Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

Synthesis of Fully Alternating Polycarbonate with Low Tg from Bio-based Fatty Acid and Carbon Dioxide

Ying-Ying Zhang, Xing-Hong Zhang*, Ren-Jian Wei, Bin-Yang Du, Zhi-Qiang Fan, Guo-Rong Qi

MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou, 310027, China. Fax & Tel: +86 571 87953732; E-mail: xhzhang@zju.edu.cn

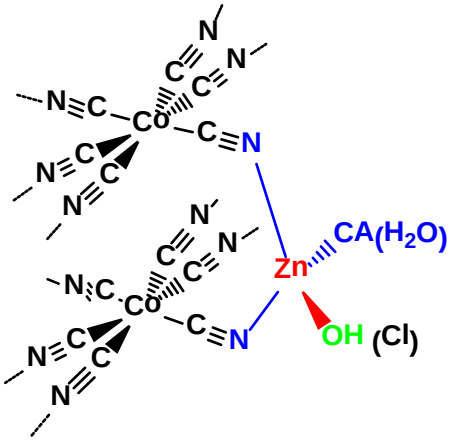

Figure S1. The proposed structure of the active site of Zn-Co (III) DMCC catalyst. The tetrahedral $(CN)_2Zn{-}OH$ structure is proposed as the initiating group of this catalyst (CA represents the complexing agent used during the preparation of the catalyst).

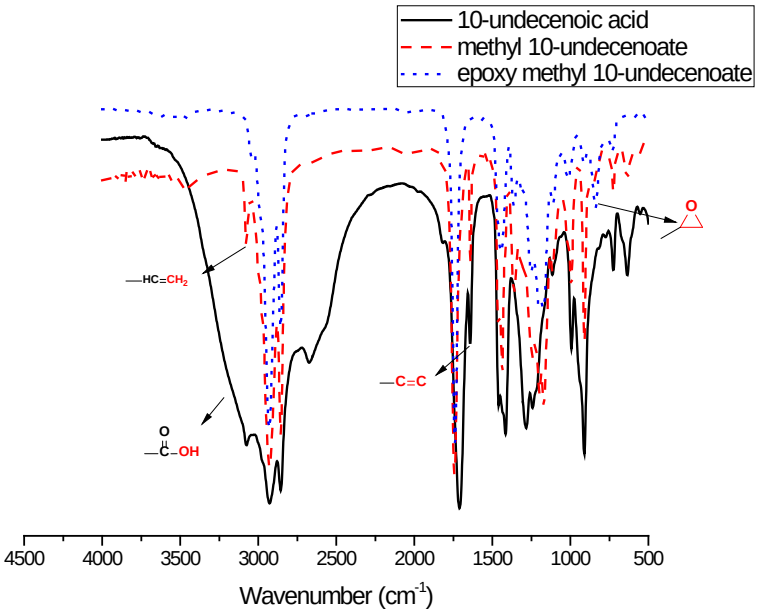

Figure S2. FTIR spectra of 10-undecenoic acid, methyl 10-undecenoate and epoxy methyl 10-undecenoate.

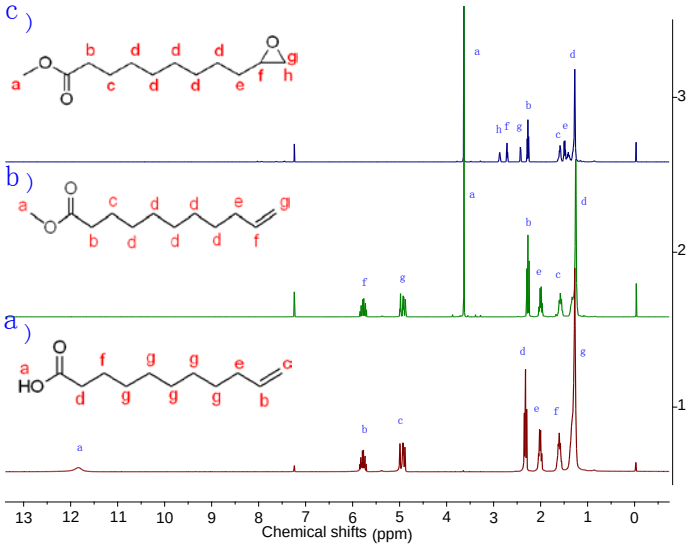

Figure S3. ^{1}H NMR spectra of a) 10-undecenoic acid , b) methyl 10-undecenoate and c) epoxy methyl 10-undecenoate ($CDCl_3$, 500 MHz).

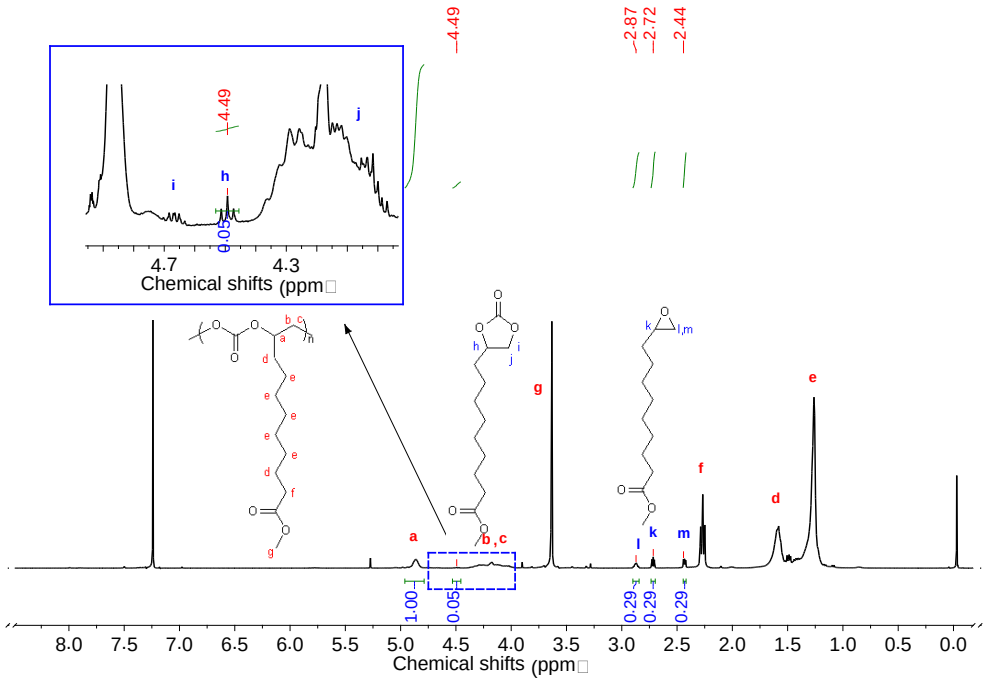

Figure S4. ^{1}H NMR spectrum of the crude copolymer at 40^{o}C (entry 2, Table 1).

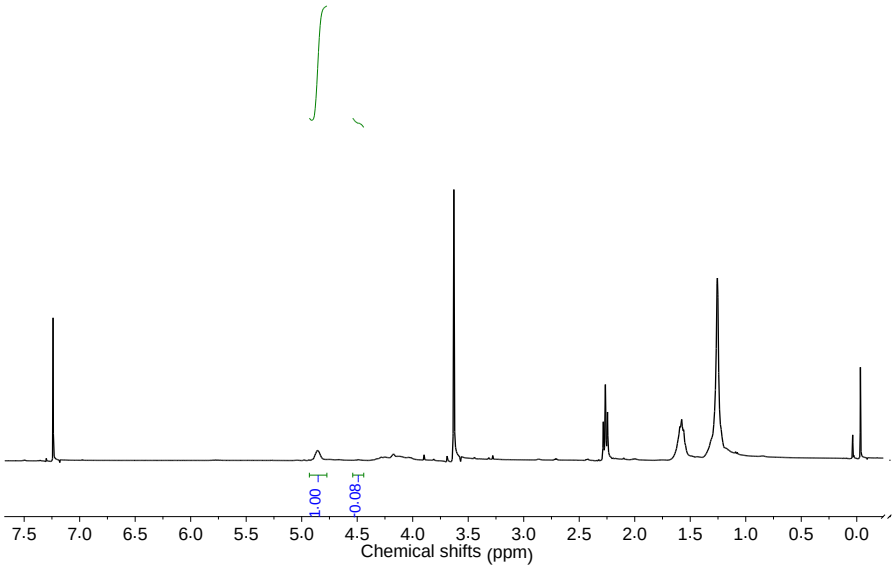

Figure S5. ^{1}H NMR spectrum of crude copolymer at 50^{o}C (entry 3, Table 1).

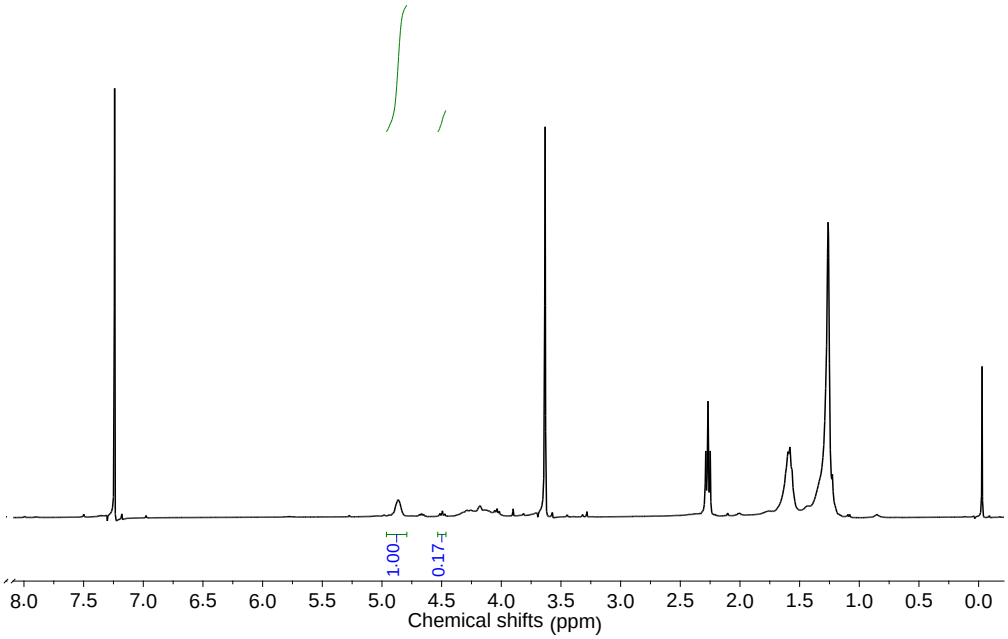

Figure S6. ^{1}H NMR spectrum of crude copolymer at 60^{o}C (entry 4, Table 1).

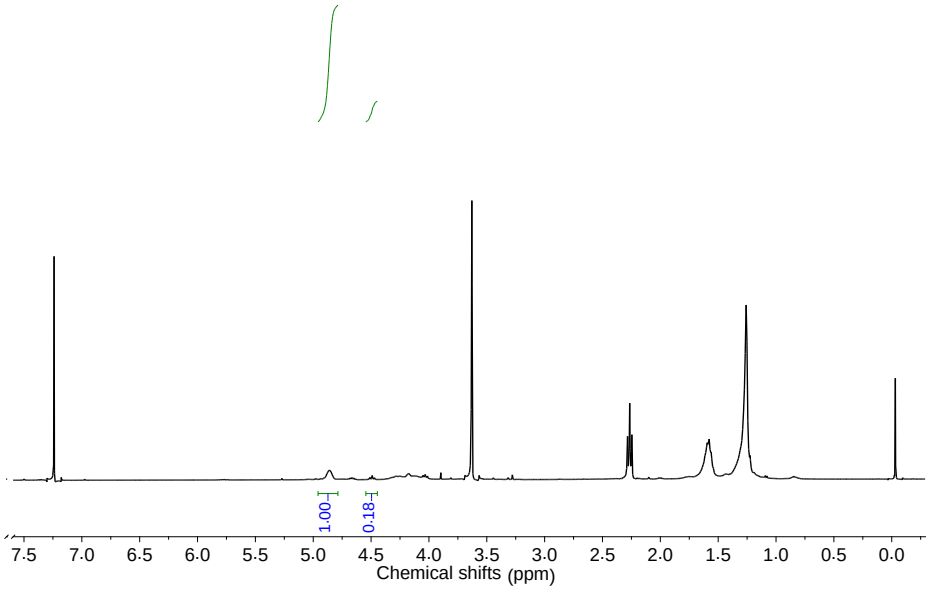

Figure S7. ^{1}H NMR spectrum of crude copolymer at 70^{o}C (entry 5, Table 1).

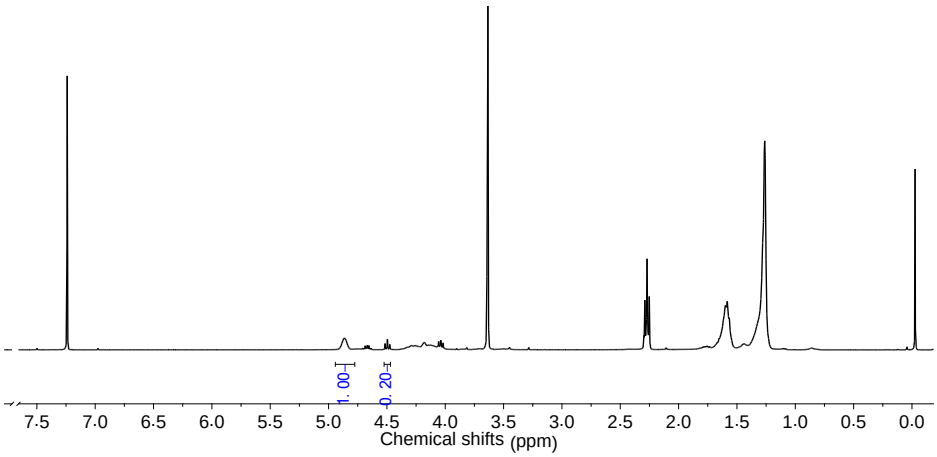

Figure S8. ^{1}H NMR spectrum of crude copolymer at 80^{o}C (entry 6, Table 1).

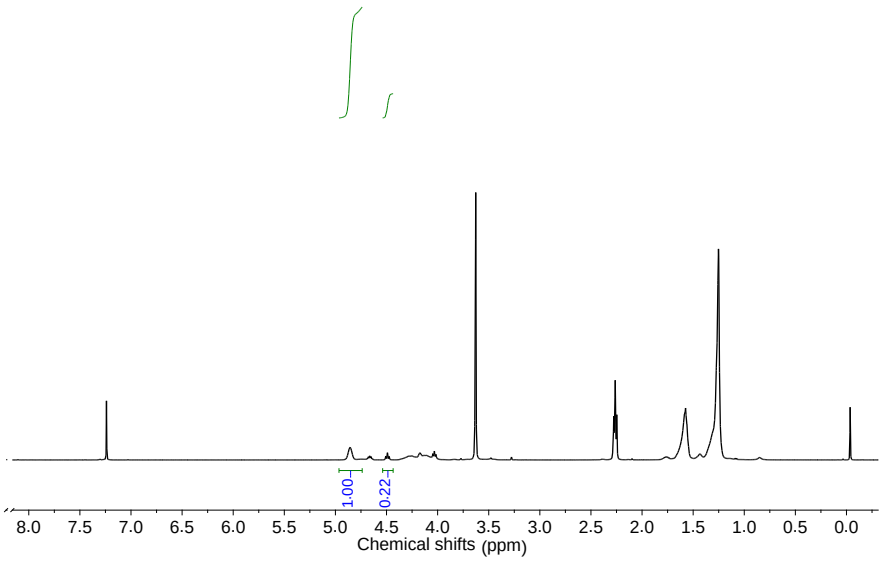

Figure S9. ^{1}H NMR spectrum of crude copolymer at 90^{o}C (entry 7, Table 1).

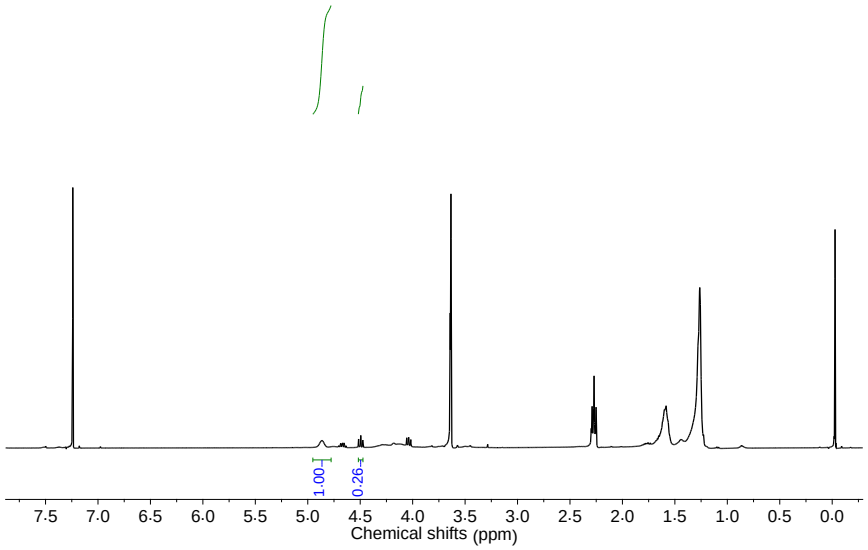

Figure S10. ^{1}H NMR spectrum of the crude copolymer at 100^{o}C (entry 8, Table 1).

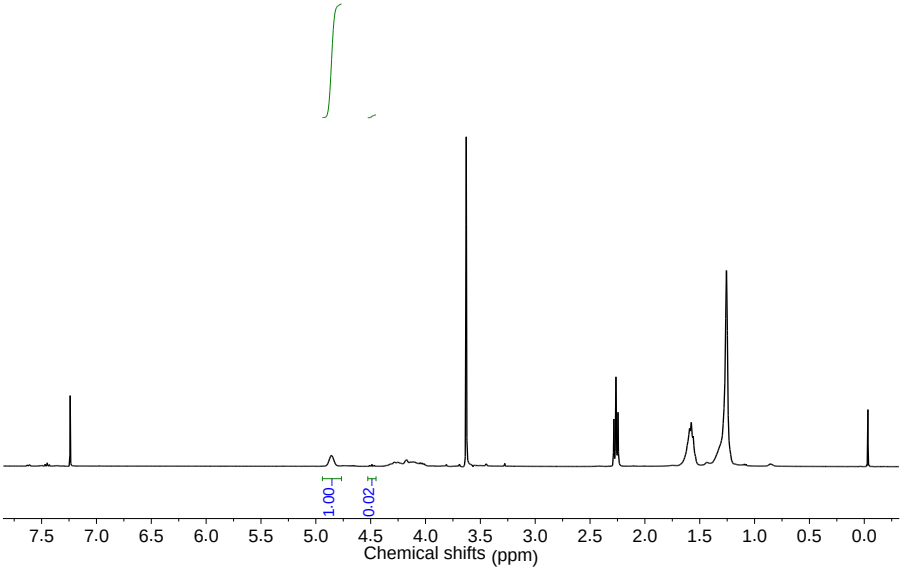

Figure S11. ^{1}H NMR spectrum of the crude copolymer at 50^{o}C (entry 9, Table 1).

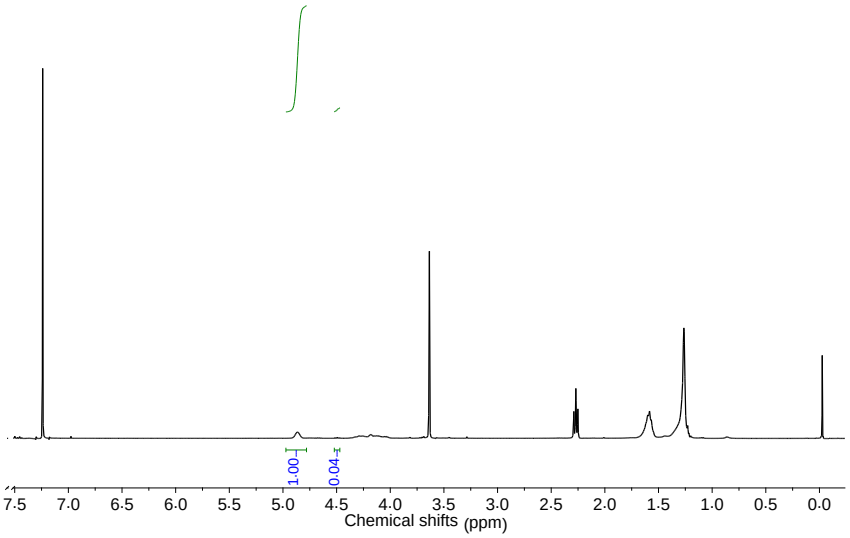

Figure S12. ^{1}H NMR spectrum of the crude copolymer at 50^{o}C (entry 10, Table 1).

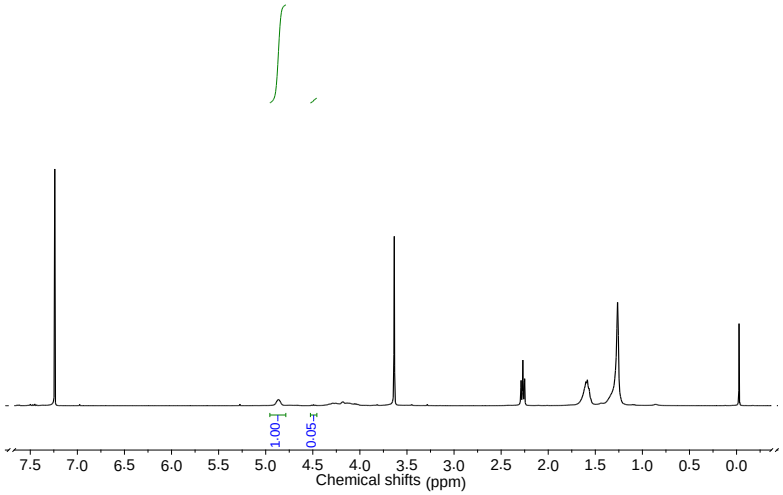

Figure S13. ^{1}H NMR spectrum of the crude copolymer at 50^{o}C (entry 11, Table 1).

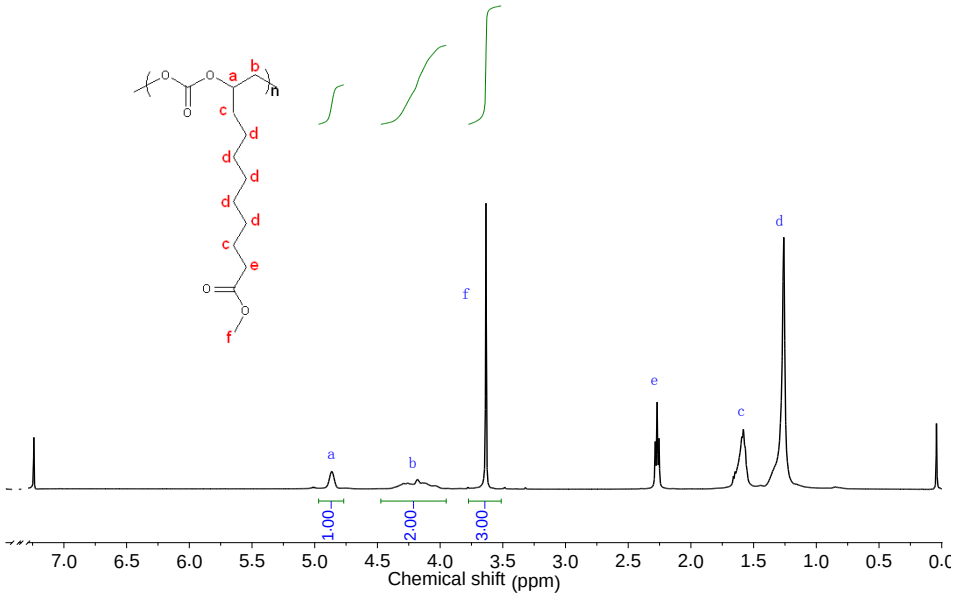

Figure S14. ^{1}H NMR spectrum of the purified copolymer at 40^{o}C (entry 2, Table 1).

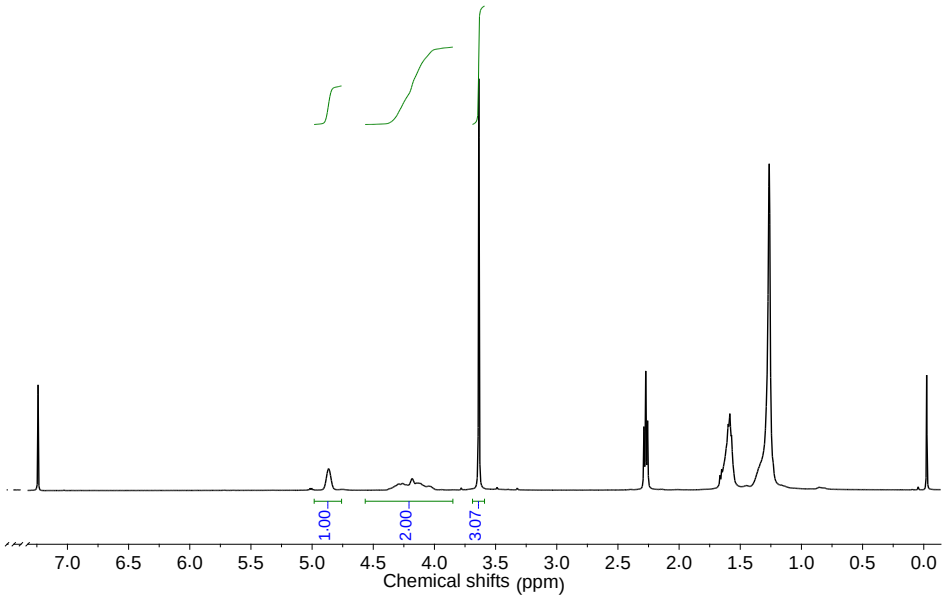

Figure S15. ^{1}H NMR spectrum of purified copolymer at 50^{o}C (entry 3, Table 1).

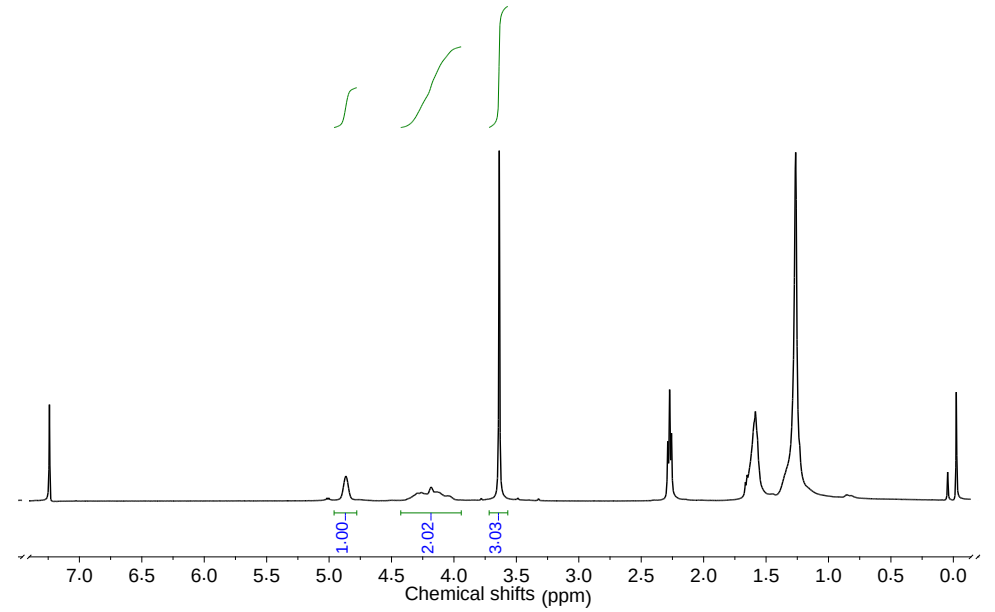

Figure S16. ^{1}H NMR spectrum of purified copolymer at 60^{o}C (entry 4, Table 1).

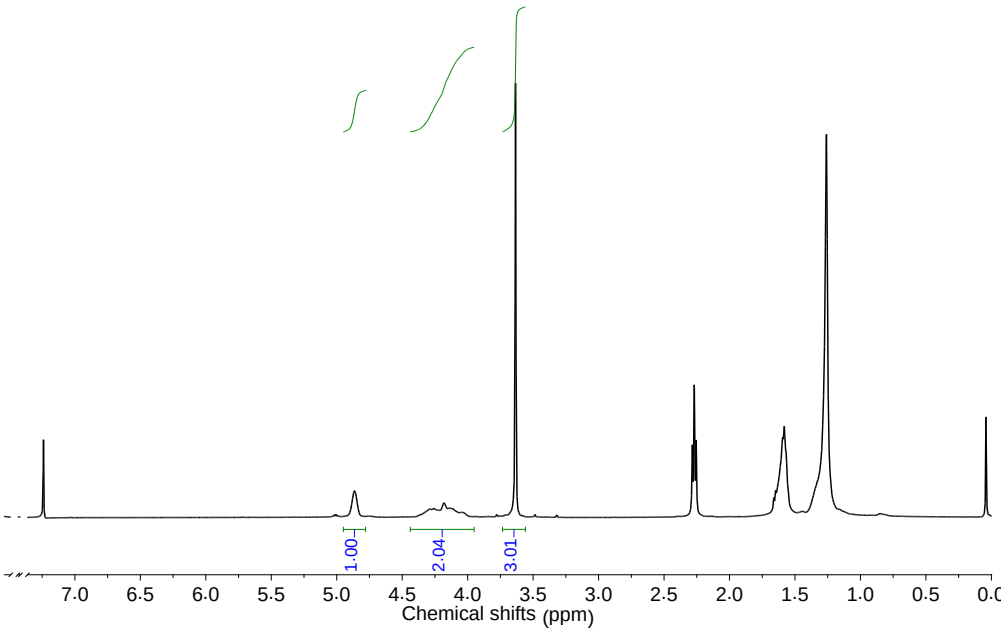

Figure S17. ^{1}H NMR spectrum of purified copolymer at 70^{o}C (entry 5, Table 1).

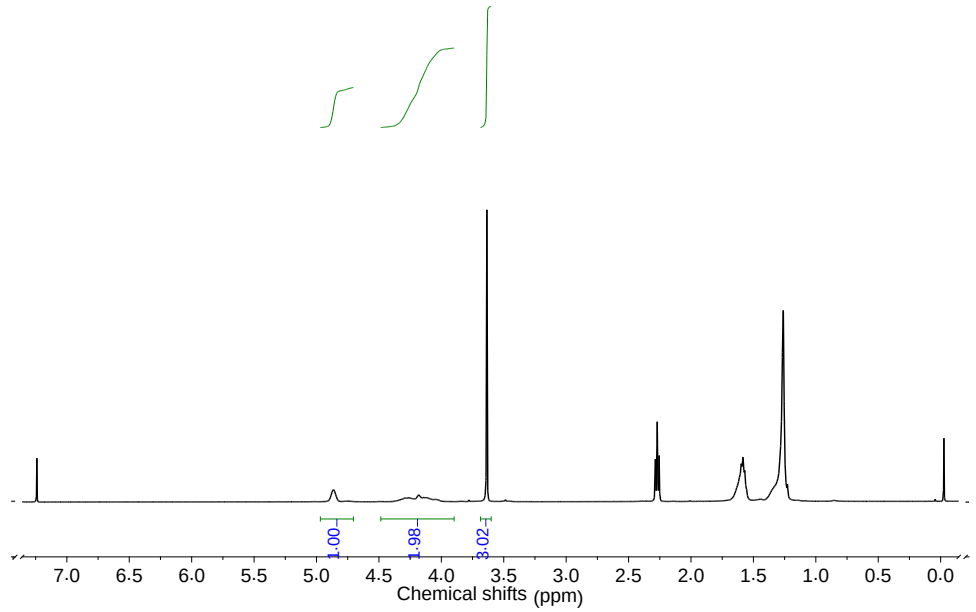

Figure S18. ^{1}H NMR spectrum of purified copolymer at 80^{o}C (entry 6, Table 1).

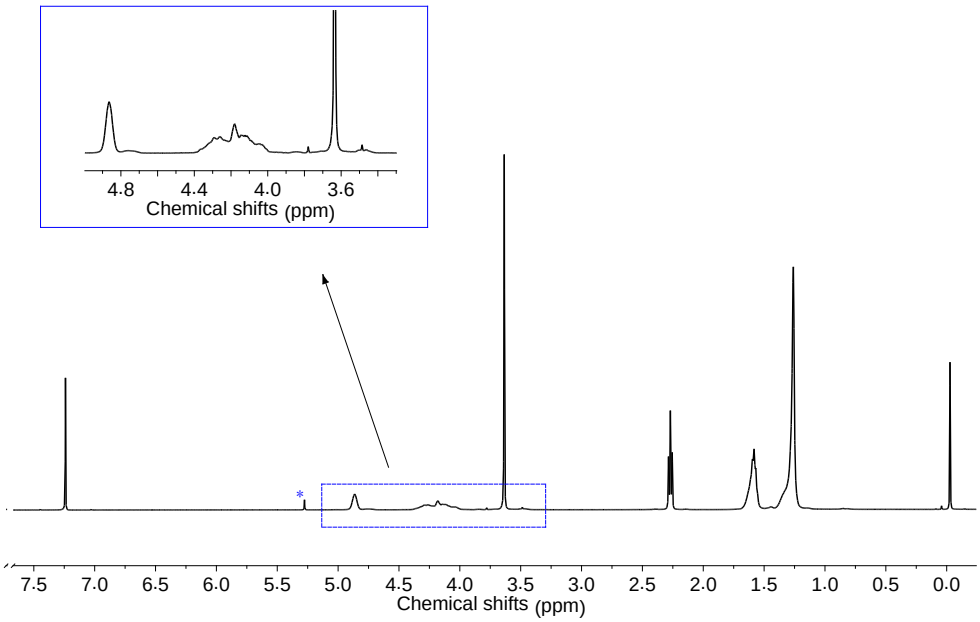

Figure S19. ^{1}H NMR spectrum of purified copolymer at 90^{o}C (entry 7, Table 1).

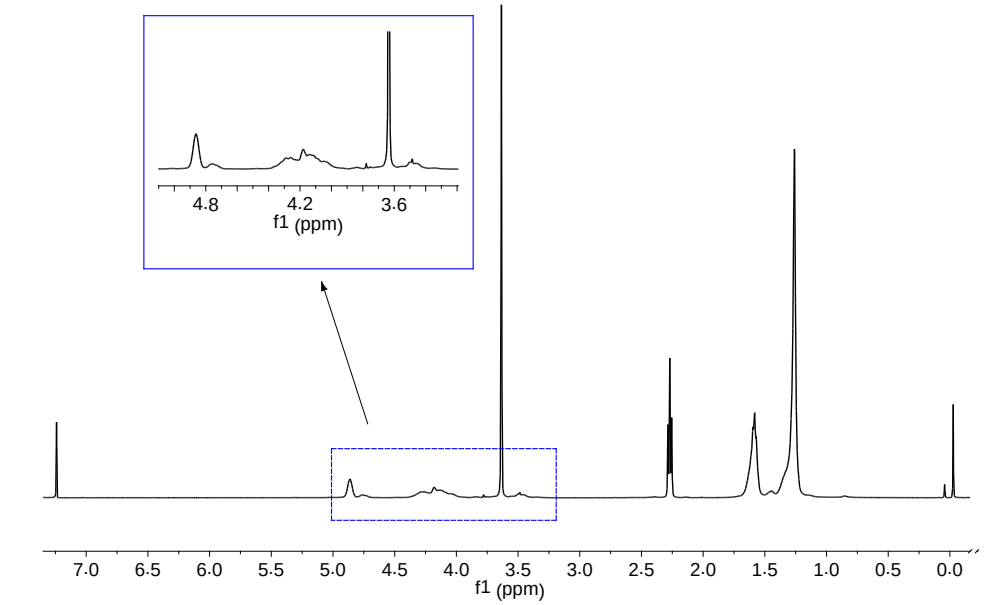

Figure S20. ^{1}H NMR spectrum of the purified copolymer at 100^{o}C (entry 8, Table 1).

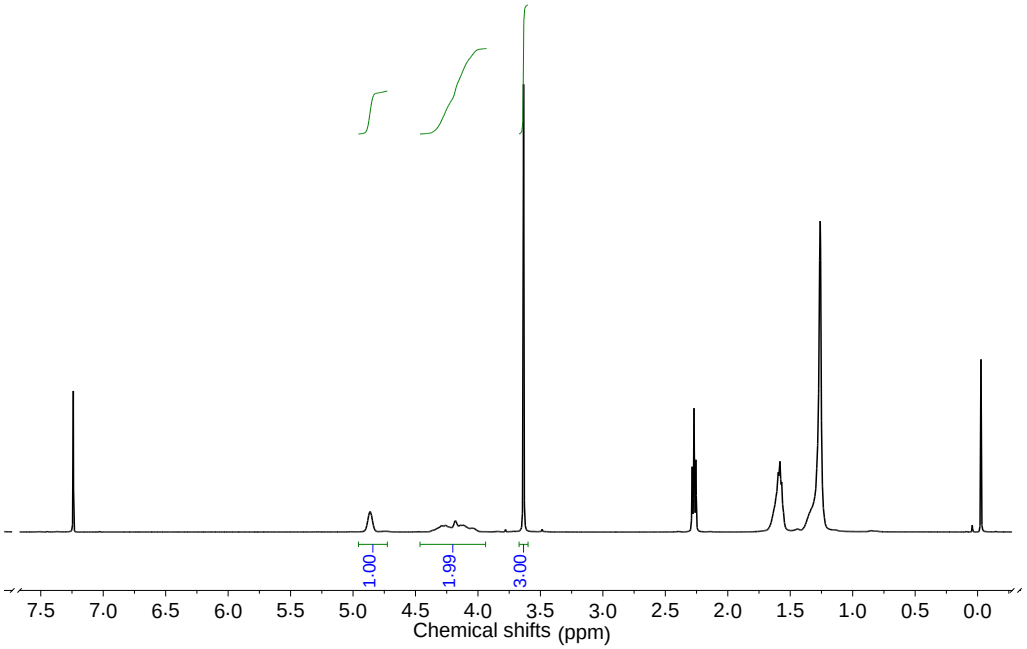

Figure S21. ^{1}H NMR spectrum of the purified copolymer at 50^{o}C (entry 9, Table 1).

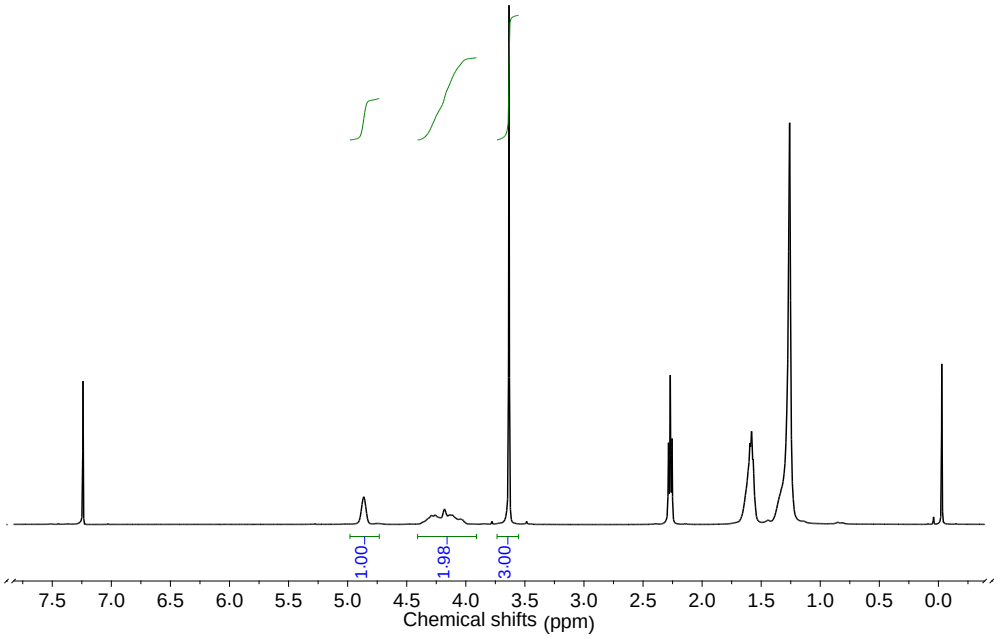

Figure S22. ^{1}H NMR spectrum of the purified copolymer at 50^{o}C (entry 10, Table 1).

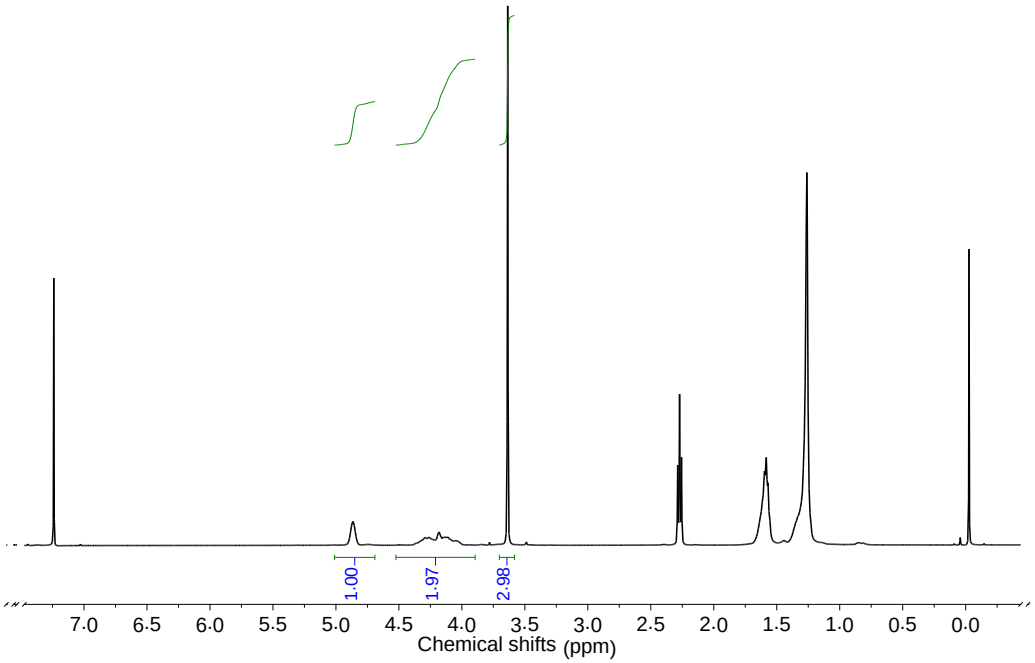

Figure S23. ^{1}H NMR spectrum of the purified copolymer at 50^{o}C (entry 11, Table 1).

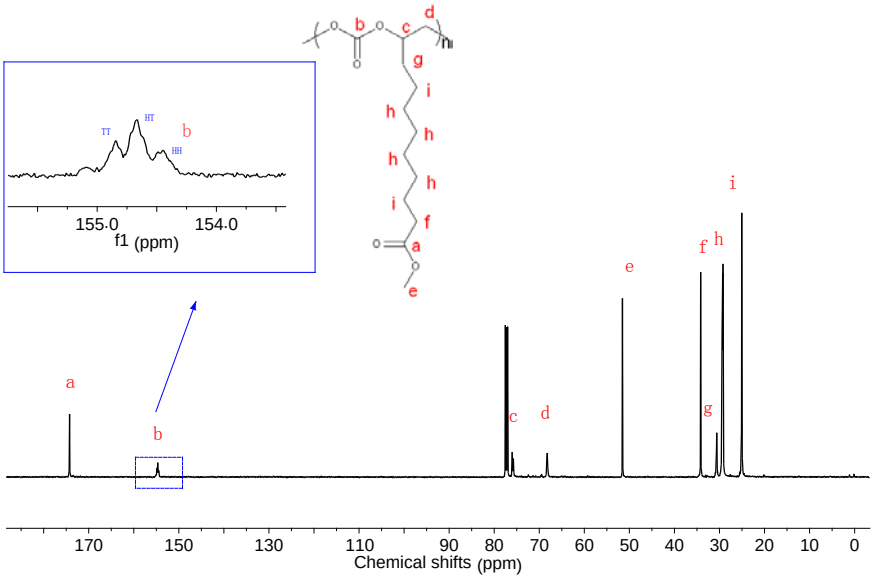

Figure S24. ^{13}C NMR spectrum of purified copolymer of entry 5 in Table 1 in $CDCl_3$. HH = head-to-head, HT = head-to-tail, TT = tail-to-tail.

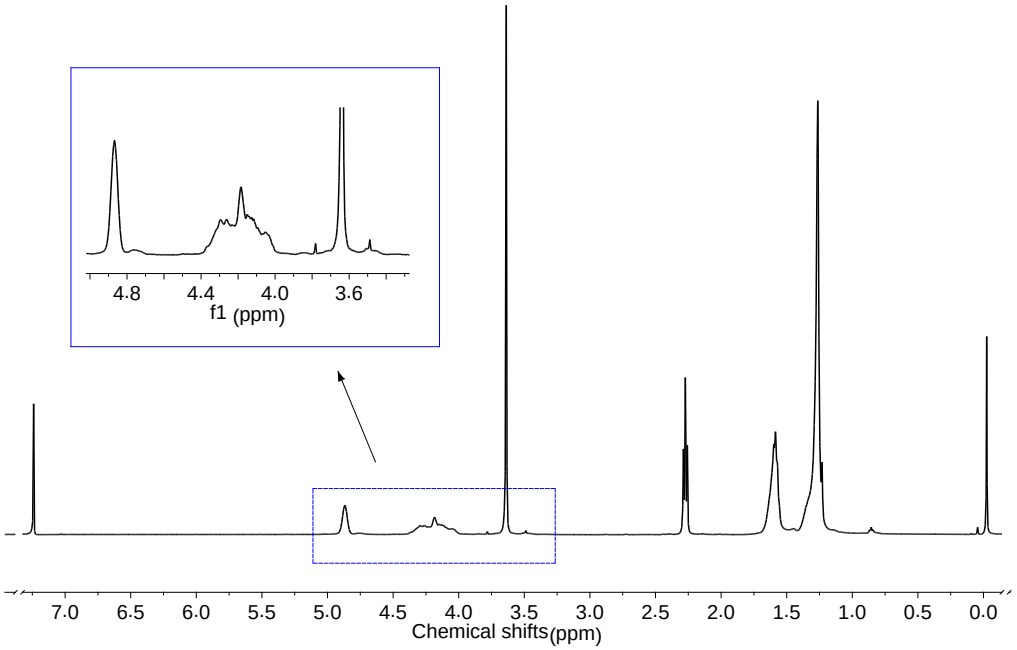

Figure S25. ^{1}H NMR spectrum of the purified copolymer with a low M_n of 2000 (GPC) and a Fco_2% of 95.2% (90°C, 5h for ESI−MS analyses).

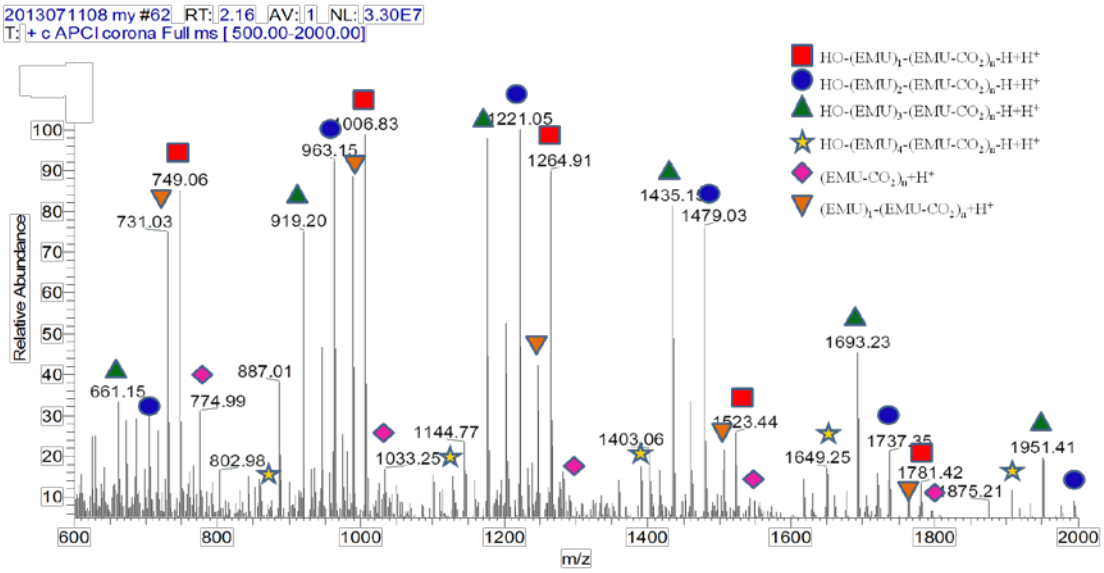

Figure S26. ESI-MS spectrum of the EMU-CO_2 copolymer with with a low M_n of 2000 (GPC) and a Fco_2% of 95.2%. Note that all the m/z species in the range of 600-2000 were captured, and polymers with M_n > 2000 (because wide PDI, as seen in Figure S25) could not be detected due to the limitation of the ESI instrument.

Table S1. m/z species of the EMU-CO2 copolymer (ESI full ms [600-2000]).

Species	Mark	m/z
HO-(EMU)$_1$ -(EMU-CO_2)$_n$-H +H^+	■	749,1007,1265,1523,1781
(17+214+258n+1+1, n=2,3,4,5,6)		
HO-(EMU)$_2$ -(EMU-CO_2)$_n$-H +H^+	●	705,963,1221,1479,1737,1995
(17+214*2+258n+1+1, n=1,2,3,4,5,6)		
HO-(EMU)$_3$ -(EMU-CO_2)$_n$-H +H^+	▲	661,919,1177,1435,1693,1951
(17+214*3+258n+1+1, n=0,1 ,2,3,4,5)		
HO-(EMU)$_4$ -(EMU-CO_2)$_n$-H +H^+	★	875,1133,1391,1649,1907
(17+214*4+258n+1+1, n=0,1 ,2,3,4)		
(EMU-CO_2)$_n$ +H^+	◆	775,1033,1291,1549,1807
(258n+1, n=3,4,5,6,7)		
(EMU)$_1$-(EMU-CO_2)$_n$ +H^+	▼	731,989,1247,1505,1763
(214+258n+1, n=2,3,4,5,6)		

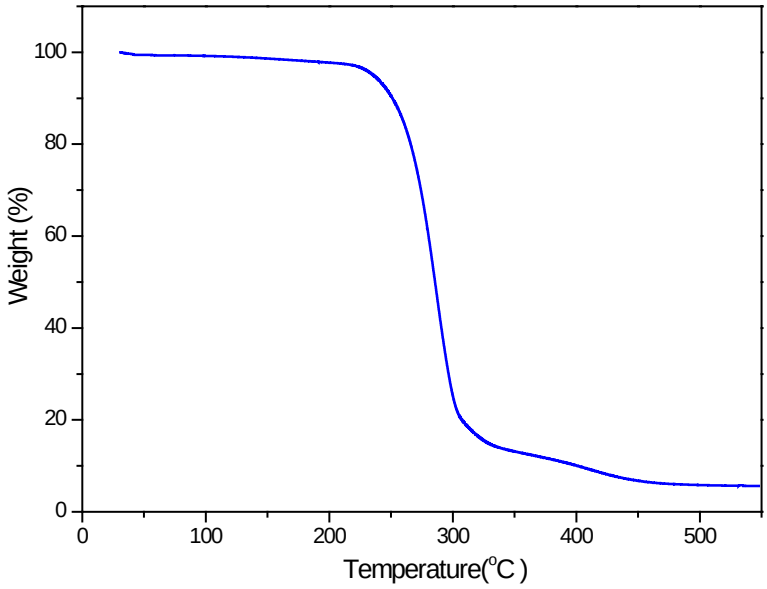

Figure S27. TGA plot of purified polycarbonate (entry 3, Table 1).

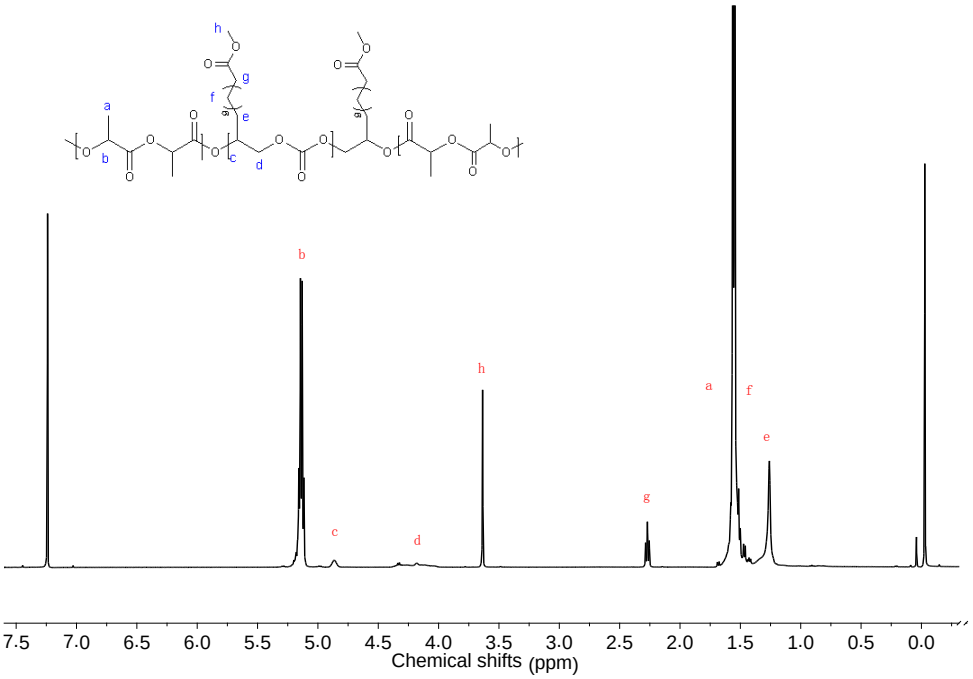

Figure S28. Representative ^{1}H NMR spectroscopy of the obtained (L-lactide-*b*-polycarbonate-*b*-L-lactide) in $CDCl_3$.

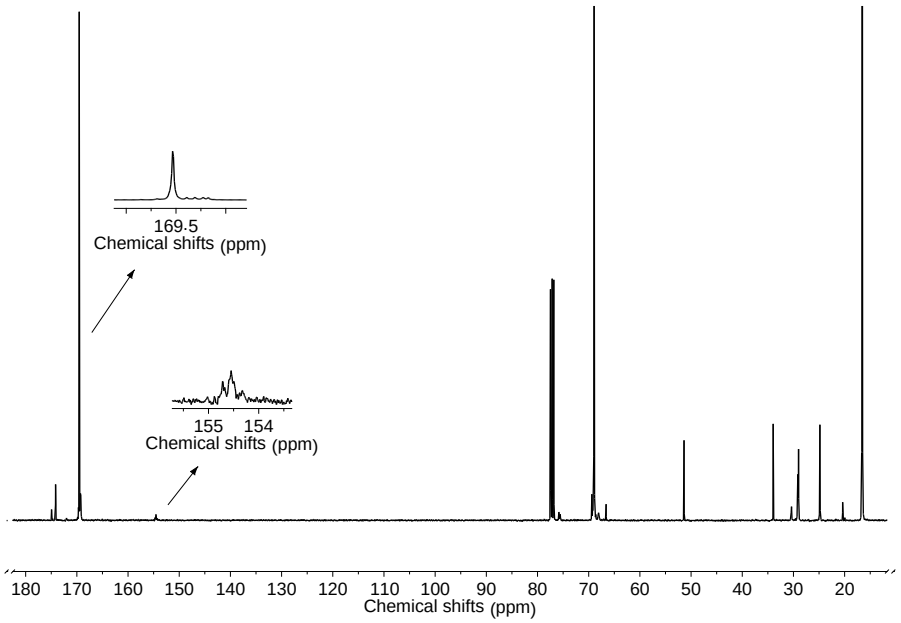

Figure S29. Representative ^{13}C NMR spectroscopy of the obtained poly (L-lactide-*b*-polycarbonate-*b*-L-lactide) in $CDCl_3$.

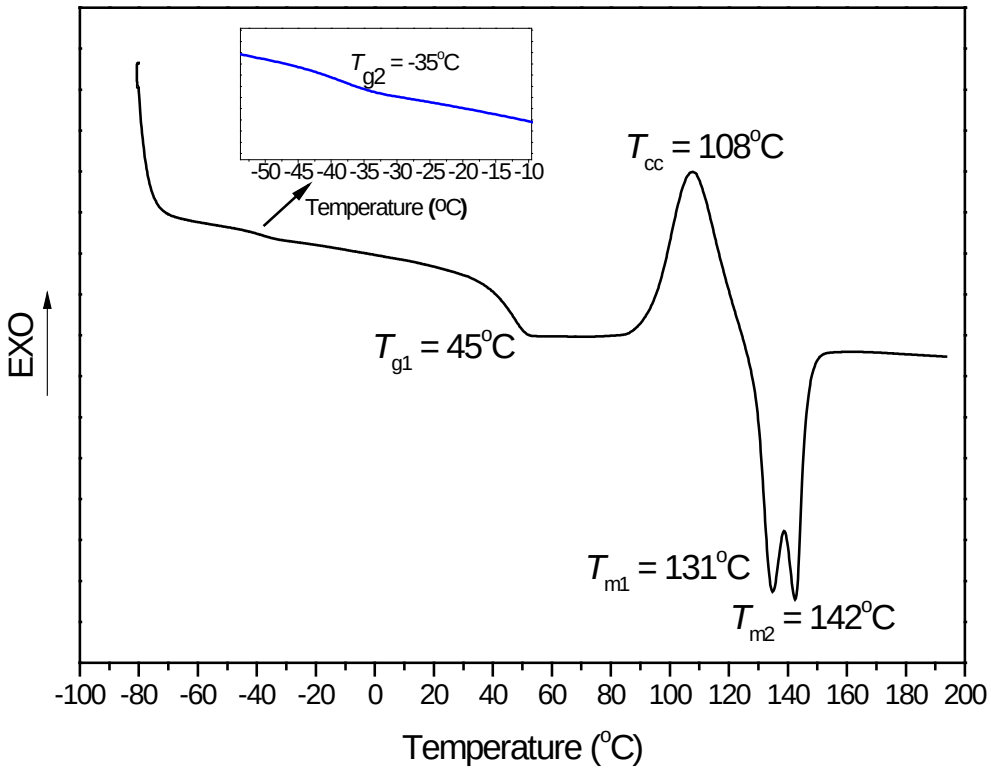

Figure S30. DSC thermograms for the obtained poly(L-lactide-*b*-polycarbonate-*b*-L-lactide). (The weight of test sample was 8.60 mg, heating rate of 20°C/min from -80-200°C under N_2 atmosphere.)