Electronic Supplementary Material (ESI) for Polymer Chemistry.

Alkali Metal Carbonates Catalyzed Copolymerization of Anhydrides and Epoxides: Simple, Efficient and Versatile Approach to Well-Defined Alternating Polyesters

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Table S1. Kinetic study for ROAP of PA and CHO induced by Cs_2CO_3.[a]

Run	Time (min)	Conv. [b] (%)	$M_{n,GPC}$ [c] (kg/mol)	M_w/M_n [c]
1	20	21.0	1.2	1.30
2	40	38.8	2.4	1.27
3	60	50.6	2.6	1.24
4	80	65.8	3.4	1.25
5	100	76.4	4.1	1.27
6	240	100	5.3	1.15

[a)]The polymerizations were conducted in bulk at 100 °C, BnOH was used as the initiator (10.4 μL, 0.1 mmol), $[Cs_2CO_3]$:[BnOH]:[PA]:[CHO] = 0.2:1:100:500. [b)]Determined by ^1H NMR. [c)]Determined by gel permeation chromatography (GPC) in THF against polystyrene standard.

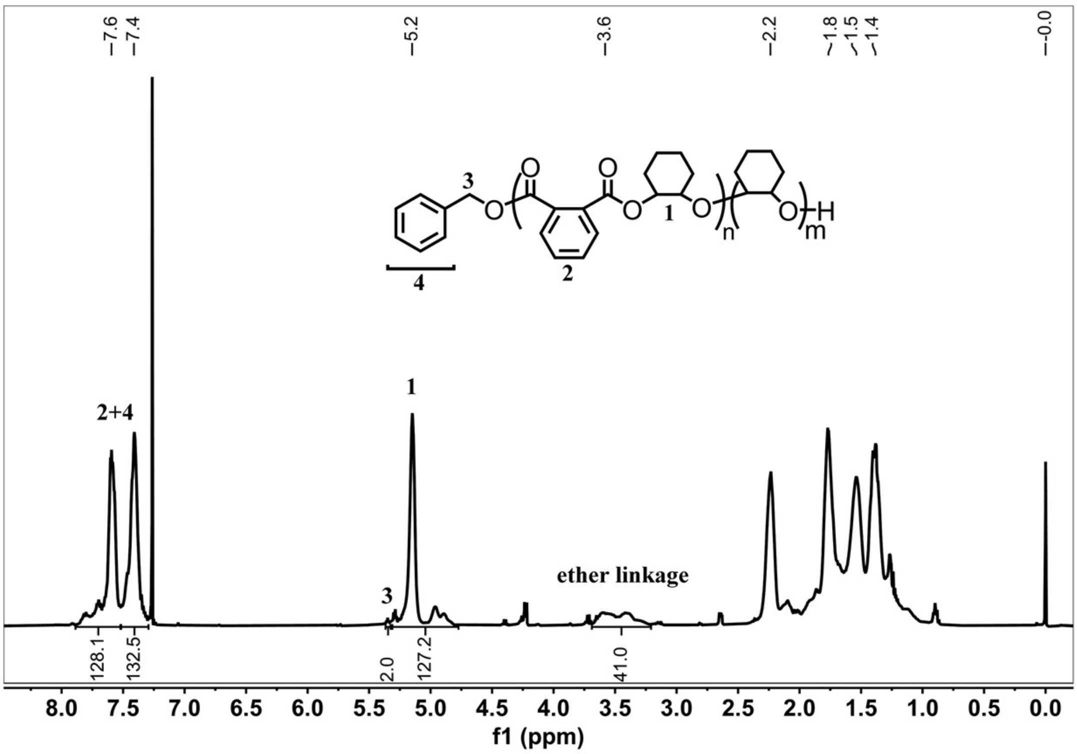

Fig. S1. ^1H NMR of poly(PA-*alt*-CHO) catalyzed by Na_2CO_3 at 100 °C, [C]:[I]:[PA]:[CHO] = 0.2:1:100:500 (Table 1, Run 2; 25 °C, $CDCl_3$).

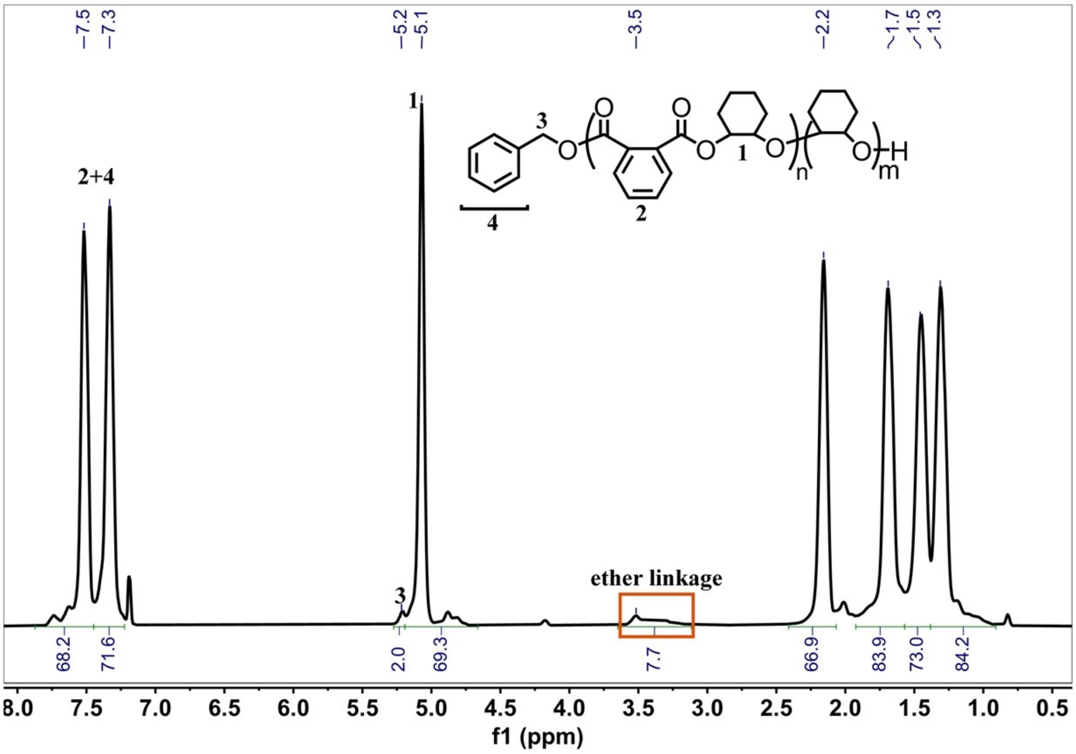

Fig. S2. [1]H NMR of poly(PA-*alt*-CHO) catalyzed by K_2CO_3 at 100 °C, [C]:[I]:[PA]:[CHO] = 0.3:1:50:250 (Table 1, Run 3; 25 °C, $CDCl_3$).

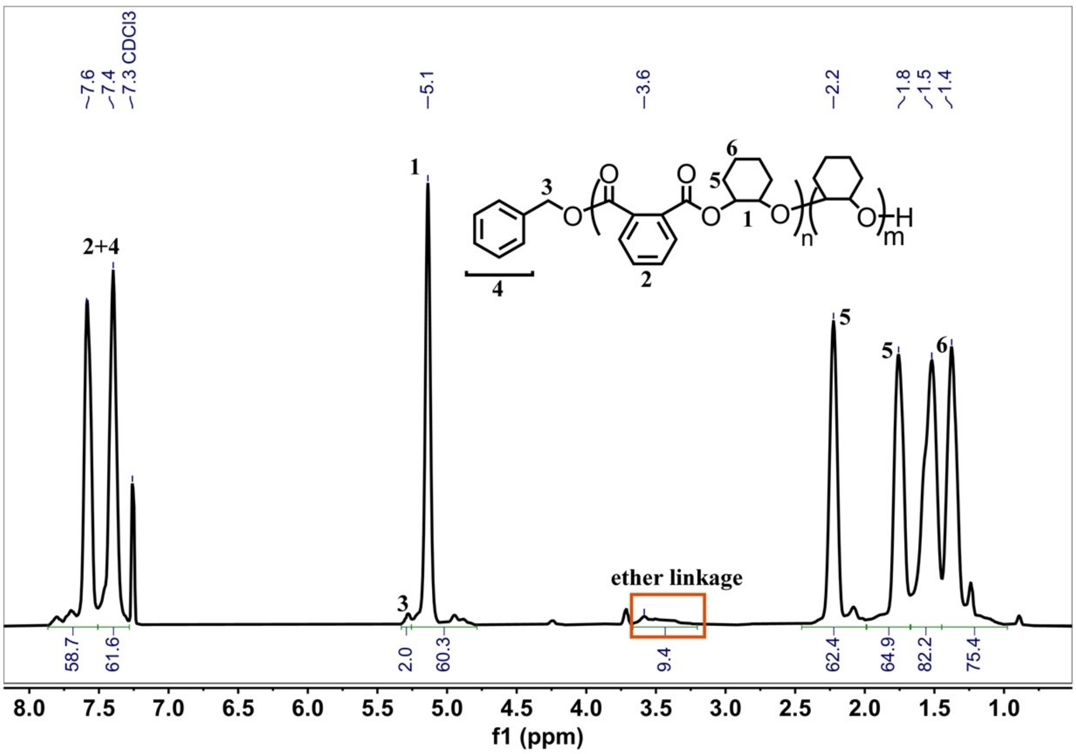

Fig. S3. [1]H NMR of poly(PA-*alt*-CHO) catalyzed by K_2CO_3 at 60 °C, [C]:[I]:[PA]:[CHO] = 0.3:1:50:250 (Table 1, Run 4; 25 °C, $CDCl_3$).

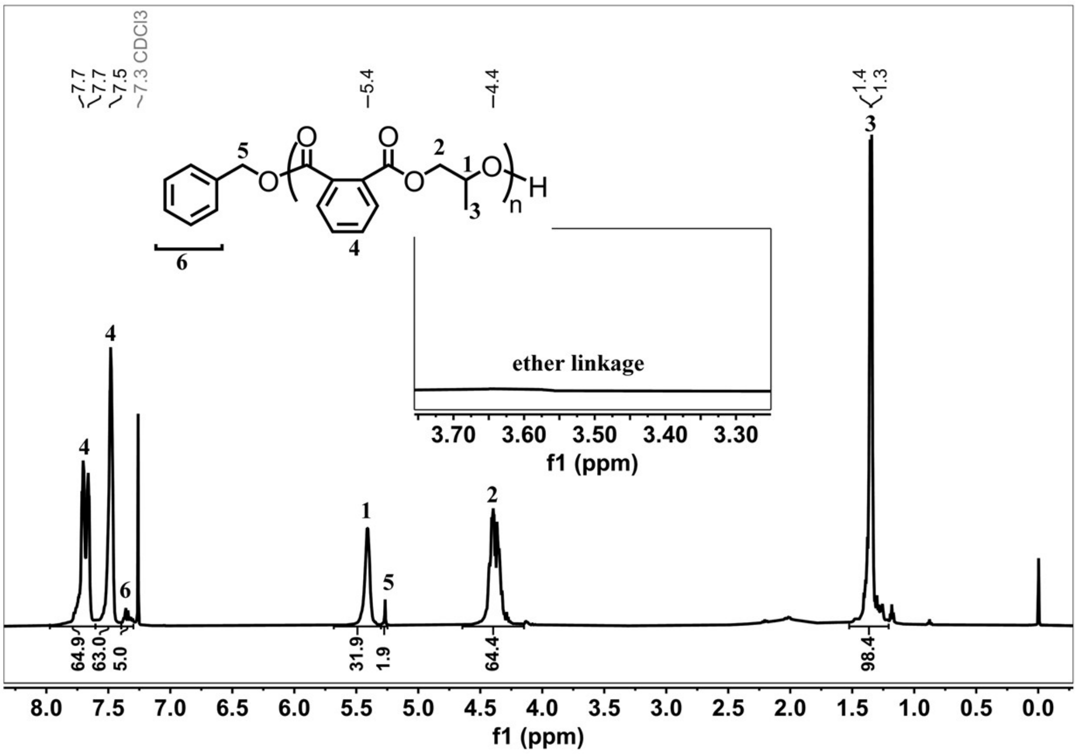

Fig. S4. [1]H NMR of poly(PA-*alt*-PO) catalyzed by K_2CO_3 at 60 °C, [C]:[I]:[PA]:[PO] = 0.3:1:50:250 (Table 1, Run 7; 25 °C, $CDCl_3$).

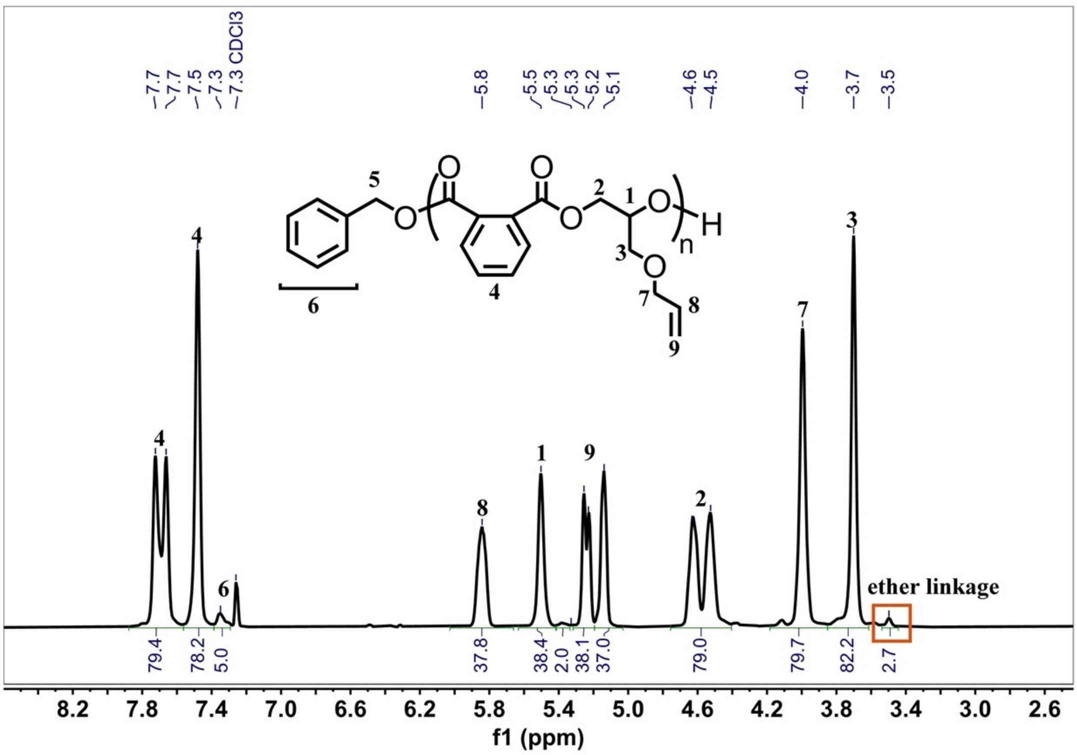

Fig. S5. [1]H NMR of poly(PA-*alt*-AGE) catalyzed by K_2CO_3 at 100 °C, [C]:[I]:[PA]:[AGE] = 0.3:1:50:250 (Table 1, Run 8; 25 °C, $CDCl_3$).

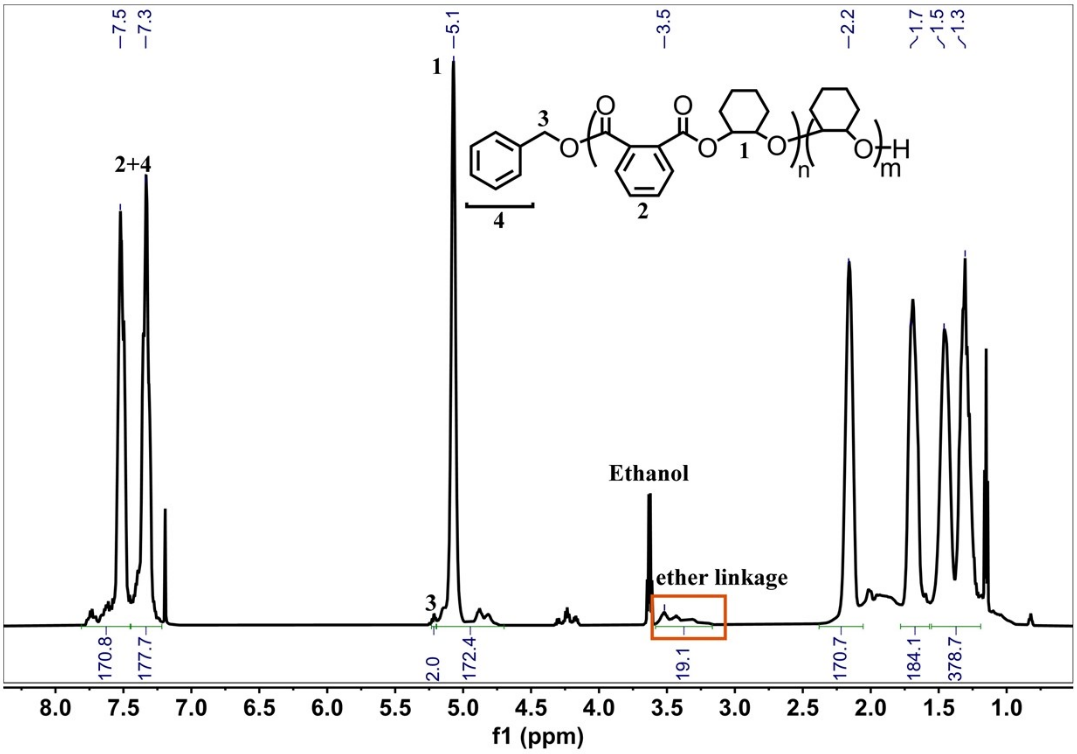

Fig. S6. [1]H NMR of poly(PA-*alt*-CHO) catalyzed by Cs_2CO_3 at 100 °C, [C]:[I]:[PA]:[CHO] = 0.2:1:100:500 (Table 1, Run 5; 25 °C, $CDCl_3$).

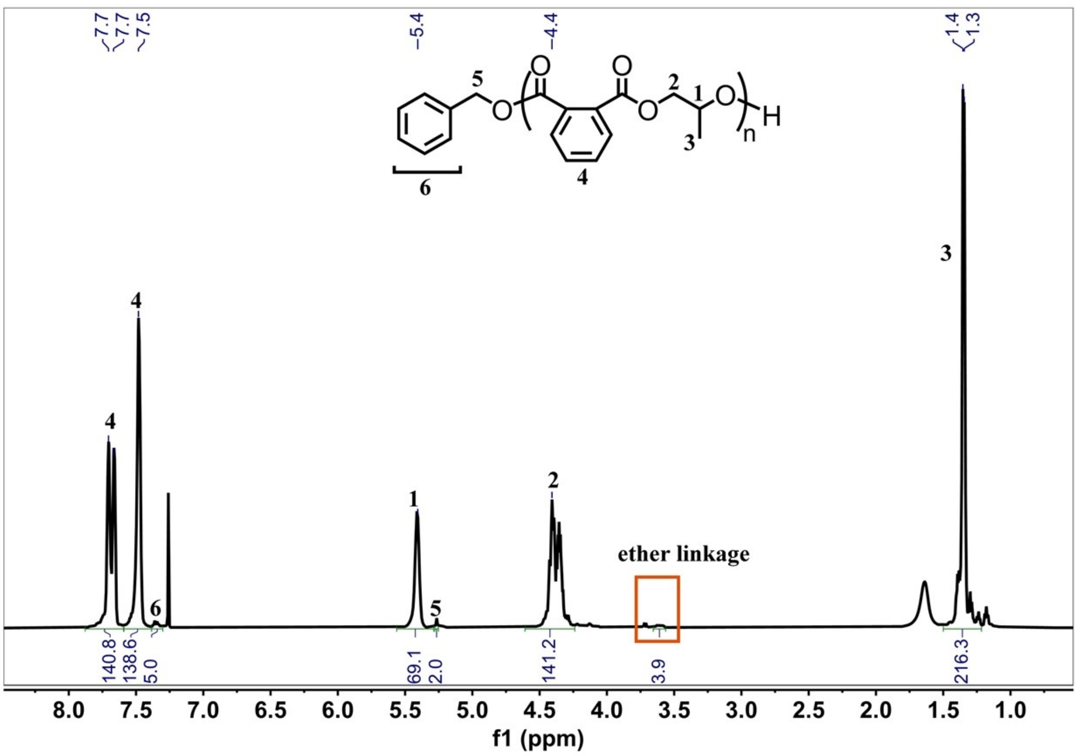

Fig. S7. [1]H NMR of poly(PA-*alt*-PO) catalyzed by Cs_2CO_3 at 100 °C, [C]:[I]:[PA]:[PO] = 0.2:1:100:500 (Table 1, Run 9; 25 °C, $CDCl_3$).

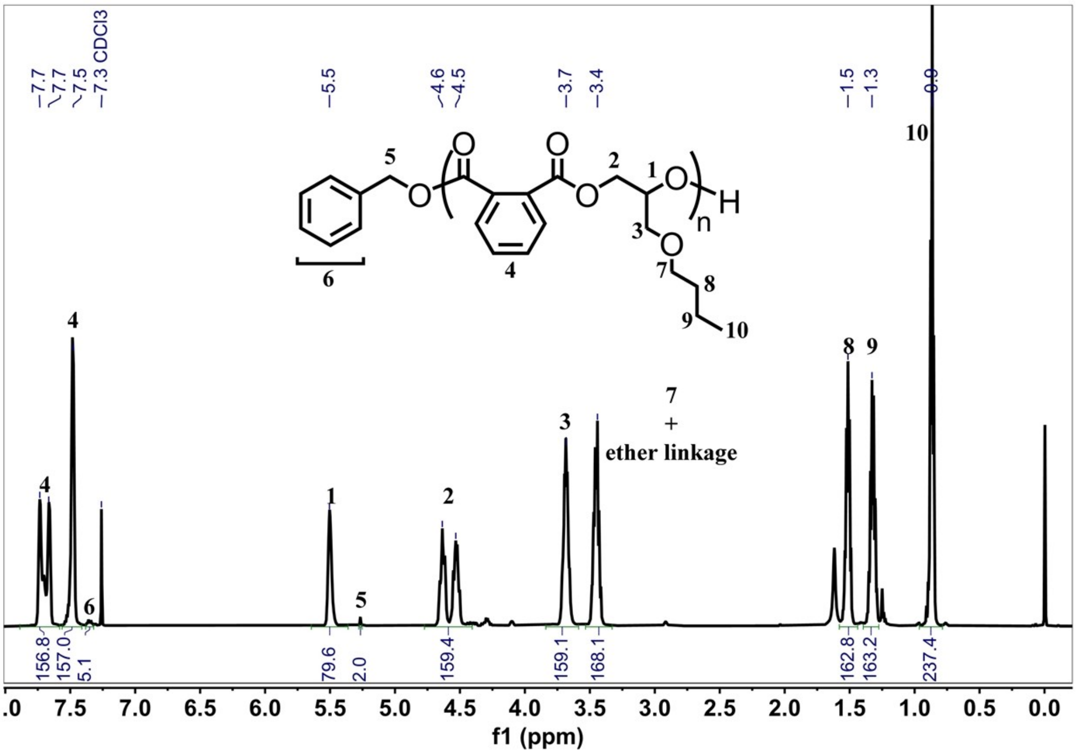

Fig. S8. [1]H NMR of poly(PA-*alt*-BGE) catalyzed by Cs_2CO_3 at 100 °C, [C]:[I]:[PA]:[BGE] = 0.2:1:100:500 (Table 1, Run 10; 25 °C, $CDCl_3$).

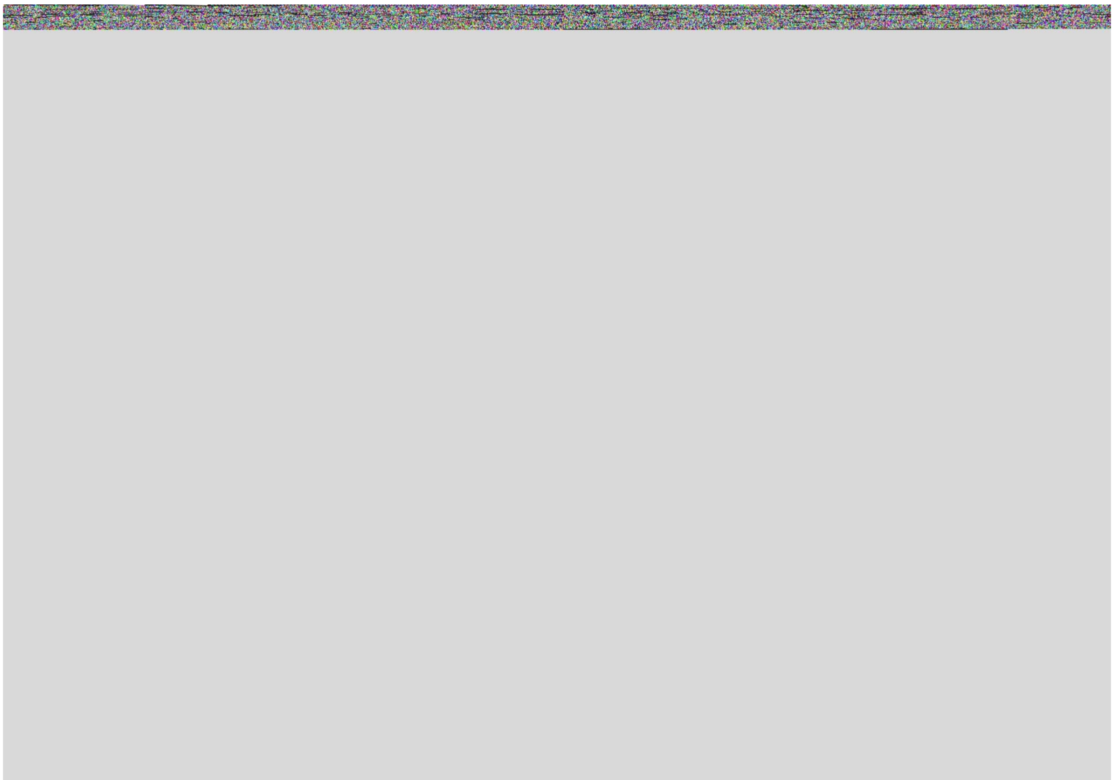

Fig. S9. [1]H NMR of poly(PA-*alt*-AGE) catalyzed by Cs_2CO_3 at 100 °C, [C]:[I]:[PA]:[AGE] = 0.2:1:100:500 (Table 1, Run 11; 25 °C, $CDCl_3$).

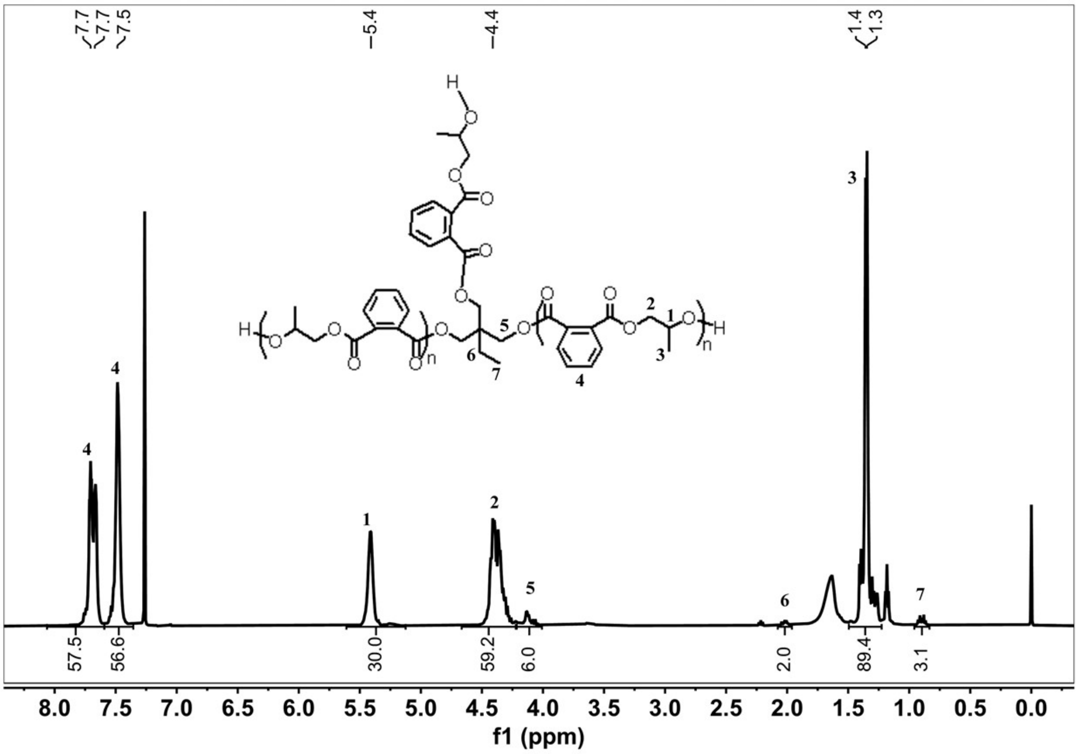

Fig. S10. [1]H NMR of poly(PA-*alt*-PO) catalyzed by Cs_2CO_3 at 100 °C, [C]:[I]:[PA]:[PO] = 0.2:1:100:500 (Table 2, Run 2; 25 °C, $CDCl_3$).

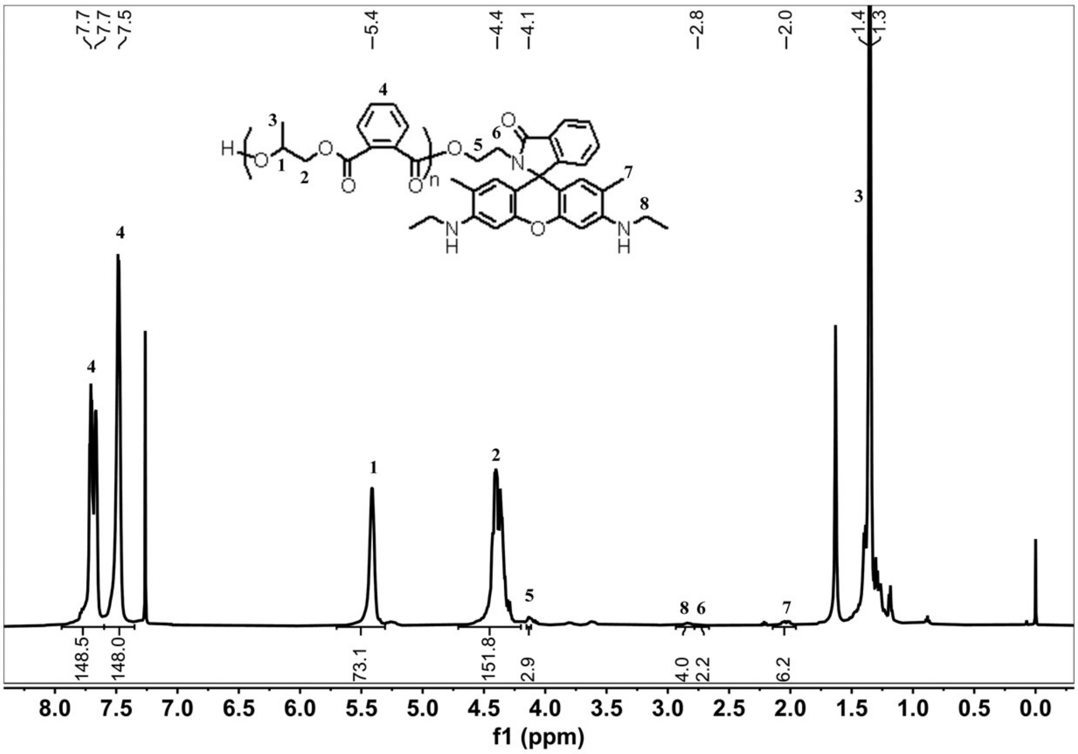

Fig. S11. [1]H NMR of poly(PA-*alt*-PO) catalyzed by Cs_2CO_3 at 100 °C, [C]:[I]:[PA]:[PO] = 0.2:1:100:500 (Table 2, Run 3; 25 °C, $CDCl_3$).

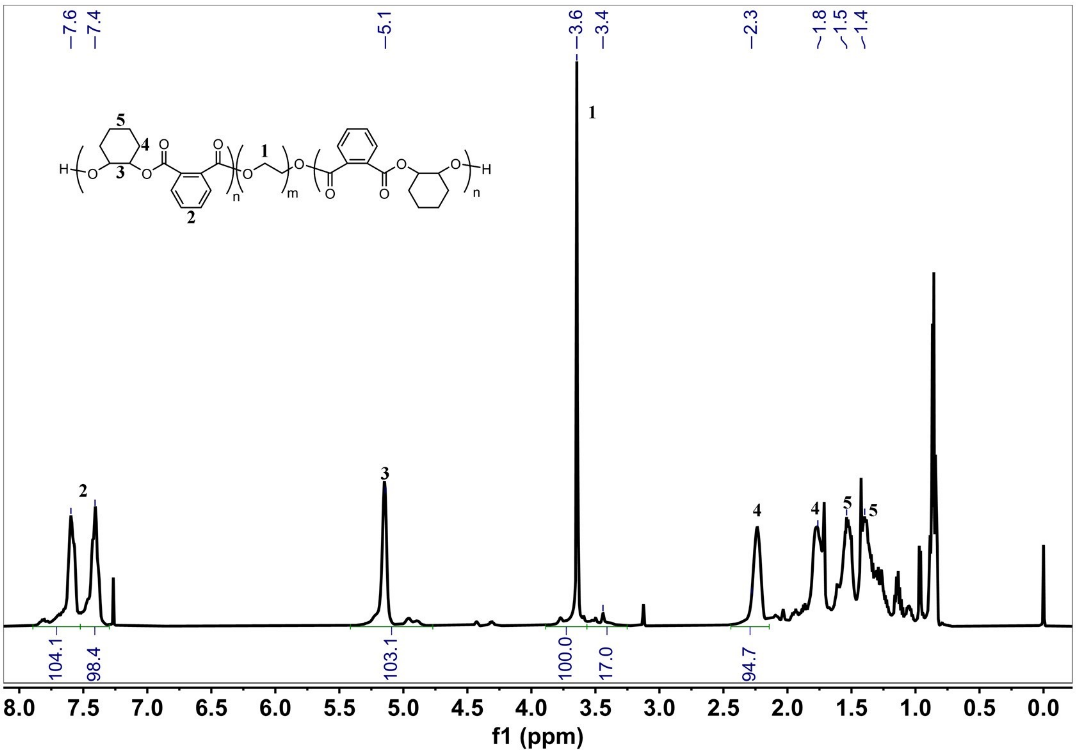

Fig. S12. ^{1}H NMR of poly(PA-*alt*-CHO)-*b*-PEG-*b*-poly(PA-*alt*-CHO) catalyzed by Cs_2CO_3 at 100 °C, [C]:[I]:[PA]:[CHO] = 0.2:1:100:500 (Table 2, Run 4; 25 °C, $CDCl_3$).

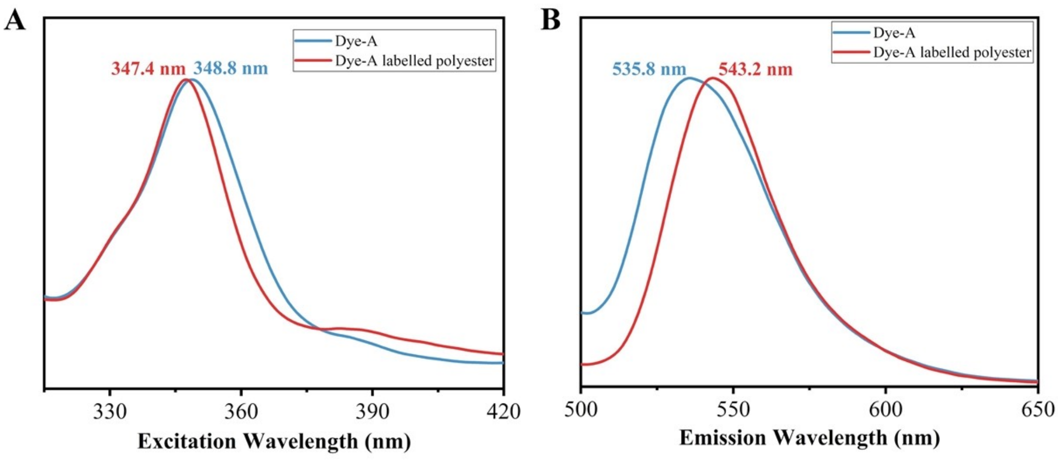

Fig. S13. The excitation spectrum (A) and emission spectrum (B) for Dye-A and Dye-A labelled poly(PA-*alt*-PO).

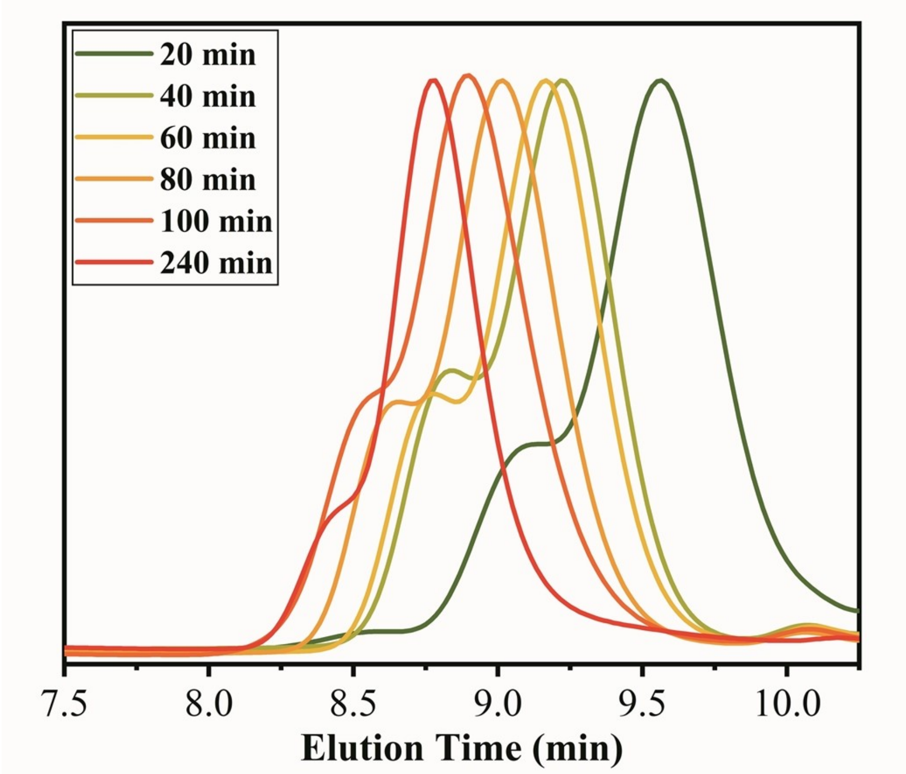

Fig. S14. Evolution of GPC curves for the kinetic studies (Table S1).

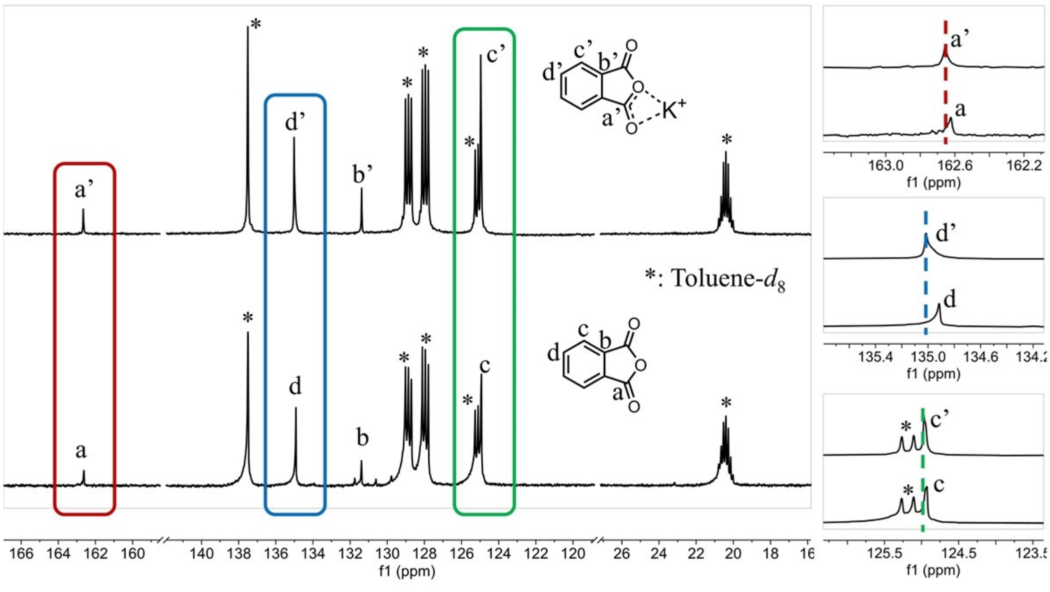

Fig. S15. The comparison of the ^{13}C NMR spectra of PA (bottom) and PA/K_2CO_3 (top).

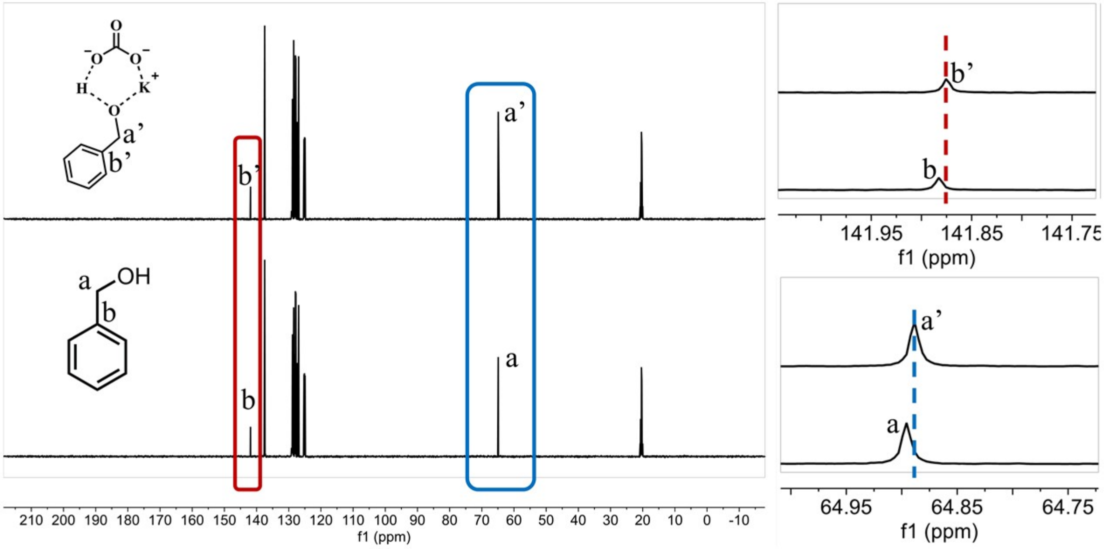

Fig. S16. The comparison of the ^{13}C NMR spectra of BnOH (bottom) and BnOH/K_2CO_3 (top).

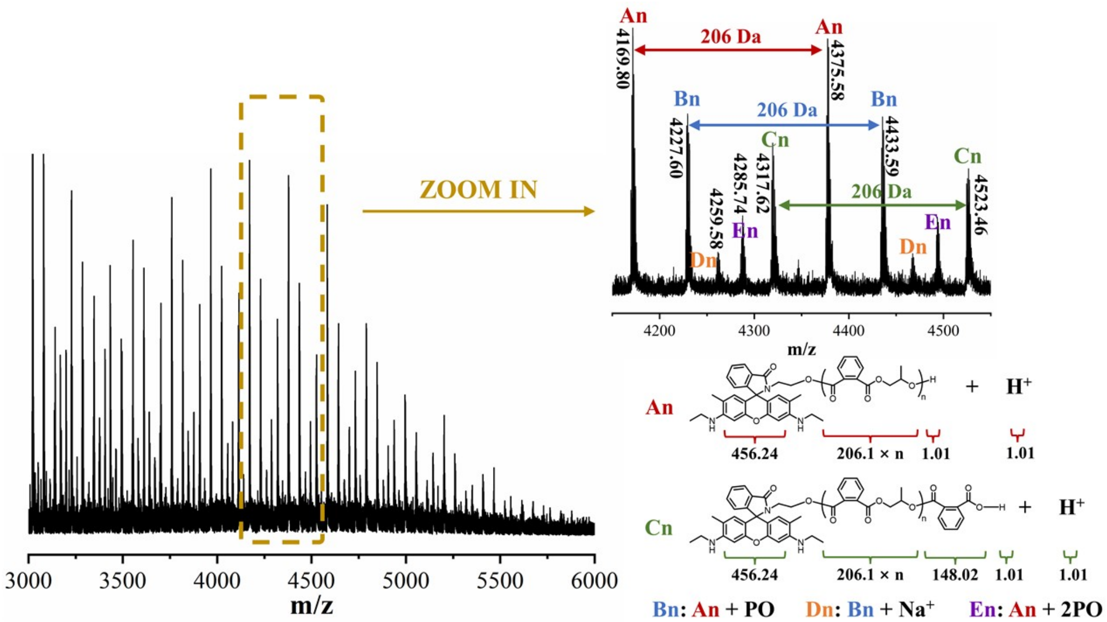

Fig. S17. The MALDI-TOF analysis of the oligomer poly(PA-*alt*-PO) initiated by dye-A ([Cs]:[dye-A]:[PA]:[PO] = 0.2:1:25:125, Conv. = 85 %, $M_{n,NMR}$ = 4.9 kg/mol, $M_{n,GPC}$ = 3.1 kg/mol, M_w/M_n = 1.43).