

Supporting Information for Manuscript Entitled

**Fast, Selective and Metal-Free Ring-Opening
Polymerization to Synthesize Polycarbonate/Polyester
Copolymers with High Incorporation of Ethylene
Carbonate by Organocatalytic Phosphazene Base**

Chuanzhi Wei, Xinhui Kou, Shaofeng Liu,* and Zhibo Li*

Key Laboratory of Biobased Polymer Materials, Shandong Provincial Education
Department; College of Polymer Science and Engineering, Qingdao University of
Science and Technology, Qingdao 266042, China.

*Corresponding Author: E-mail: shaofengliu@qust.edu.cn and zbli@qust.edu.cn

Table S1. Copolymerization of EC and CL at different times.^a

run	Time (s)	EC conv. ^b (%)	CL conv. ^b (%)	EC inserted ^c (mol%)
1	5	21	34	42.0
2	10	29	49	38.5
3	20	34	58	37.9
4	30	36	62	37.5
5	40	37	67	35.2
6	60	38	69	37.3
7	80	40	72	36.2
8	100	40	74	35.7
9	120	40	75	35.2

^aConditions: **CTPB** 0.04 mmol; EC/CL/B/I = 500:500:1:1; [EC]₀ was 2.0 mol L⁻¹; 20 °C in toluene; the base and initiator were mixed firstly in toluene, followed by addition of monomers. ^bDetermined by ¹H NMR of reaction solution. ^cDetermined by ¹H NMR of resulted polymer.

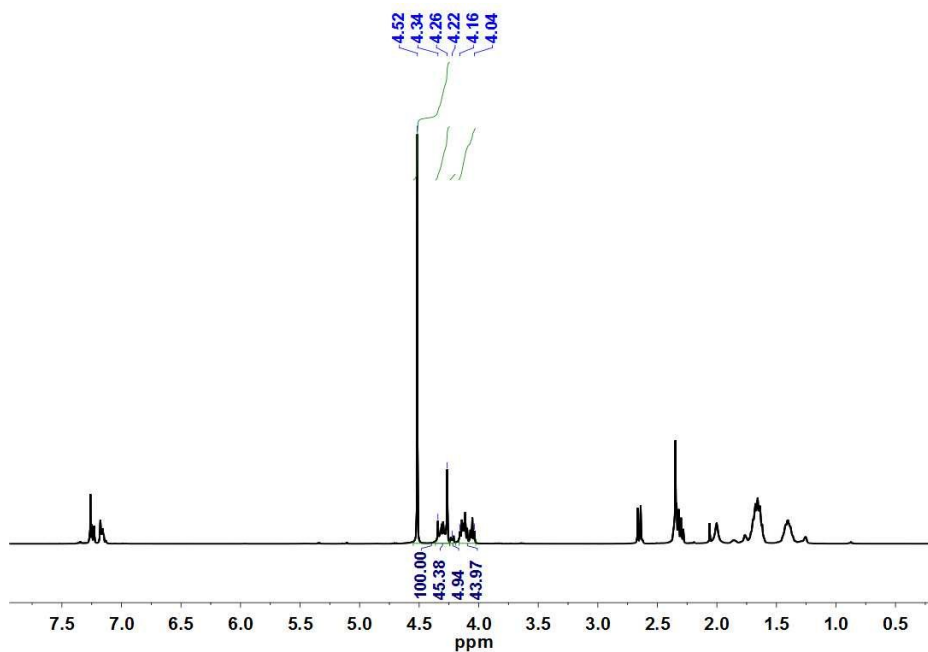


Figure S1. In situ ^1H NMR spectrum of polymerization mixture in Table 1, run 3 (conv.: EC 45% and CL 90%).

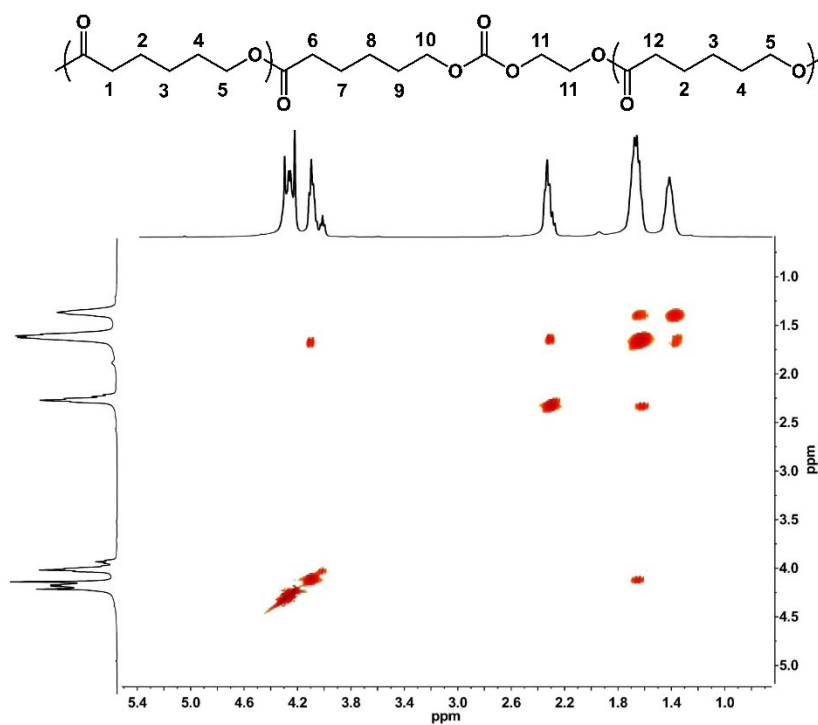


Figure S2. ^1H - ^1H COSY NMR spectrum of P(EC-*co*-CL) copolymer obtained in Table 1 run 3.

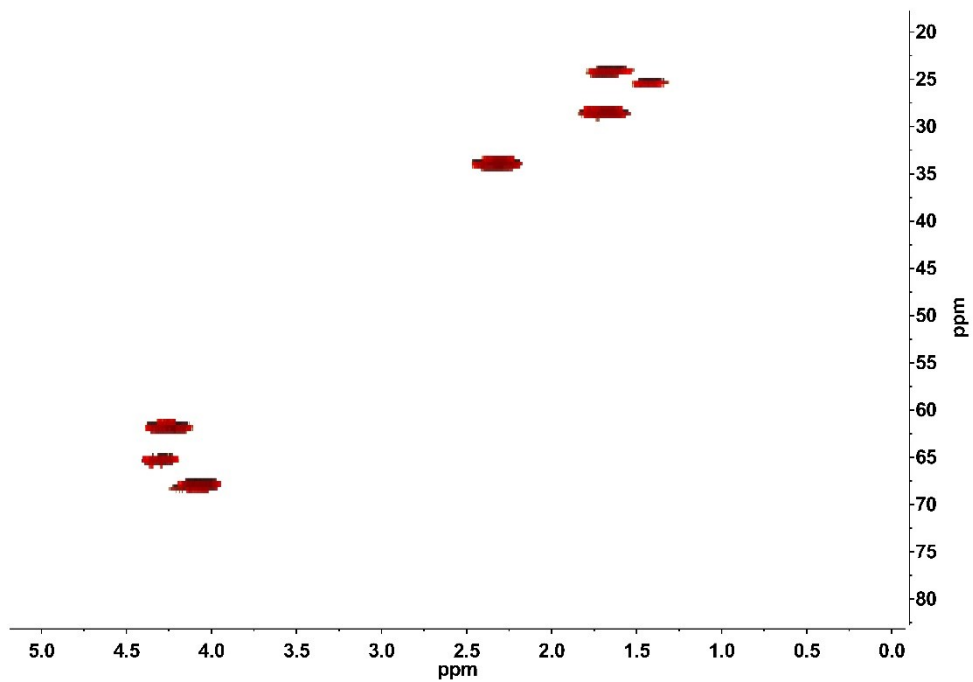


Figure S3. ^1H - ^{13}C HSQC NMR spectrum of P(EC-*co*-CL) copolymer obtained in Table 1 run 3.

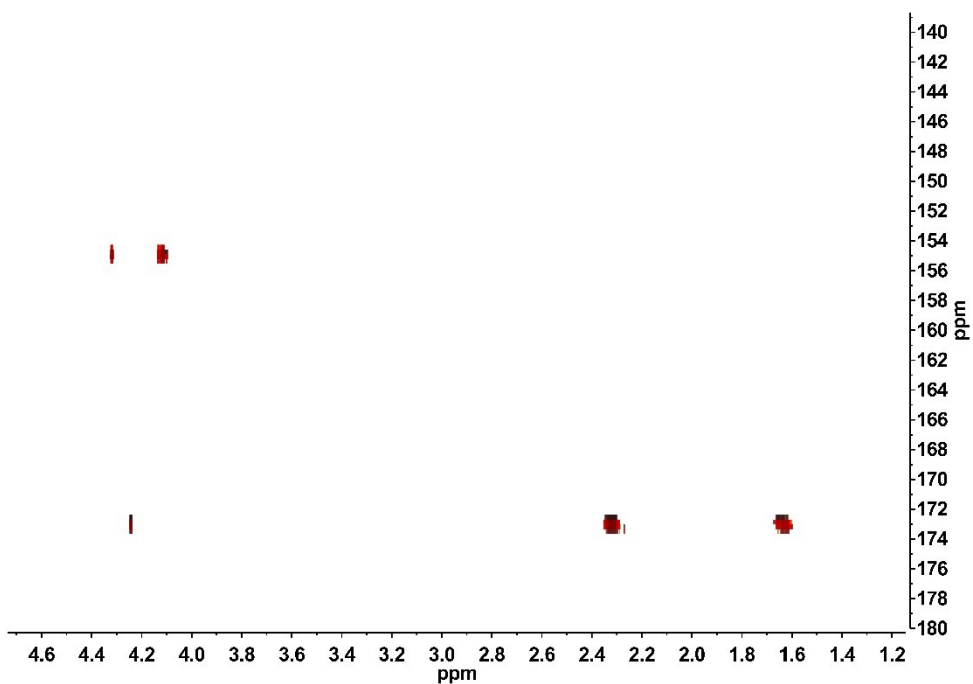


Figure S4. ^1H - ^{13}C HMBC NMR spectrum of P(EC-*co*-CL) copolymer obtained in Table 1 run 3.

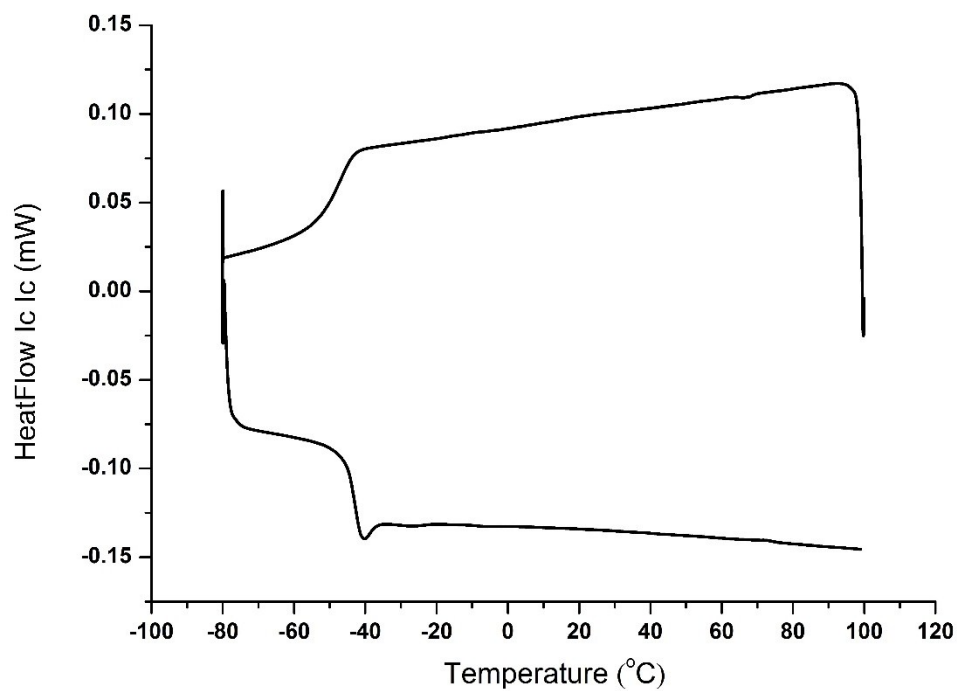


Figure S5. DSC trace of a P(EC-co-CL) copolymer with a 35% mol% of EC (Table 1 run 3).

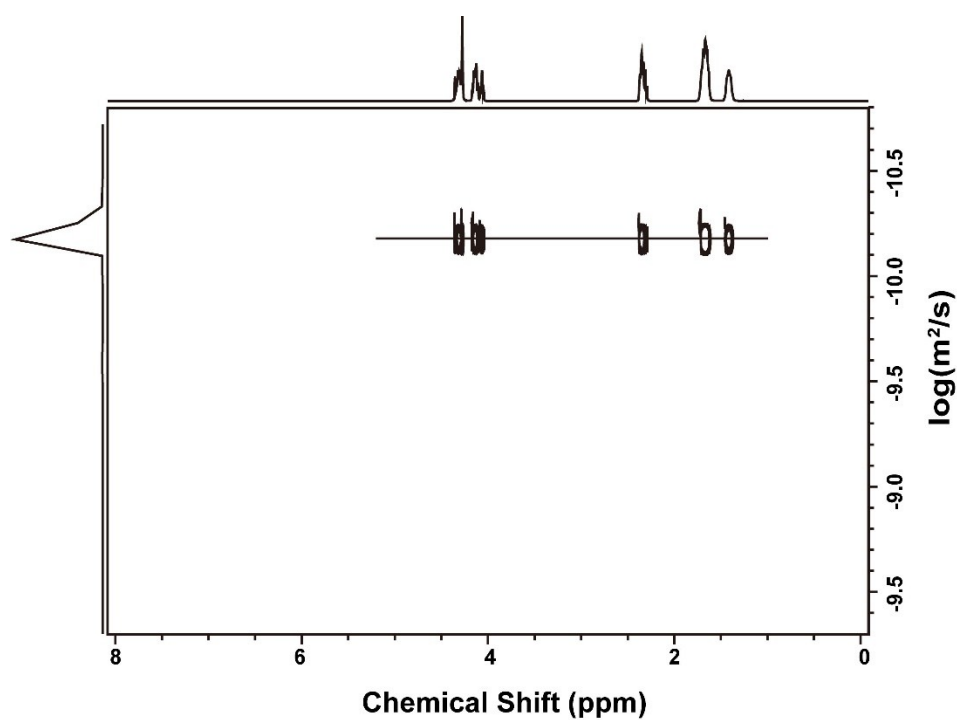


Figure S6. DOSY NMR spectrum of a P(EC-co-CL) copolymer in CDCl_3 (Table 1 run 3).

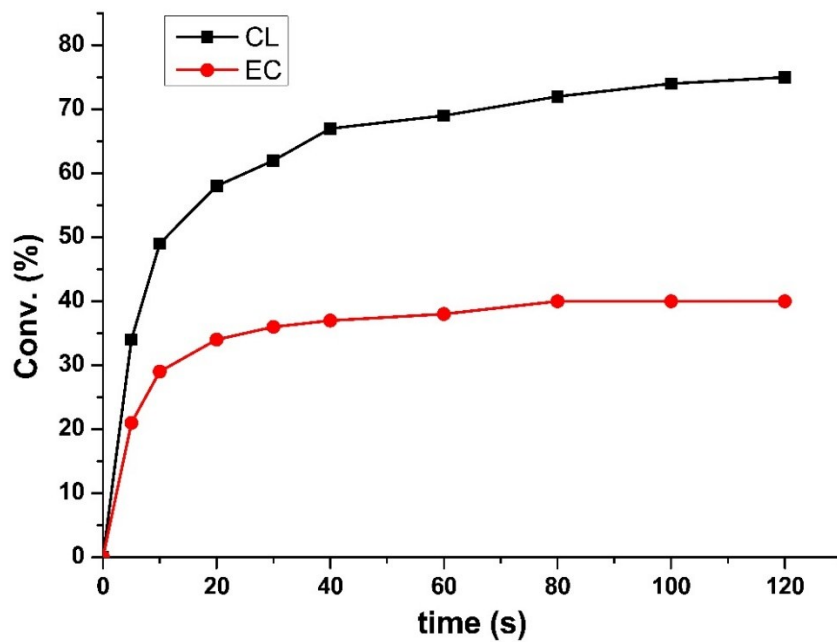


Figure S7. Conversions of CL and EC at different polymerization times with EC/CL/CTPB/BnOH = 500/500/1/1 in Table S1.

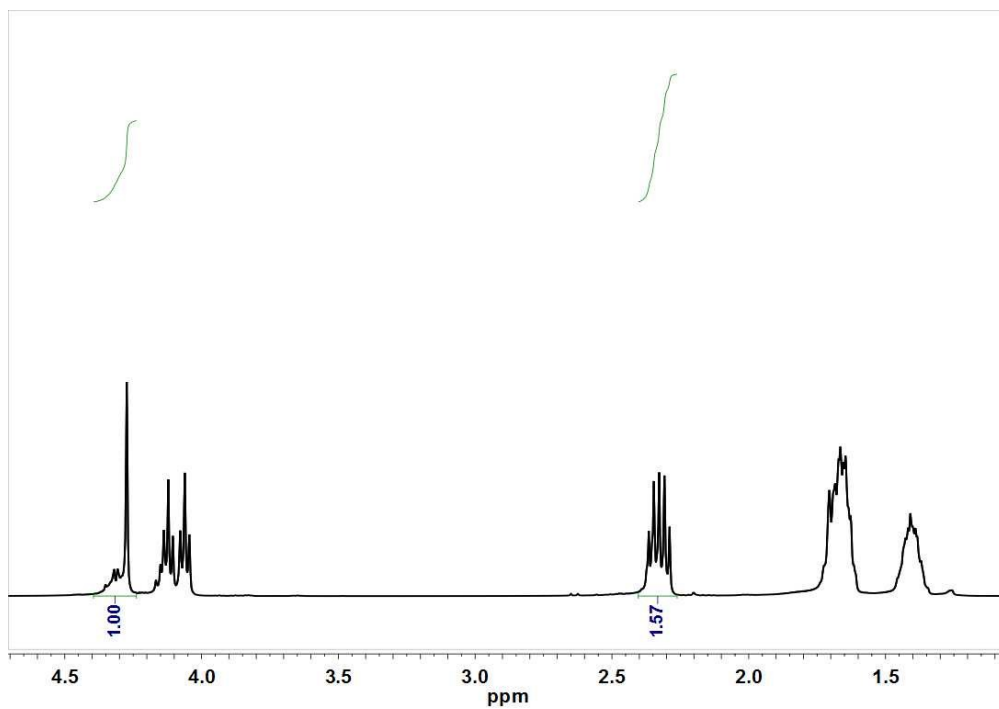


Figure S8. ^1H NMR spectrum (400 MHz, CDCl_3 , 25 $^\circ\text{C}$) of P(EC-*co*-CL) copolymer with a 24 mol% incorporation of EC prepared by CTPB/BnOH (Table 1, run 2).

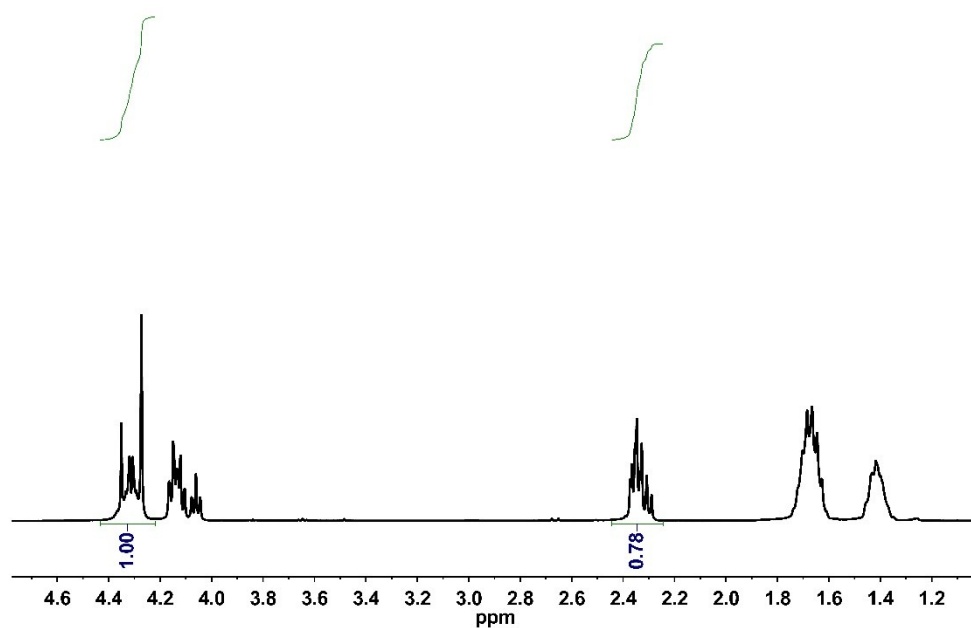


Figure S9. ¹H NMR spectrum (400 MHz, CDCl₃, 25 °C) of P(EC-co-CL) copolymer with a 39 mol% incorporation of EC prepared by **CTPB**/BnOH (Table 1, run 4).

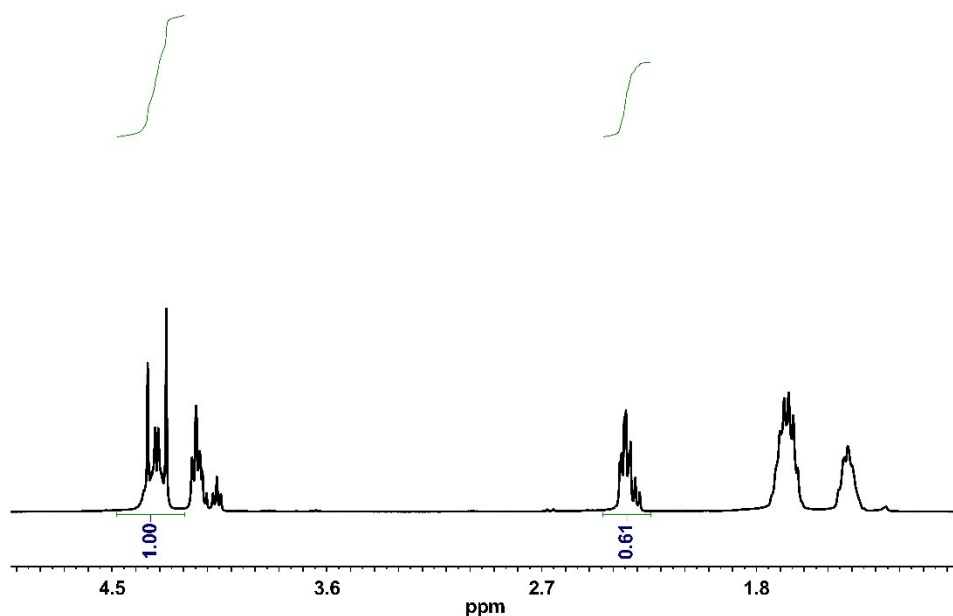


Figure S10. ¹H NMR spectrum (400 MHz, CDCl₃, 25 °C) of P(EC-co-CL) copolymer with a 45 mol% incorporation of EC prepared by **CTPB**/BnOH (Table 1, run 5).

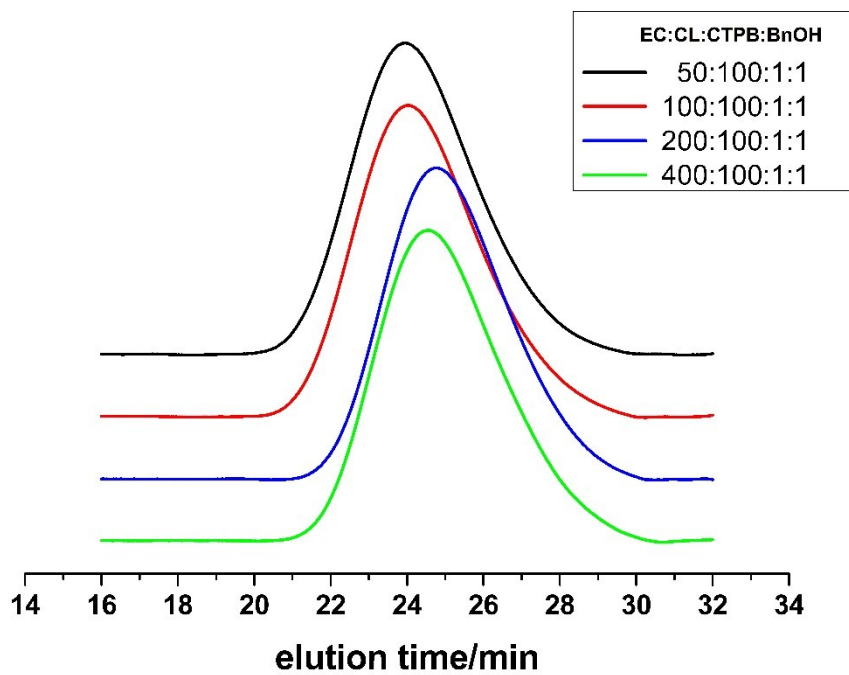


Figure S11. SEC curves of P(EC-*co*-CL) with different EC incorporation (Table 1, runs 2-5).

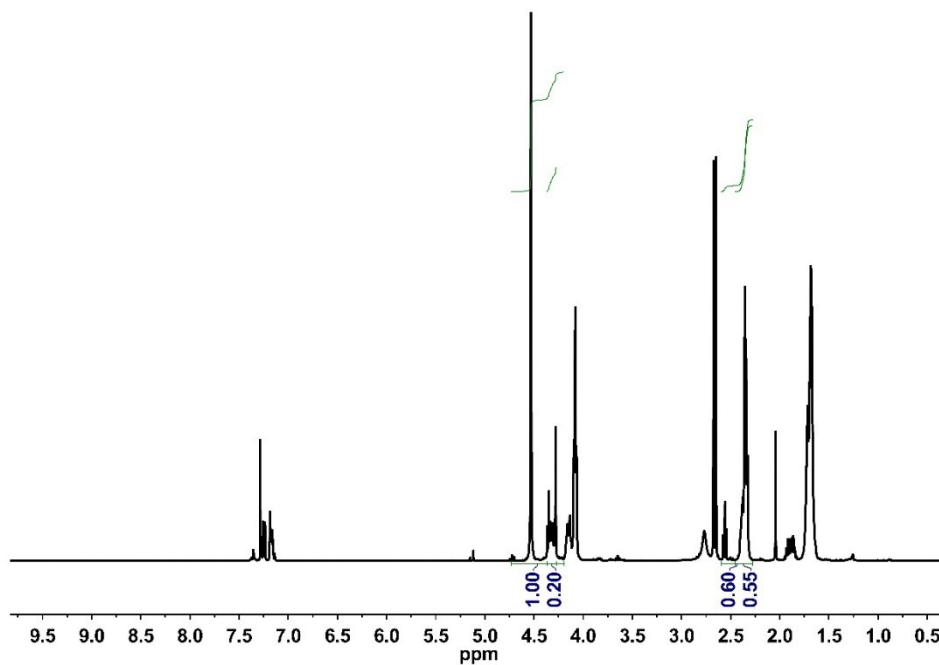


Figure S12. In situ ^1H NMR spectrum of polymerization mixture in Table 1, run 12 (conv.: EC 20% and VL 92%).

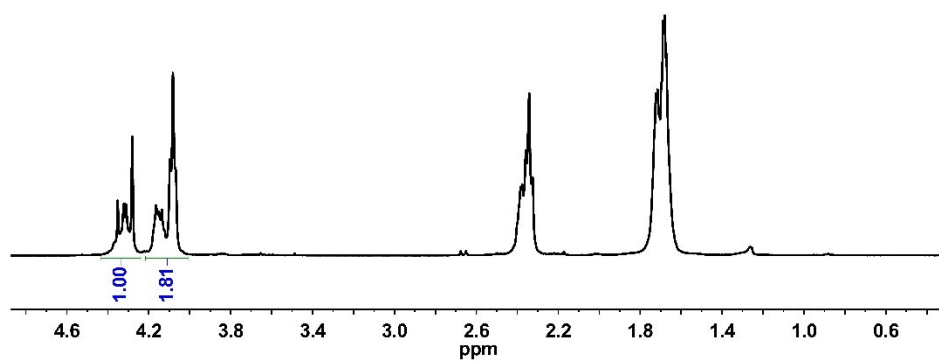


Figure S13. ^1H NMR spectrum (400 MHz, CDCl_3 , 25 $^\circ\text{C}$) of P(EC-*co*-VL) copolymer with a 22 mol% incorporation of EC prepared by **CTPB**/BnOH (Table 1, run 13).

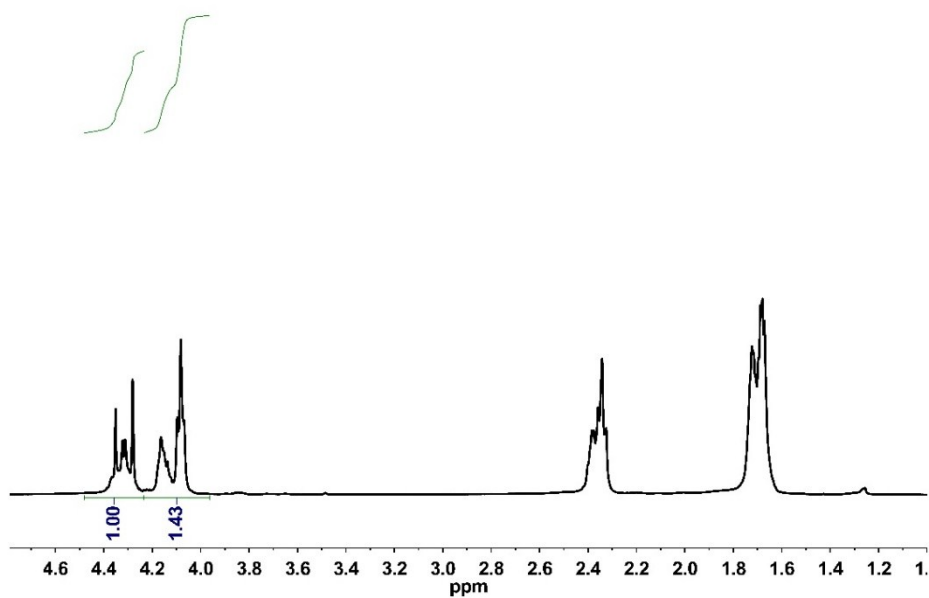


Figure S14. ^1H NMR spectrum (400 MHz, CDCl_3 , 25 $^\circ\text{C}$) of P(EC-*co*-VL) copolymer with a 26 mol% incorporation of EC prepared by **CTPB**/BnOH (Table 1, run 14).

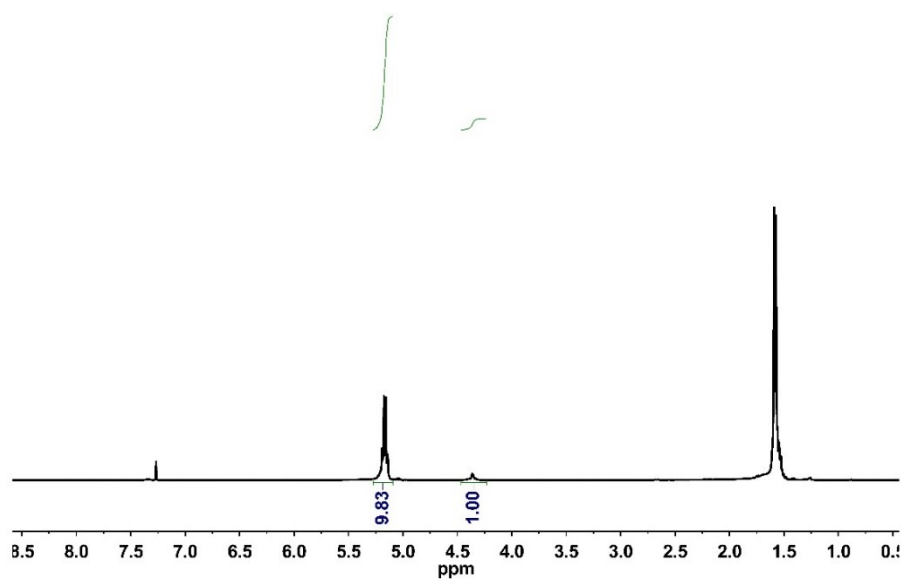


Figure S15. ^1H NMR spectrum (400 MHz, CDCl_3 , 25 $^\circ\text{C}$) of P(EC-*co*-LA) copolymer with a 4.8 mol% incorporation of EC prepared by CTPB/BnOH (Table 1, run 15).

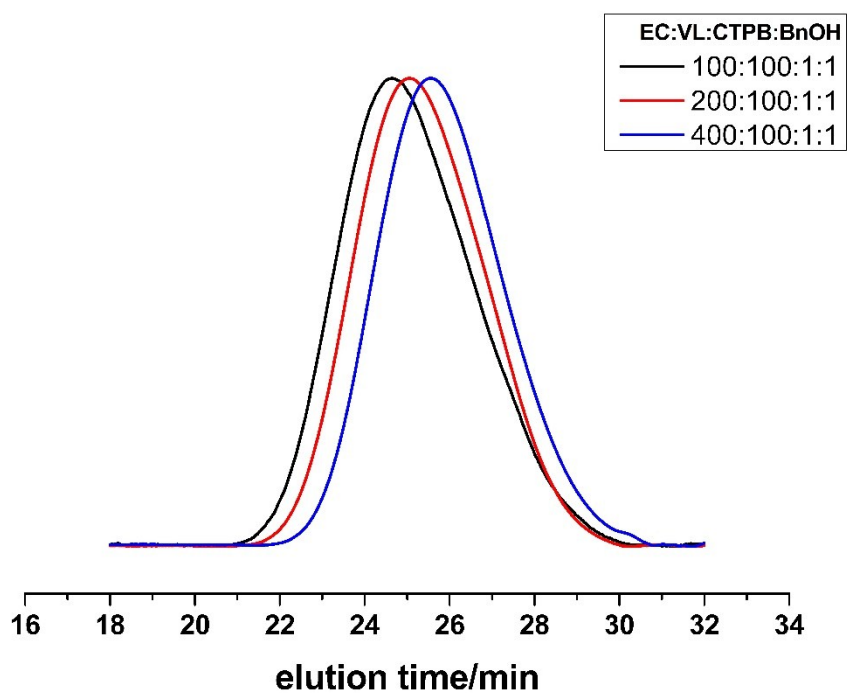


Figure S16. SEC curves of P(EC-*co*-VL) copolyesters obtained in Table 1, runs 12–14.