$  NMR( $\text{CDCl}_3$ ) spectrum of the product taken at 50 min of reaction.



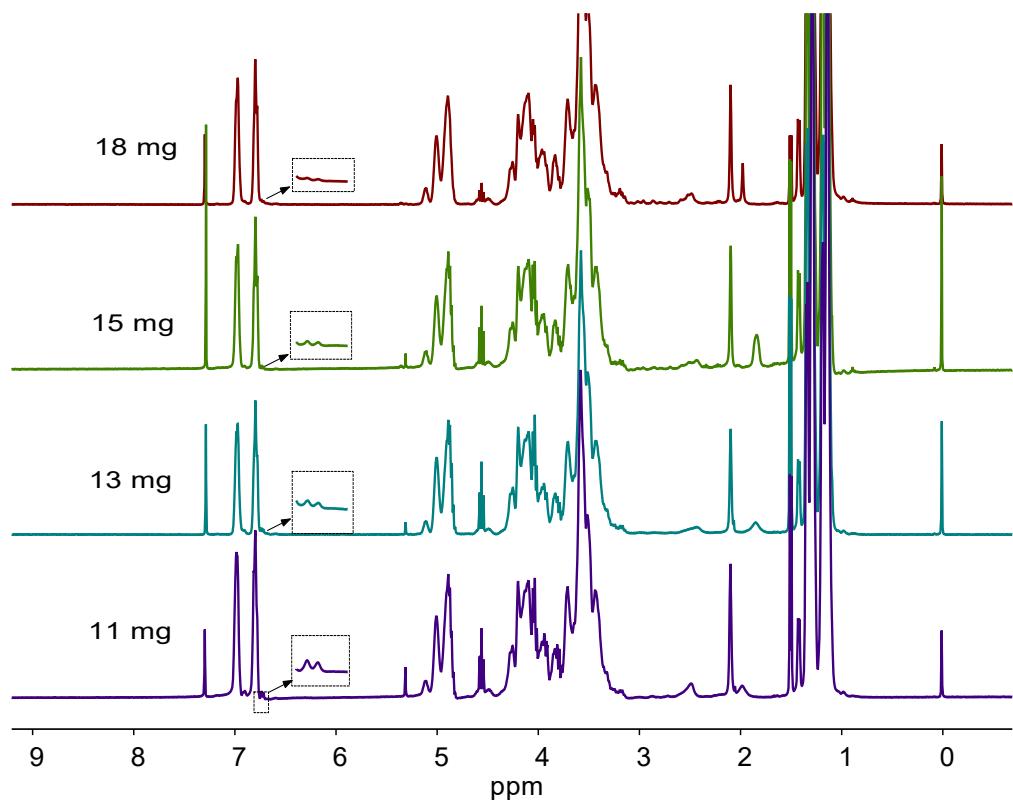
**Figure S8.**  $^1\text{H}$  NMR (DMSO) spectra of the products collected at different reaction periods. Copolymerizations were carried out at 95 °C, 4 MPa with PO (50 mL, 41.5 g, 0.72 mol), 13 mg DMC,  $n_{\text{THPE}}:n_{\text{PO}}=1:38$  (5.8 g THPE).



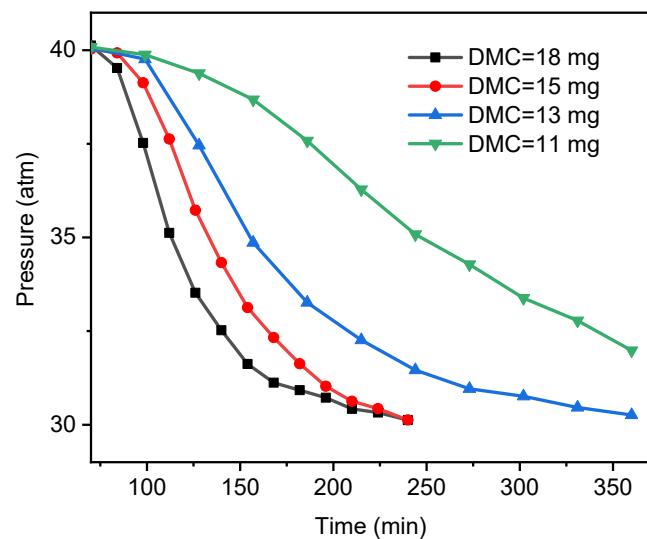
**Figure S9.** The  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) of the product collected at 70 min of polymerization. Copolymerizations were carried out at 95 °C, 4 MPa with 18 mg DMC, PO (50 mL, 41.5 g, 0.72 mol),  $n_{\text{THPE}}:n_{\text{PO}}=1:38$  (5.8 g THPE).



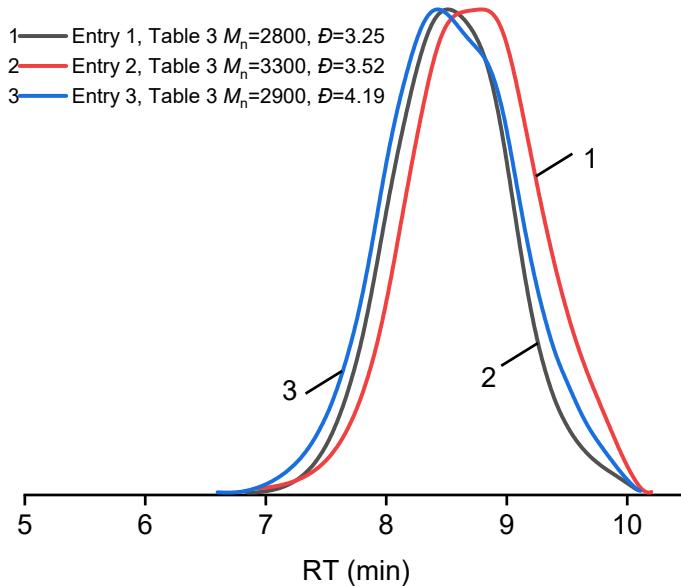
**Figure S10.** GPC curves of products obtained by using different dosages of DMC catalyst (Entries 1–4, Table 9).



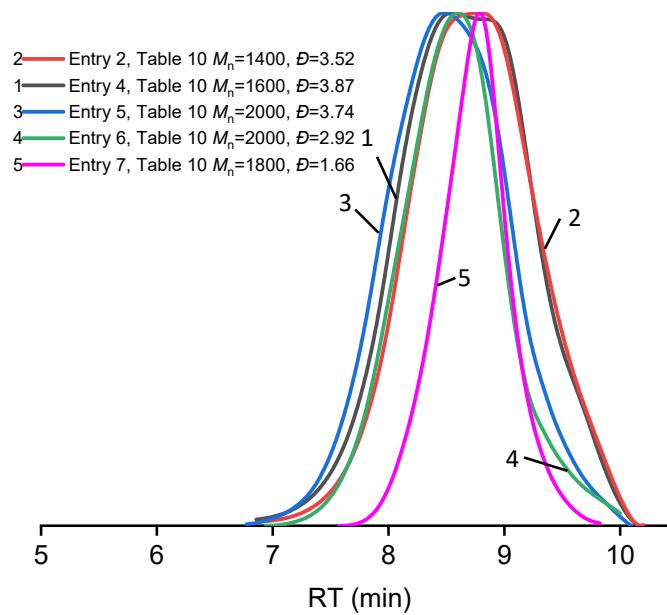
**Figure S11.** <sup>1</sup>H NMR spectra of products obtained by using different dosages of DMC catalyst (Entries 1–4, Table 9).



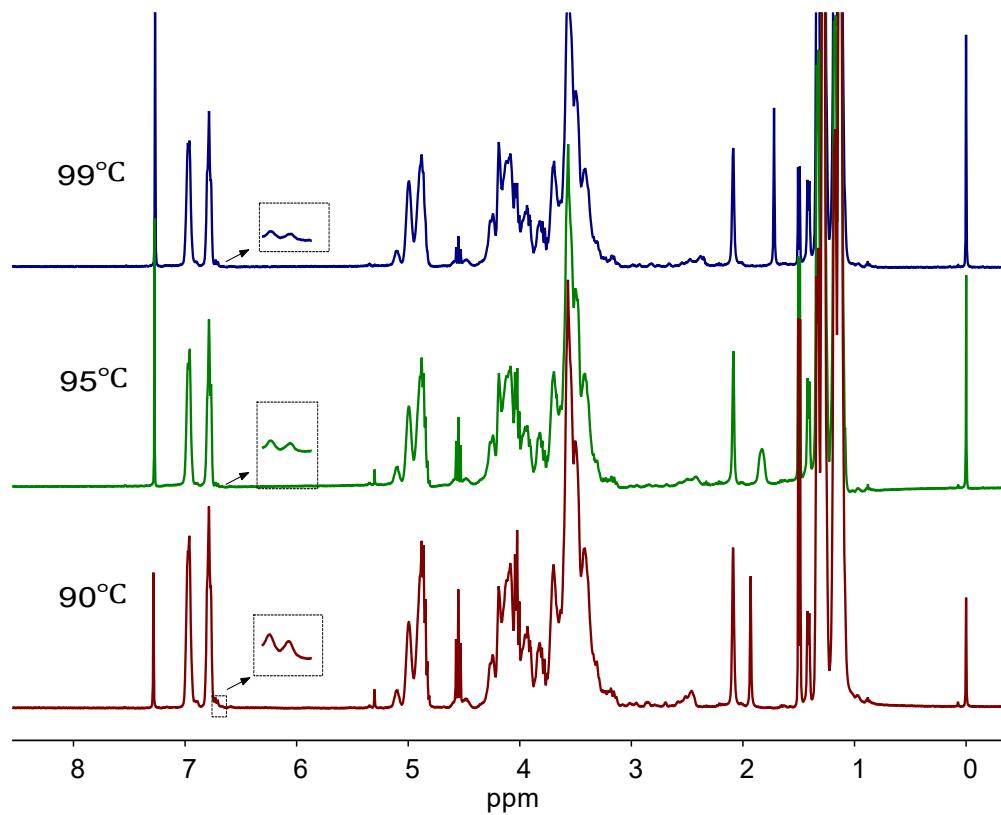
**Figure S12.** The variation of CO<sub>2</sub> pressure during the copolymerization under different dosages of DMC catalyst (Entries 1–4, Table 9).



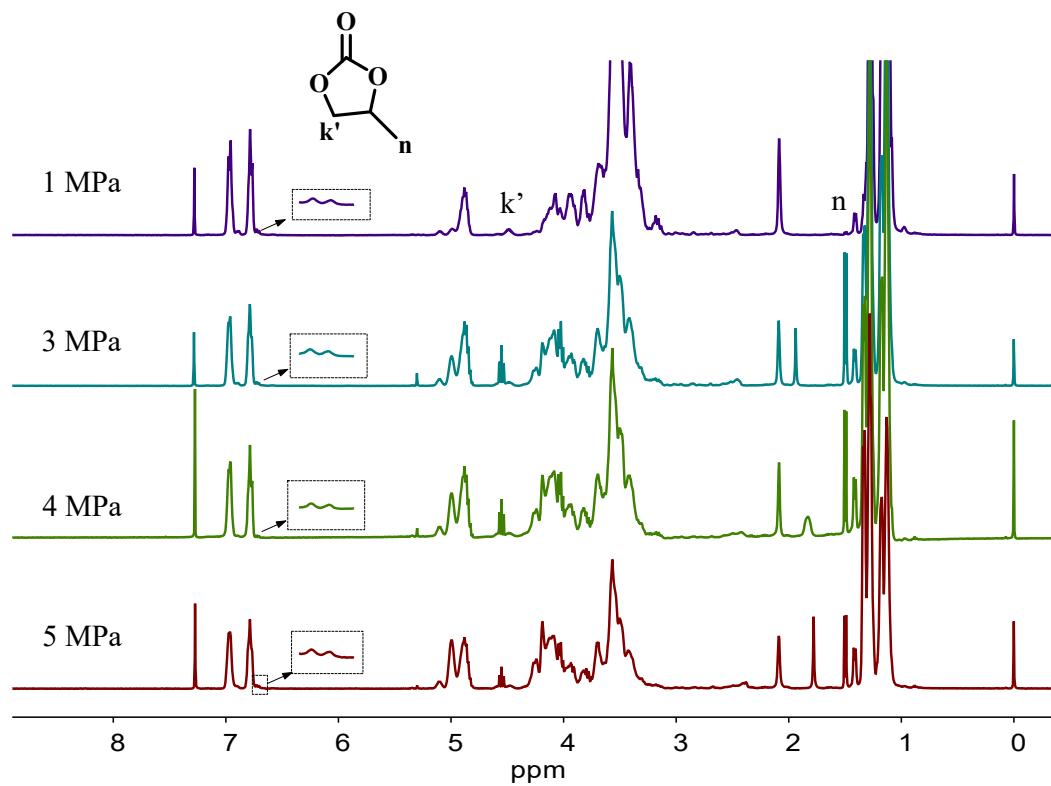
**Figure S13.** GPC curves of products obtained by using different temperatures (Entries 1–3, Table 10).



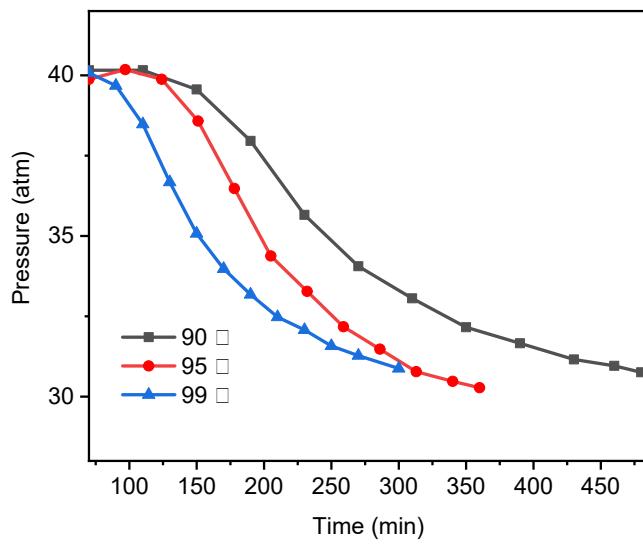
**Figure S14.** GPC curves of products obtained by using different pressures of  $\text{CO}_2$  (Entries 2, 4–7, Table 10).



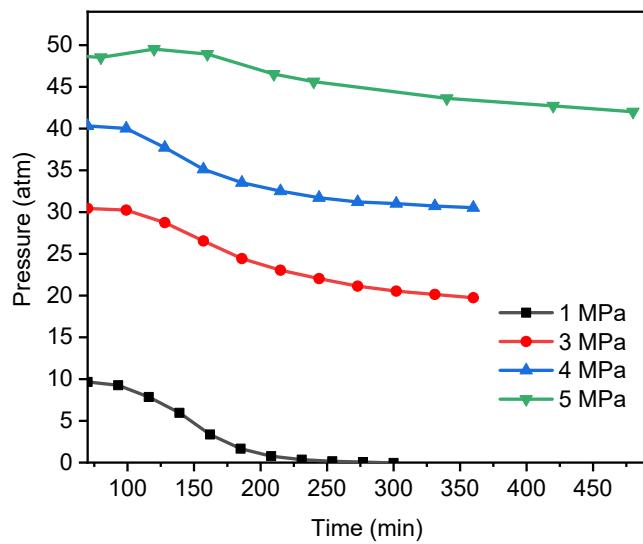
**Figure S15.** <sup>1</sup>H NMR spectra of products obtained by using different temperatures (Entries 1–3, Table 10).



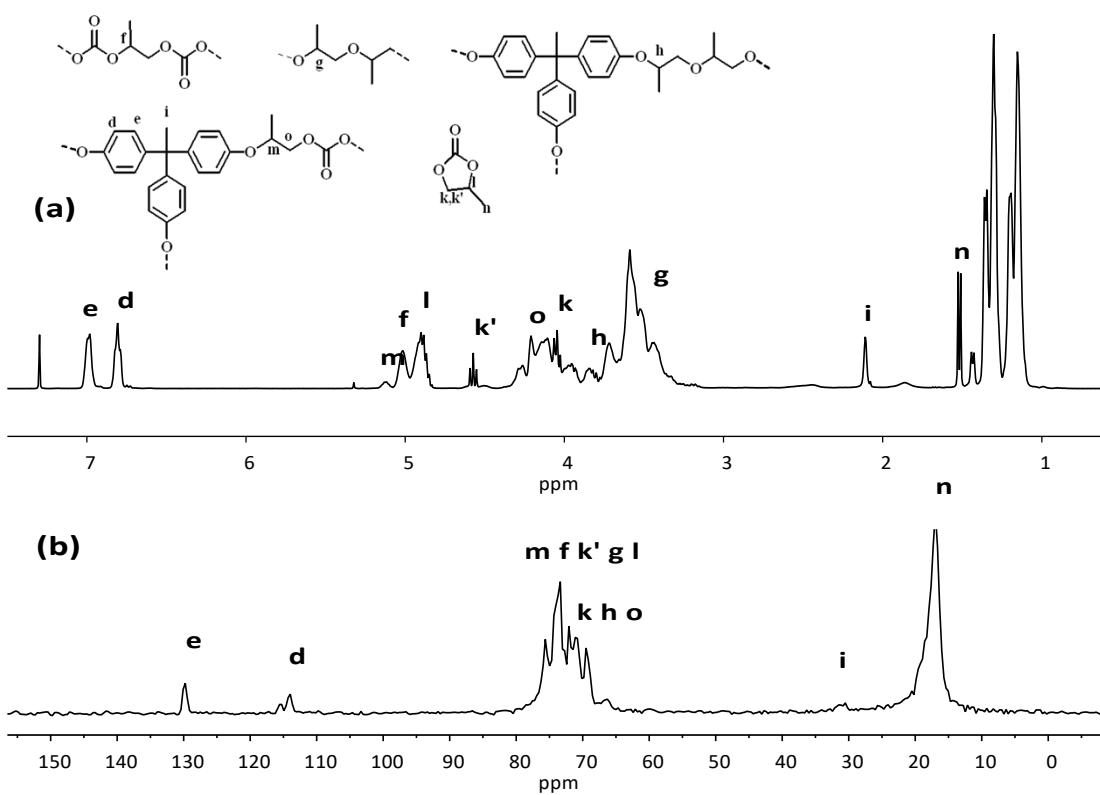
**Figure S16.** <sup>1</sup>H NMR spectra of products obtained by using different pressures of  $\text{CO}_2$  (Entries 2, 4–6, Table 10).



**Figure S17.** The variation of CO<sub>2</sub> pressure during the copolymerizations under different temperatures (Entries 1–3, Table 10).



**Figure S18.** The variation of CO<sub>2</sub> pressure during the copolymerizations under different CO<sub>2</sub> pressures (Entries 2, 4–6, Table 10).



**Figure S19.** <sup>1</sup>H and <sup>13</sup>C NMR ( $\text{CDCl}_3$ ) spectra of the product (Entry 3, Table 9). Copolymerizations were carried out at 95 °C, 4 MPa with 13 mg DMC PO (50 mL, 41.5 g, 0.72 mol),  $n_{\text{THPE}}:n_{\text{PO}}=1:38$  (5.8 g THPE).