Electronic Supplementary Material (ESI) for Polymer Chemistry.

–Supporting Information for the manuscript entitled–

"Iodine and alkali metal alkoxides: A simple and versatile catalyst system for fully alternating polyesters synthesis from phthalic anhydride and epoxides"

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Figure S1. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298K) of P(PA-*alt*-CHO) copolymer derived by the action of I_2 and *t*BuOK (I_2/*t*BuOK/PA/CHO = 1:1:100:400), (entry15, Table 1).

Figure S2. ^{13}C NMR spectrum ($CDCl_3$, 400 MHz, 298K) of P(PA-*alt*-CHO) copolymer derived by the action of I_2 and *t*BuOK (I_2/*t*BuOK/PA/CHO = 1:1:100:400), (entry15, Table 1).

Figure S3. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298K) of P(PA-*alt*-*t*BGE)copolymer derived by the action of I_2 and *t*BuOK (I_2/*t*BuOK/PA/*t*BGE = 1:1:100:400), (entry 1, Table 2).

Figure S4. ^{13}C NMR spectrum ($CDCl_3$, 400 MHz, 298K) of P(PA-*alt*-*t*BGE) copolymer derived by the action of I_2 and *t*BuOK (I_2/*t*BuOK/PA/*t*BGE = 1:1:100:400), (entry 1, Table 2).

Figure S5. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298K) of P(PA-*alt*-PGE) copolymer derived by the action of I_2 and *t*BuOK (I_2/*t*BuOK/PA/PGE = 1:1:100:400), (entry 4, Table 2).

Figure S6. ^{13}C NMR spectrum ($CDCl_3$, 400 MHz, 298K) of P(PA-*alt*-PGE) copolymer derived by the action of I_2 and *t*BuOK (I_2/*t*BuOK/PA/PGE = 1:1:100:400), (entry 4, Table 2).

Figure S7. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298K) of P(PA-*alt*-AGE) copolymer derived by the action of I_2 and *t*BuOK (I_2/tBuOK/PA/AGE = 2:1:100:400), (entry7, Table 2).

Figure S8. ^{13}C NMR spectrum ($CDCl_3$, 400 MHz, 298K) of P(PA-*alt*-AGE) copolymer derived by the action of I_2 and tBuOK (I_2/tBuOK/PA/AGE = 1:1:100:400), (entry7, Table 2).

Figure S9. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298K) of P(PA-*alt*-PO) copolymer derived by the action of I_2 and *t*BuOK (I_2/*t*BuOK/PA/PO = 1:1:100:400), (entry 13, Table 2).

Figure S10. ^{13}C NMR spectrum ($CDCl_3$, 400 MHz, 298K) of P(PA-*alt*-PO) copolymer derived by the action of I_2 and *t*BuOK (I_2/*t*BuOK/PA/PO = 1:1:100:400), (entry 13, Table 2).

Figure S11. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298K) of P(PA-*alt*-SO) copolymer derived by the action of I_2 and *t*BuOK (I_2/*t*BuOK/PA/SO = 1:1:100:400), (entry 10, Table 2).

Figure S12. ^{13}C NMR spectrum ($CDCl_3$, 400 MHz, 298K) of P(PA-*alt*-SO) copolymer derived by the action of I_2 and *t*BuOK (I_2/*t*BuOK/PA/SO = 1:1:100:400), (entry 10, Table 2).

Figure S13. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298K) of P(PA-*alt*-CHO) copolymer derived by the action of I_2 and *t*BuOK (I_2/*t*BuOK/PA/PO = 1:1:100:400), at 70 °C. (entry 10, Table 2).

Figure S14. GPC trace of purified product P(PA-*alt*-CHO) copolymer derived by the action of I_2 and CH_3OK (I_2/CH_3OK/PA/CHO = 1:1:100:300), (entry 3, Table 1).

Figure S15. GPC trace of purified product P(PA-*alt*-CHO) copolymer derived by the action of I_2 and *t*BuOLi (I_2/*t*BuOLi/PA/CHO = 1:1:100:400), (entry 6, Table 1).

Figure S16. GPC trace of purified product P(PA-*alt*-CHO) copolymer derived by the action of I_2 and *t*BuONa (I_2/*t*BuONa/PA/CHO = 1:1:100:400), (entry 7, Table 1).

Figure S17. GPC trace of purified product P(PA-*alt*-CHO) copolymer derived by the action of I_2 and CH_3OK (I_2/CH_3OK/PA/CHO = 1:1:100:400), (entry 8, Table 1).

Figure S18. GPC trace of purified product P(PA-*alt*-CHO) copolymer derived by the action of I_2 and *i*PrOK (I_2/*i*PrOK /PA/CHO = 1:1:100:400), (entry 12, Table 1).

Figure S19. GPC trace of purified product P(PA-*alt*-CHO) copolymer derived by the action of I_2 and *t*BuOLi(I_2/*t*BuOLi/PA/CHO = 1:1:100:400), (entry 13, Table 1).

Figure S20. GPC trace of purified product of P(PA-*alt*-CHO) copolymer derived by the action of I_2 and *t*BuONa (I_2/*t*BuONa/PA/CHO = 1:1:100:400), (entry 14, Table 1).

Figure S21. GPC trace of purified product P(PA-*alt*-CHO) copolymer derived by the action of I_2 and *t*BuOK (I_2/*t*BuOK/PA/CHO = 1:1:100:400), (entry15, Table 1).

Figure S22. GPC trace of purified product P(PA-*alt*-CHO) copolymer derived by the action of I_2 and *i*PrONa (I_2/*i*PrONa /PA/CHO = 1:1:100:400), (entry 20, Table 1).

Figure S23. GPC trace of purified product P(PA-*alt*-CHO) copolymer derived by the action of I_2 and CH_3OK (I_2/CH_3OK/PA/CHO = 1:1:100:300), (entry 24, Table 1).

Figure S24. GPC trace of purified product P(PA-*alt*- *t*BGE) copolymer derived by the action of I_2 and *t*BuOK (I_2/*t*BuOK/PA/*t*BGE = 1:1:100:400), (entry 1, Table 2).

Figure S25. GPC trace of purified product P(PA-*alt*- *t*BGE) copolymer derived by the action of I_2 and *t*BuOK (I_2/*t*BuOK /PA/*t*BGE = 1:1:250:800), (entry 2, Table 2).

Figure S26. GPC trace of purified product P(PA-*alt*- *t*BGE) copolymer derived by the action of I_2 and *t*BuOK (I_2/*t*BuOK /PA/*t*BGE = 1:1:500:1200), (entry 3, Table 2).

Figure S27. GPC trace of purified product P(PA-*alt*-PGE) copolymer derived by the action of I_2 and *t*BuOK (I_2/*t*BuOK /PA/PGE = 1:1:100:400), (entry 4, Table 2).

Figure S28. GPC trace of purified product P(PA-*alt*-PGE) copolymer derived by the action of I_2 and *t*BuOK (I_2/*t*BuOK /PA/PGE = 1:1:250:800), (entry 5, Table 2).

Figure S29. GPC trace of purified product of P(PA-*alt*-PGE) copolymer derived by the action of I_2 and *t*BuOK (I_2/*t*BuOK/PA/PGE = 1:1:500:1200), (entry 6, Table 2).

Figure S30. GPC trace of purified product P(PA-*alt*-AGE) copolymer derived by the action of I_2 and *t*BuOK (I_2/*t*BuOK/PA/AGE = 1:1:100:400), (entry 7, Table 2).

Figure S31. GPC trace of purified product P(PA-*alt*-AGE) copolymer derived by the action of I_2 and *t*BuOK (I_2/*t*BuOK/PA/AGE = 1:1:250:800), (entry 8, Table 2).

Figure S32. GPC trace of purified product P(PA-*alt*-AGE) copolymer derived by the action of I_2 and *t*BuOK (I_2/*t*BuOK/PA/AGE = 1:1:500:1200), (entry 9, Table 2).

Figure S33. GPC trace of purified product P(PA-*alt*-SO) copolymer derived by the action of I_2 and *t*BuOK (I_2/*t*BuOK/PA/SO = 1:1:100:400), (entry 10, Table 2).

Figure S34. GPC trace of purified product P(PA-*alt*-SO) copolymer derived by the action of I_2 and *t*BuOK (I_2/*t*BuOK/PA/SO = 1:1:250:800), Table (entry 11, Table 2).

Figure S35. GPC trace of purified product P(PA-*alt*-SO) copolymer derived by the action of I_2 and *t*BuOK (I_2/*t*BuOK/PA/SO = 1:1:500:1200), (entry 12, Table 2).

Figure S36. GPC trace of purified product P(PA-*alt*-PO) copolymer derived by the action of I_2 and *t*BuOK (I_2/*t*BuOK/PA/PO = 1:1:100:400), (entry 13, Table 2).

Figure S37. GPC trace of purified product P(PA-*alt*-PO) copolymer derived by the action of I_2 and *t*BuOK (I_2/*t*BuOK/PA/PO = 1:1:250:800), (entry 14, Table 2).

Figure S38. GPC trace of purified product P(PA-*alt*-PO) copolymer derived by the action of I_2 and *t*BuOK (I_2/*t*BuOK/PA/PO = 1:1:500:1200), (entry 15, Table 2).

Figure S39. Regiostructures of polyesters: tail-to-tail (TT), head-to-tail (HT), and head-to-head (HH) junctions, P(PO-*alt*-PA)polymer.

Figure S40. MALDI-TOF MS spectrum of the short P(PA-*alt*-AGE) precursor synthesized by the catalysis of I_2/*t*BuOK.

Figure S41. MALDI-TOF MS spectrum of the short P(PA-*alt*-*t*BGE) precursor synthesized by the catalysis of I_2/*t*BuOK.

Figure S42. Overlap of ^{1}H NMR monitoring of copolymerization PA/CHO and catalysed by I_2/*t*BuOK catalyst system with the ratio I_2/*t*BuOK/NA/CHO = 1:1:100:400 (Entry 3 to 6, Table 4.2) with respect 0.5 h, 1 h, 2 h, and 2.5 h of reaction time.

Figure S43. TGA and derivative thermogravimetry (DTG) curves of of P(PA-*alt*-AGE) copolymer derived by the action of I_2/*t*BuOK (I_2/*t*BuOK/PA/AGE = 1:1:100:400), (entry 7, Table 4.3).

Figure S44. TGA and derivative thermogravimetry (DTG) curves of P(PA-*alt*-CHO) copolymer derived by the action of I_2/*t*BuOK (I_2/*t*BuOK/PA/CHO = 1:1:500:1200), (entry 26 Table 4.1).

Table S1. ROAC of phthalic anhydride with cyclohexane oxide at various temperature and time.

EXPERIMENTAL DETAILS

Monomers and catalysts used for copolymerization were purchased from Aldrich. CHO, *t*BGE, PO, PGE, AGE and SO were dried over CaH_2 overnight, vacuum-distilled, and stored in the glovebox for further use. PA was sublimed twice prior to use. The deuterated solvent for NMR studies *i.e* $CDCl_3$ was acquired from Aldrich and purified by distilling over calcium hydride then stored in a glove box. The common reagents, common solvents were acquired locally and purified by usual methods. Toluene and THF were dried by refluxing over sodium/benzophenone for at least 24 h and freshly distilled prior to use. All manipulations for the preparation of polyesters were carried out using either standard Schlenk techniques or glovebox techniques under a dry argon atmosphere. All ^1H and ^{13}C NMR were recorded on a Bruker Avance 400 MHz or 500 MHz spectrometers with chemical shifts given in parts per million (ppm) using residual solvent peak at 7.26 ppm as reference in the case of $CDCl_3$. MALDI-TOF MS spectra were recorded on a Bruker Daltonics instrument using trans-2-[3-(4-t-butyl-phenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) as the matrix in THF at a loading of 1:5 with potassium trifluoroacetate as ionizing agent. Molecular weights (M_n and M_w) and the MWDs (M_w/M_n) of polymer samples were determined by GPC instrument with Waters 510 pump and Waters 410 or 2414 differential refractometer as the detector. Three columns, namely WATERS STRYGEL-HR5, STRYGEL-HR4 and STRYGEL-HR3, each of dimensions (7.8 × 300 mm), were connected in series. Measurements were done in THF at 27 °C. Number average molecular weights (M_n) and MWDs (M_w/M_n) of polymers were measured relative to polystyrene standards.

General procedure for the ring-opening copolymerization of PA and different epoxides under neat condition using I_2 and *t*BuOK

Polymerizations were performed in a dry Schlenk tube or pressure tube using an outside heating bath. The vial was charged with a predetermined amount of molecular iodine (0.05 mmol, 1 equiv), potassium *tert*-butoxide (0.05 mmol, 1 equiv), epoxide (20 mmol, 400 equiv) and anhydride (5 mmol, 100 equiv), which were kept stirring for 5 min at room temperature in an argon filled glove box. The Schlenk tube or pressure tube was sealed, taken out of the glove box, and then immersed in the heating bath under the determined temperature, and stirred over the desired period of time. After a desired period, the reaction tube was removed from the heating bath and a 0.2 mL of crude sample was taken from the reaction mixture and prepared for ^{1}H NMR analysis. Then the mixture was diluted with dichloromethane and precipitated into 10 fold excess of cold methanol or ethanol or hexane, filtered, washed with methanol or hexane to remove the unreacted monomer and dried in a vacuum at room temperature to a constant weight. The final copolymers were analysed by ^{1}H and ^{13}C NMR, GPC, MALDI-TOF MS, DSC and TGA experiments.

General procedure for the ring-opening copolymerization of PA and cyclohexene oxide in toluene using I_2 and *t*BuOK

Polymerization was performed in a dry schlenk tube or pressure tube using an external heating bath. The reaction tube was charged with 5 mL of dry toluene, iodine (12.69mg, 0.05 mmol, 1 equiv), potassium *tert*-butoxide (5.61mg, 0.05 mmol, 1 equiv), dibromomethane (8.69mg, 0.05 mmol, 1 equiv), epoxide (5 mmol, 100 equiv) and phthalic anhydride (5 mmol, 100 equiv), which were kept stirring for 5 to 10 min at room temperature in an argon filled glove box. The schlenk tube or pressure tube was sealed, taken out of the glove box, and then immersed in the heating bath at 90°C and stirred over the desired period of time. After a desired period, the reaction tube was removed from the heat heating bath and cooled to room temperature. The crude reaction product was analysed by ^{1}H NMR to see the conversion.

In-situ studies for *tert*-butyl hypoiodite (*t*BuOI) and other alkyl hypoiodites synthesis:

According to previous literature method, *tert*-butyl hypoiodite (*t*BuOI) was prepared in-situ by the reaction of *tert*-butyl hypochlorite (*t*BuOCl) with NaI in 1:1 stoichiometric amount.[1] The starting reagent *t*BuOCl was also synthesized quantitatively from previous method.[2] The reaction of I_2 and *t*BuOK in THF at 70 ^oC gave *tert*-butyl hypoiodite (*t*BuOI) and KI. The aliquot was analysed by ^1H NMR and *tert*-butyl signal of *t*BuOI along with solvated THF signals were noticed (Figure S5a). After removal of THF by 6h vacuum the ^1H NMR analysis of obtained powder showed multiple signals indicating the decomposition of *t*BuOI product (Figure S5b). Hence, the in-situ formed *t*BuOI remains more stable in THF solvent. In the case of other alkyl hypoiodites we are not succeeded in in-situ ^1H NMR analysis. Because of high sensitivity to air and moisture the other alkyl hypoiodites (eg, *i*PrOI and MeOI) are decomposing while preparing NMR sample.

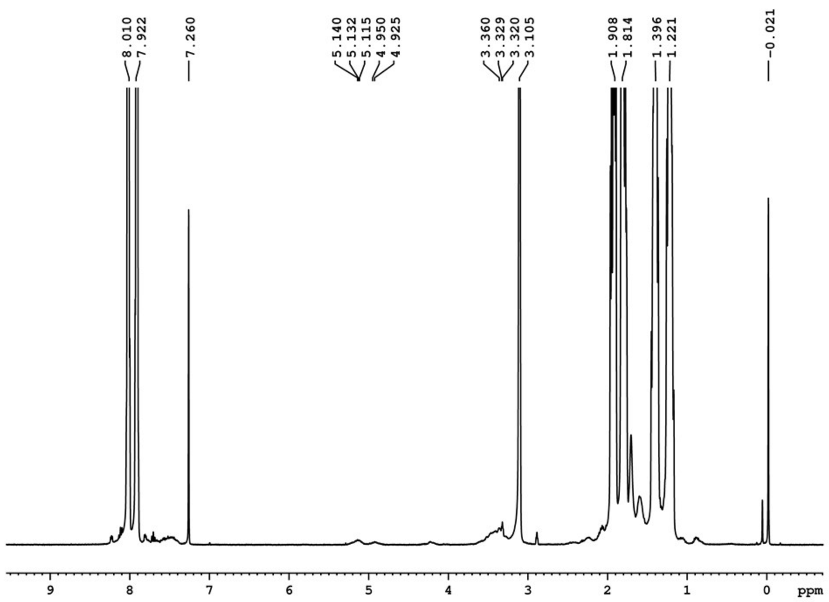


Figure S1 ^1H NMR spectrum ($CDCl_3$, 400 MHz, 298K) of crude product derived by the action of LiI (LiI/PA/CHO = 1:100:400) at 90 ^oC, 12h.

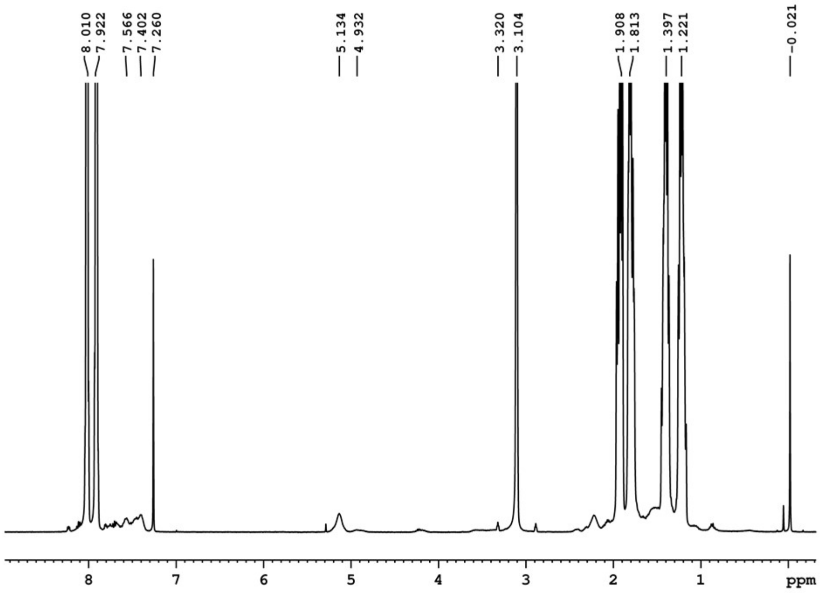


Figure S2 [1]H NMR spectrum ($CDCl_3$, 400 MHz, 298K) of crude product derived by the action of NaI (NaI/PA/CHO = 1:100:400) at 90 °C, 12h.

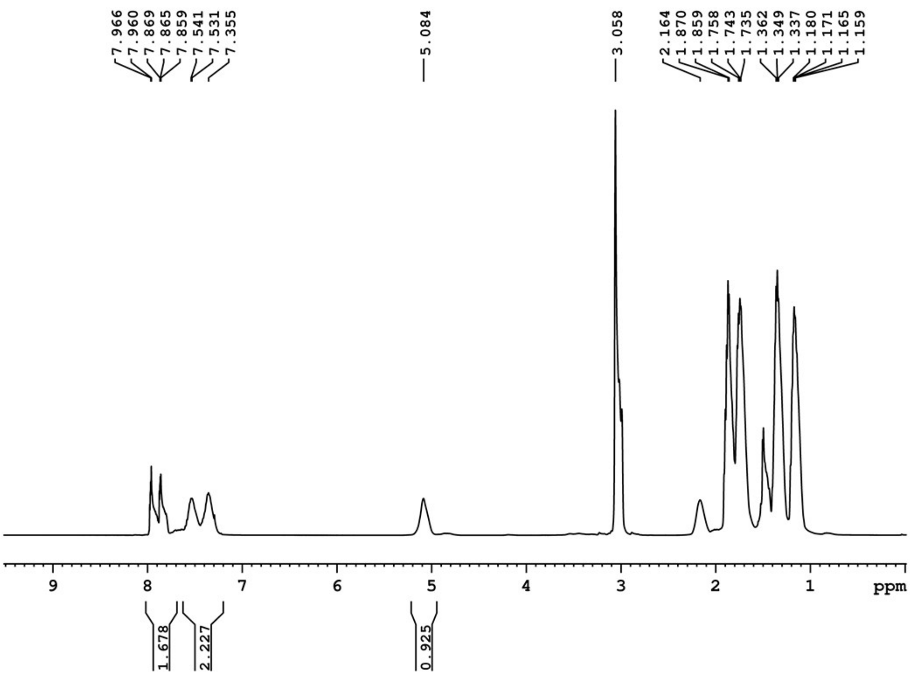


Figure S3 [1]H NMR spectrum ($CDCl_3$, 400 MHz, 298K) of crude product derived by the action of *t*BuOK (*t*BuOK/PA/CHO = 1:100:400) (entry 18, Table 1).

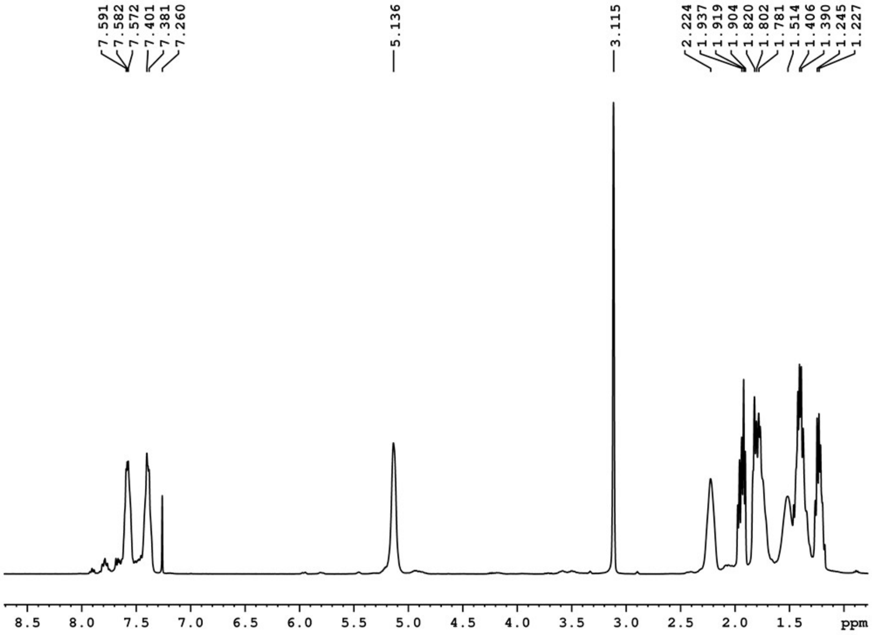


Figure S4 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298K) of crude product, P(PA-*alt*-CHO) derived by the action of KI+NaI+*t*BuOCl (KI/NaI/*t*BuOCl/PA/CHO = 1:1:1:100:400), (entry19, Table 1).

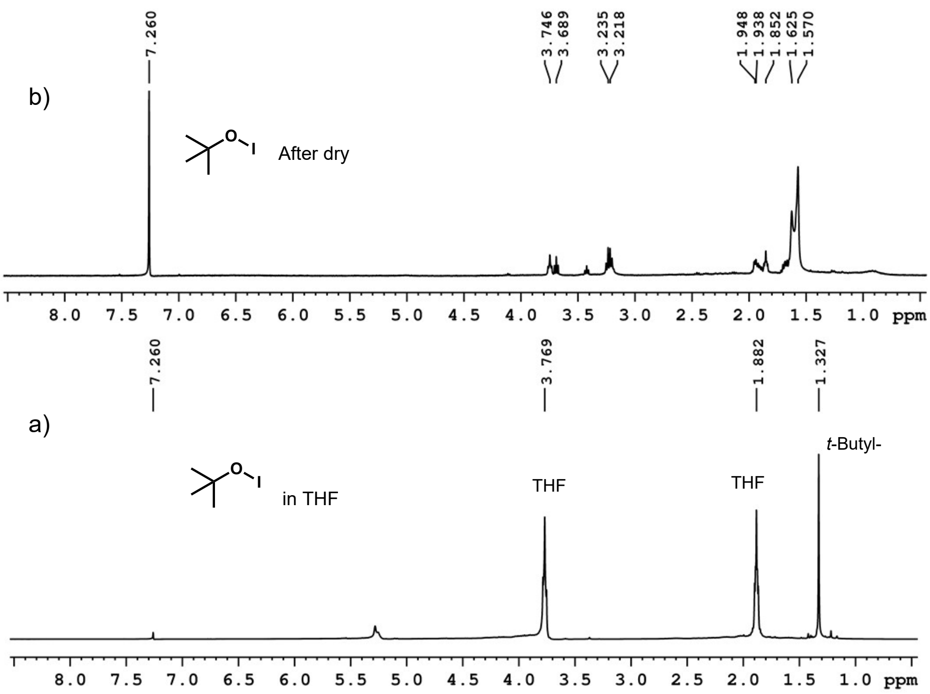


Figure S5 a) ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298K) of THF aliquot from the in-situ reaction of *t*BuOK and I_2 (1:1) in THF at 70 °C, 6h. b) After removal of THF by 6h vacuum.

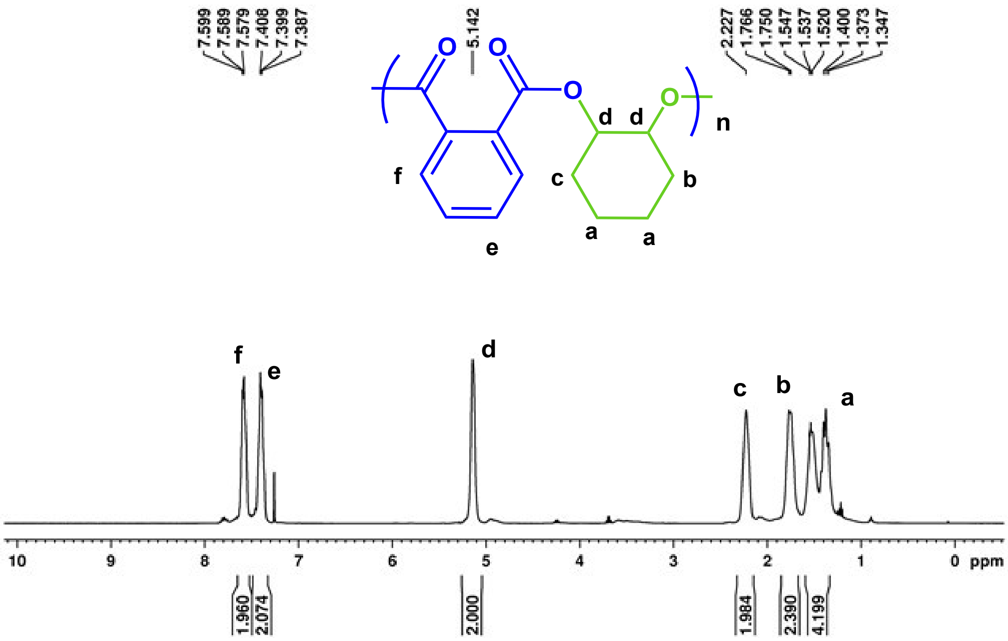


Figure S6 [1]H NMR spectrum ($CDCl_3$, 400 MHz, 298K) of purified P(PA-*alt*-CHO) copolymer derived by the action of I_2 and *t*BuOK (I_2/*t*BuOK/PA/CHO = 1:1:100:400), (entry15, Table 1).

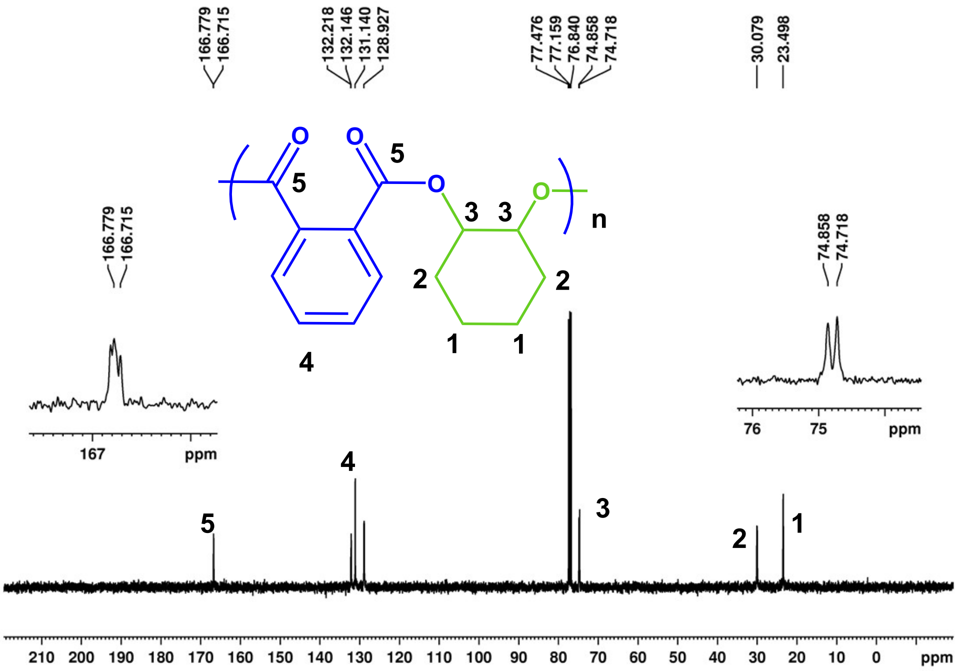


Figure S7 [13]C NMR spectrum ($CDCl_3$, 400 MHz, 298K) of P(PA-*alt*-CHO) copolymer derived by the action of I_2 and *t*BuOK (I_2/*t*BuOK/PA/*t*BGE = 1:1:100:400), (entry15, Table 1).

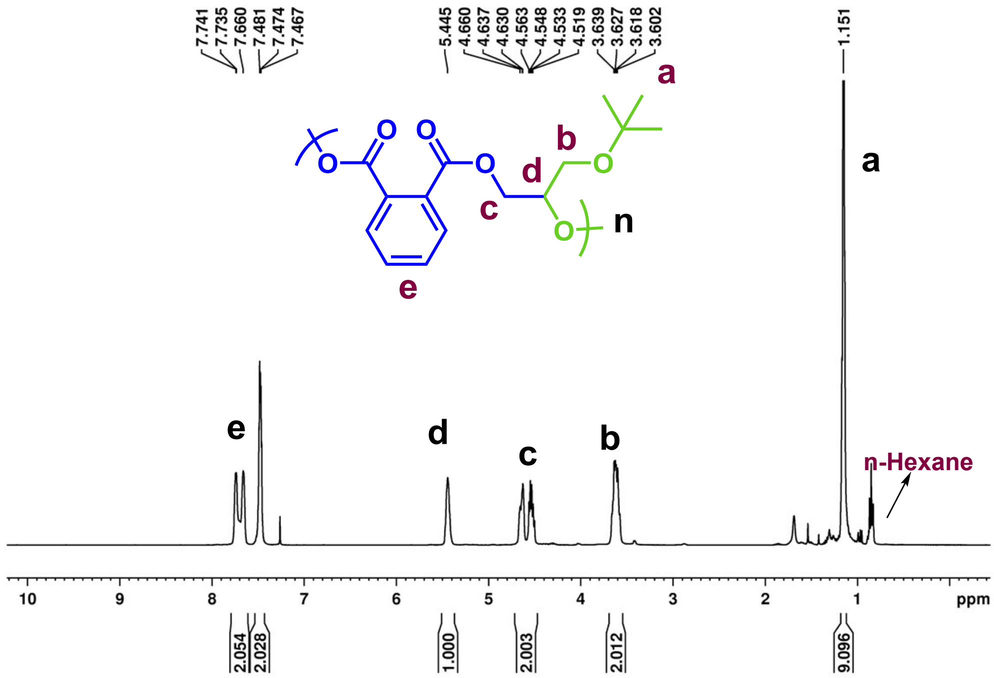


Figure S8 [1]H NMR spectrum ($CDCl_3$, 400 MHz, 298K) of P(PA-*alt*-*t*BGE)copolymer derived by the action of I_2 and *t*BuOK (I_2/*t*BuOK/PA/*t*BGE = 1:1:100:400), (entry 1, Table 2).

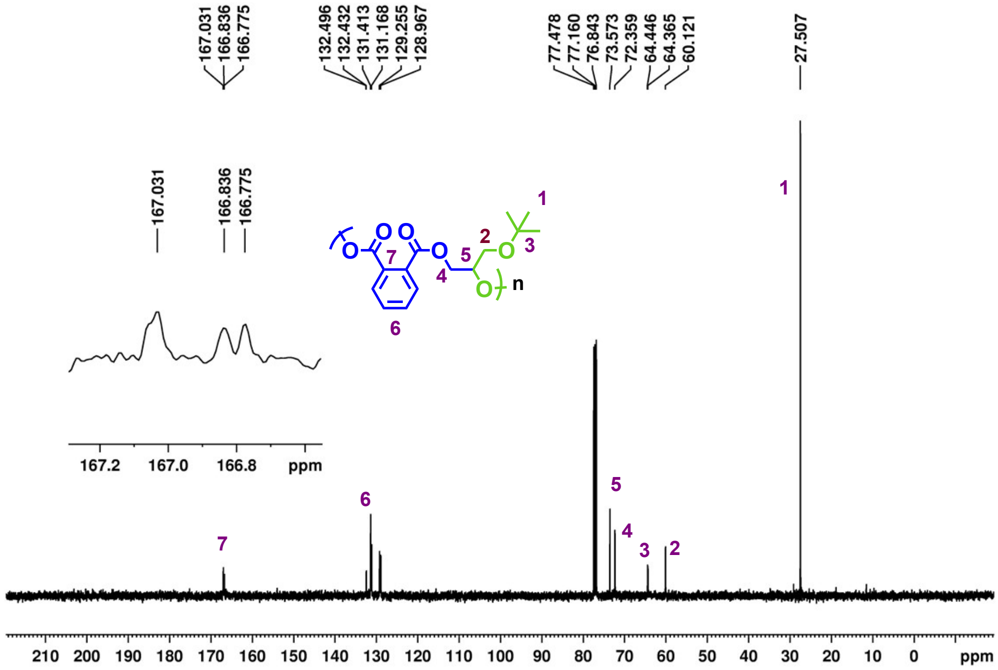


Figure S9 [13]C NMR spectrum ($CDCl_3$, 400 MHz, 298K) of P(PA-*alt*-*t*BGE) copolymer derived by the action of I_2 and *t*BuOK (I_2/*t*BuOK/PA/*t*BGE = 1:1:100:400), (entry 1, Table 2).

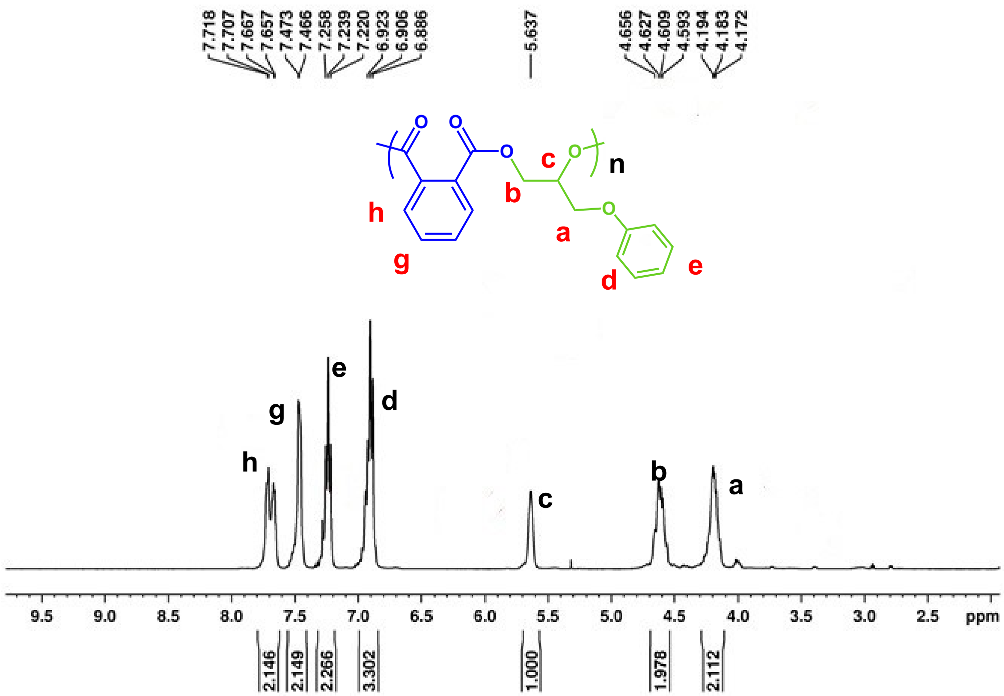


Figure S10 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298K) of P(PA-*alt*-PGE) copolymer derived by the action of I_2 and *t*BuOK (I_2/*t*BuOK/PA/PGE = 1:1:100:400), (entry 4, Table 2).

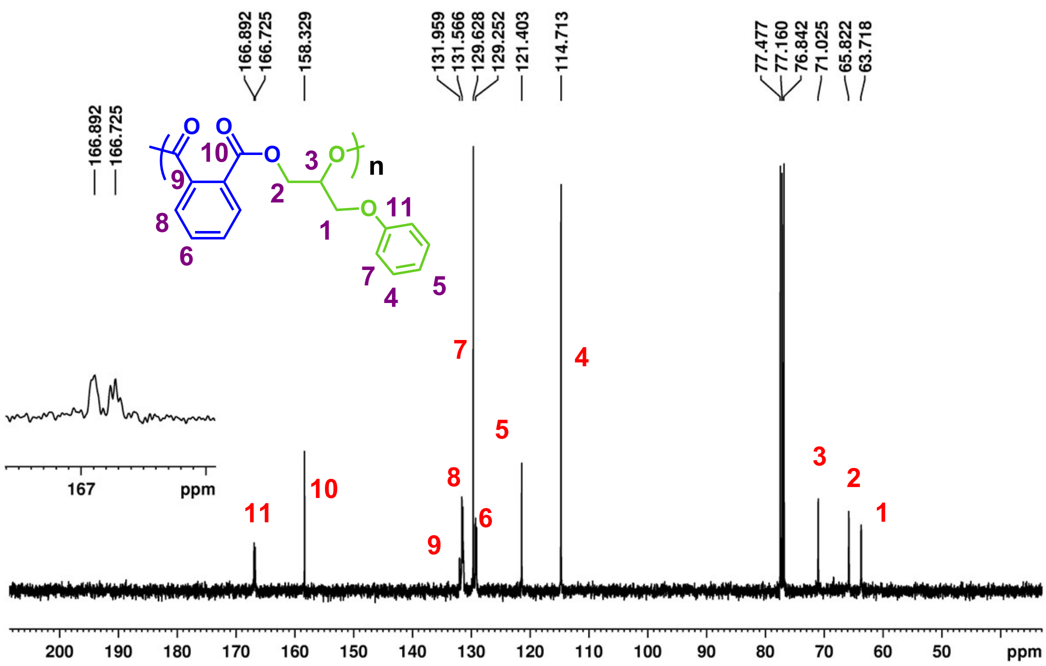


Figure S11 ^{13}C NMR spectrum ($CDCl_3$, 400 MHz, 298K) of P(PA-*alt*-PGE) copolymer derived by the action of I_2 and *t*BuOK (I_2/*t*BuOK/PA/PGE = 1:1:100:400), (entry 4, Table 2).

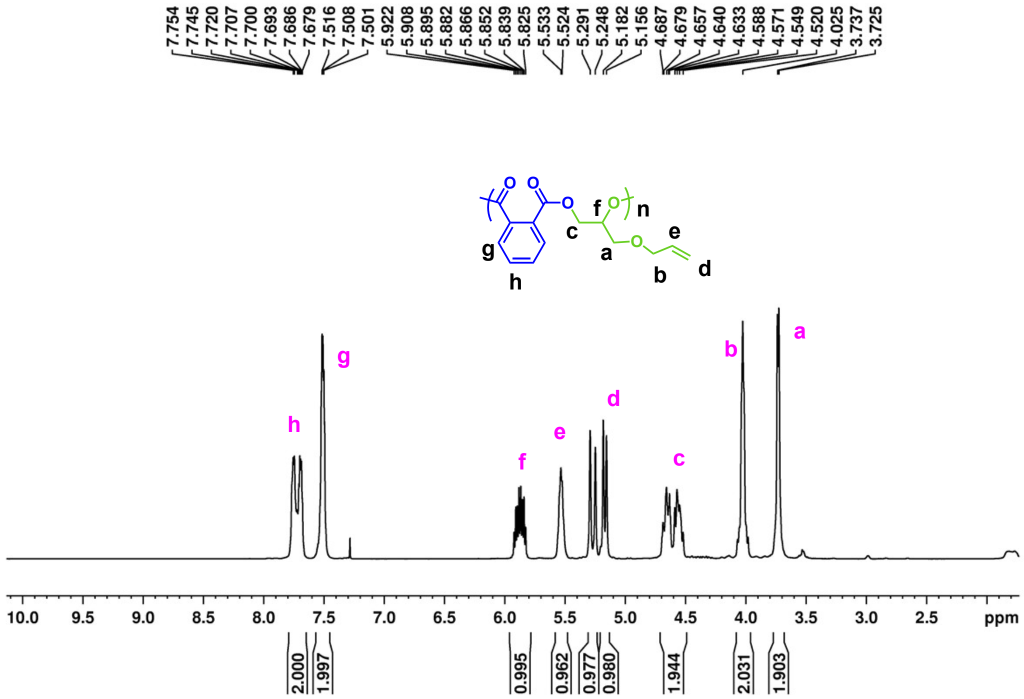


Figure S12 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298K) of P(PA-*alt*-AGE) copolymer derived by the action of I_2 and *t*BuOK (I_2/tBuOK/PA/AGE = 2:1:100:400), (entry7, Table 2).

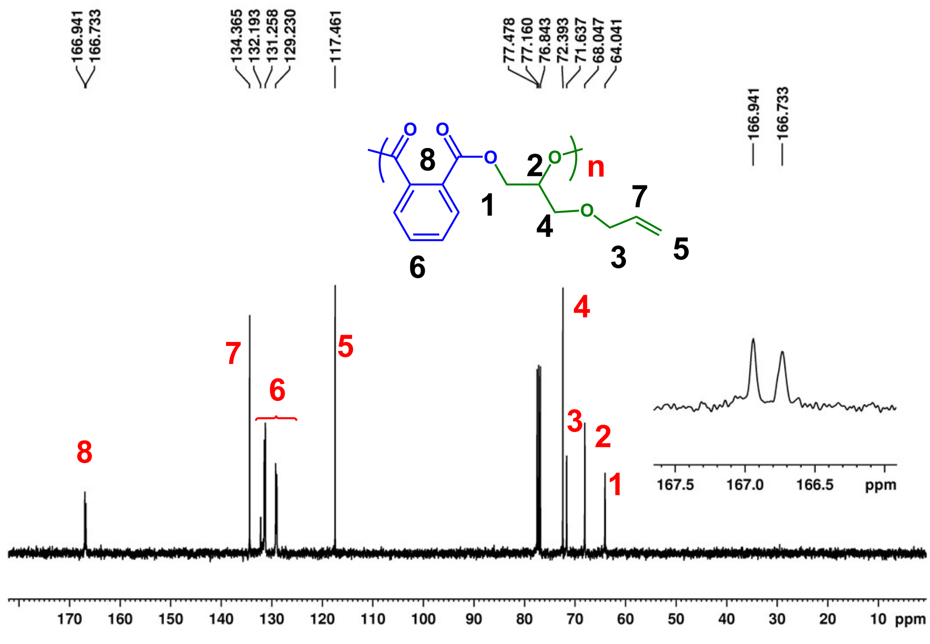


Figure S13 ^{13}C NMR spectrum ($CDCl_3$, 400 MHz, 298K) of P(PA-*alt*-AGE) copolymer derived by the action of I_2 and tBuOK (I_2/tBuOK/PA/AGE = 1:1:100:400), (entry7, Table 2).

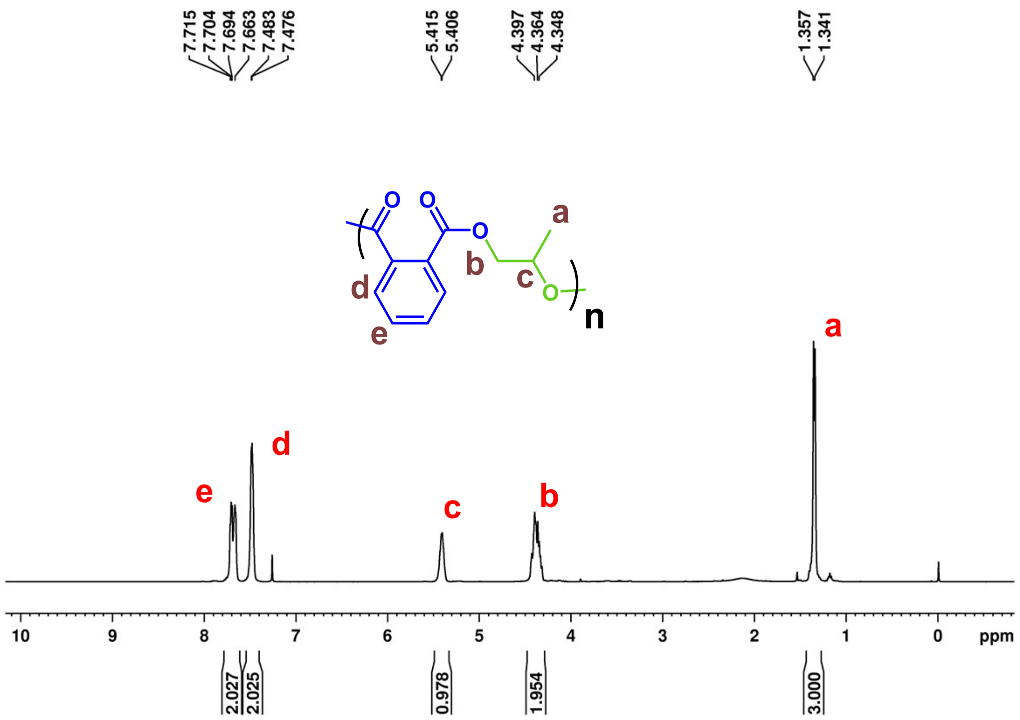


Figure S14 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298K) of P(PA-*alt*-PO) copolymer derived by the action of I_2 and *t*BuOK (I_2/*t*BuOK/PA/PO = 1:1:100:400), (entry 13, Table 2).

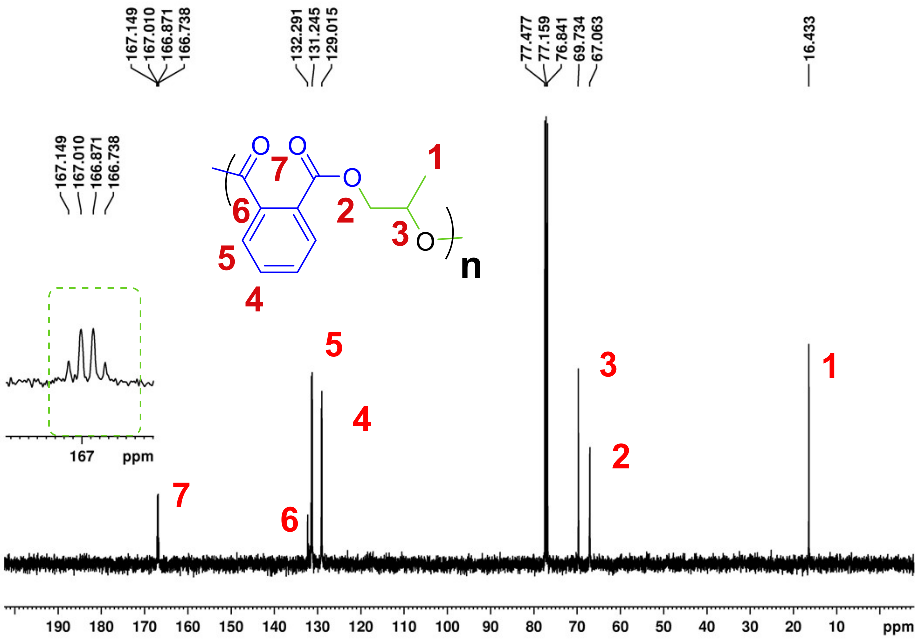


Figure S15 ^{13}C NMR spectrum ($CDCl_3$, 400 MHz, 298K) of P(PA-*alt*-PO) copolymer derived by the action of I_2 and *t*BuOK (I_2/*t*BuOK/PA/PO = 1:1:100:400), (entry 13, Table 2).

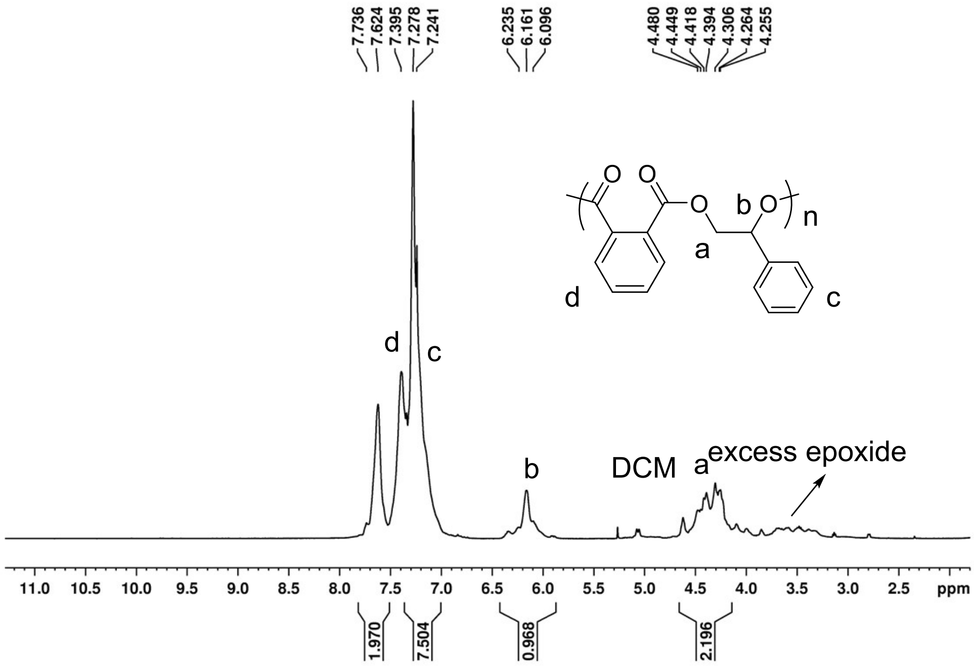


Figure S16 [1]H NMR spectrum ($CDCl_3$, 400 MHz, 298K) of P(PA-*alt*-SO) copolymer derived by the action of I_2 and *t*BuOK (I_2/*t*BuOK/PA/SO = 1:1:100:400), (entry 10, Table 2).

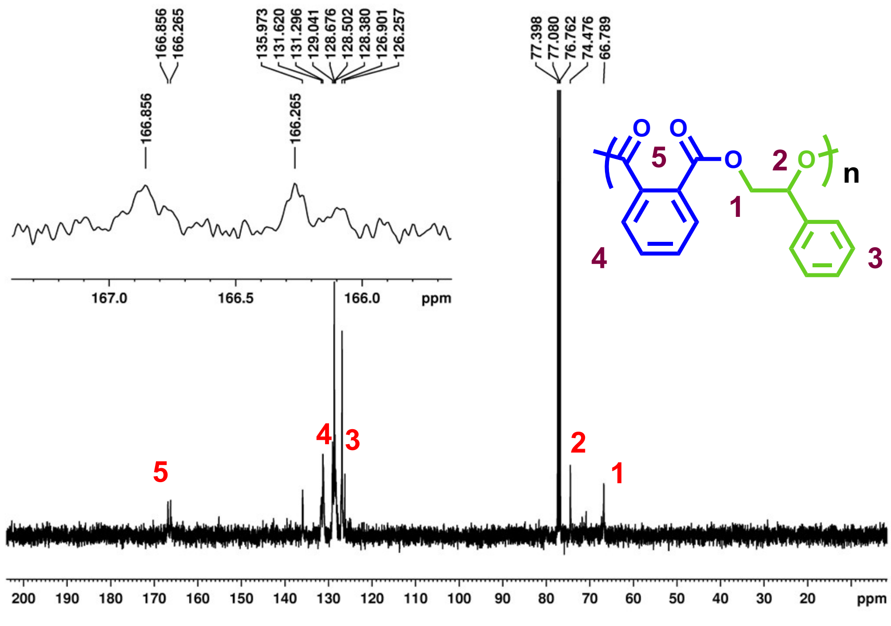


Figure S17 [13]C NMR spectrum ($CDCl_3$, 400 MHz, 298K) of P(PA-*alt*-SO) copolymer derived by the action of I_2 and *t*BuOK (I_2/*t*BuOK/PA/SO = 1:1:100:400), (entry 10, Table 2).

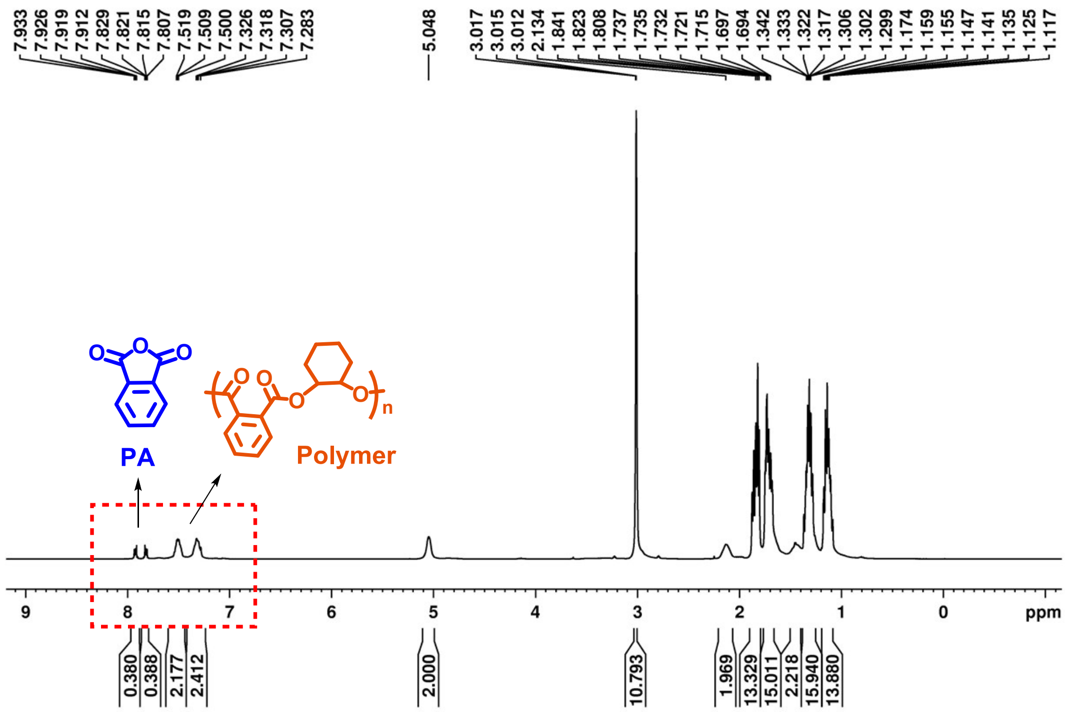
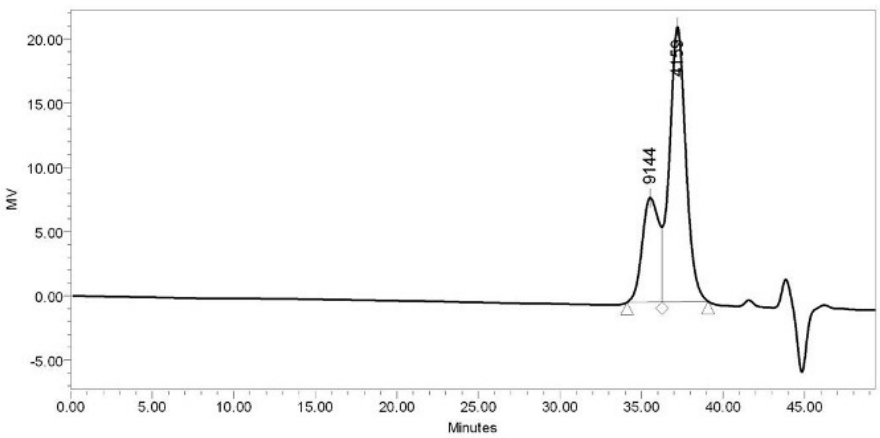


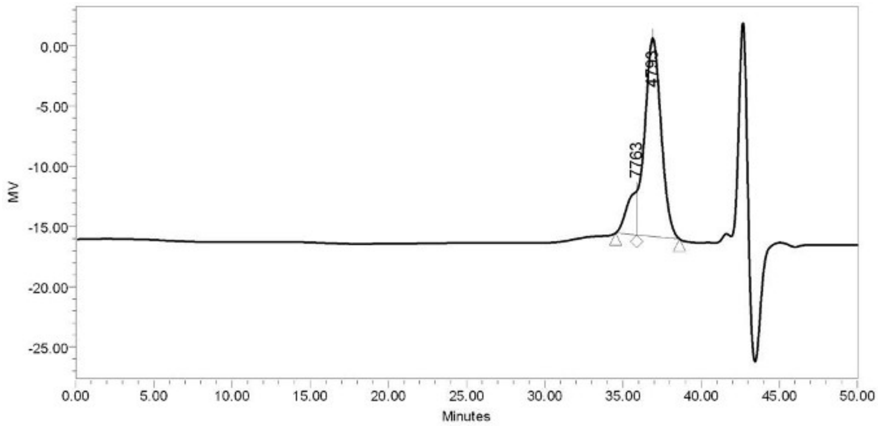
Figure S18 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298K) of P(PA-*alt*-CHO) copolymer derived by the action of I_2 and *t*BuOK (I_2/*t*BuOK/PA/PO = 1:1:100:400), at 70 °C.



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Poly dispersity	MW Marker 1	MW Marker 2
1		8906	9264	9144	9656	10078		1.040161		
2		3984	4193	4159	4396	4593		1.052442		

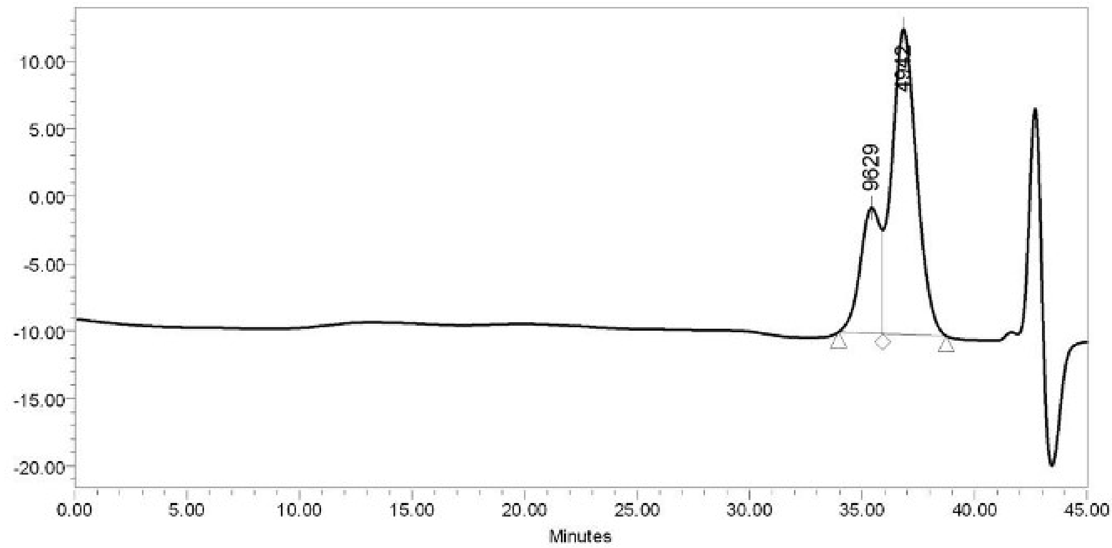
Figure S19 GPC trace of purified product, P(PA-*alt*-CHO) copolymer derived by the action of I_2 and CH_3OK (I_2/CH_3OK/PA/CHO = 1:1:100:300), (entry 3, Table 1).



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Poly dispersity	MW Marker 1	MW Marker 2
1		9379	9557	7763	9752	9962		1.018992		
2		4606	4855	4793	5106	5353		1.054183		

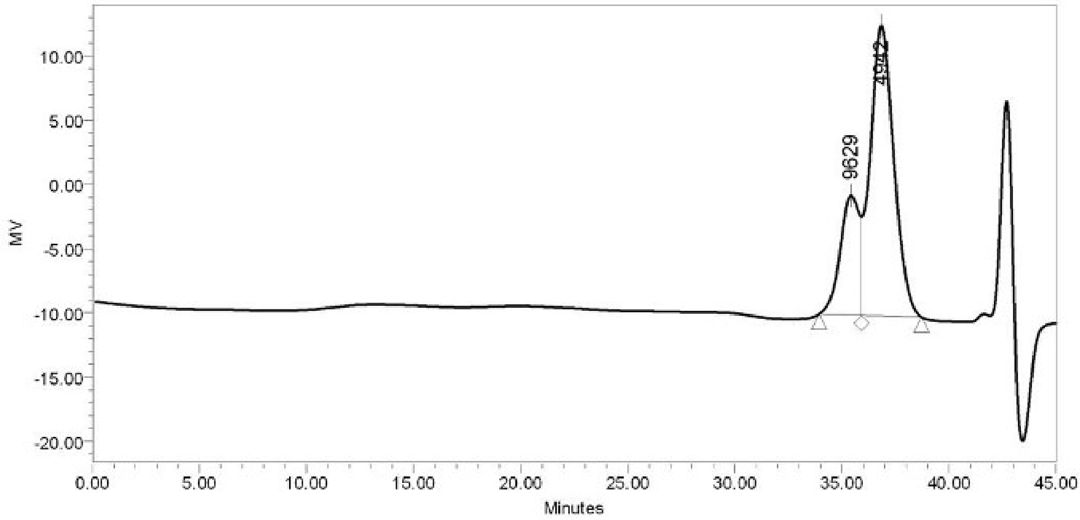
Figure S20 GPC trace of purified product P(PA-*alt*-CHO) copolymer derived by the action of I_2 and CH_3OLi (I_2/CH_3OLi/PA/CHO = 1:1:100:400), (entry 6, Table 1).



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Poly dispersity	MW Marker 1	MW Marker 2
1		9953	10281	9629	10654	11070		1.032960		
2		4643	4921	4942	5190	5446		1.059809		

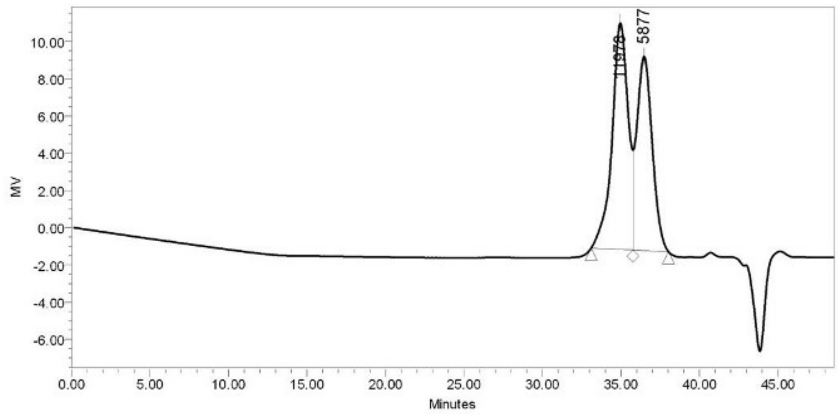
Figure S21 GPC trace of purified product P(PA-*alt*-CHO) copolymer derived by the action of I_2 and CH_3ONa (I_2/CH_3ONa/PA/CHO = 1:1:100:400), (entry 7, Table 1).



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Poly dispersity	MW Marker 1	MW Marker 2
1		9966	10300	9629	10682	11112		1.033573		
2		4647	4923	4942	5192	5448		1.059440		

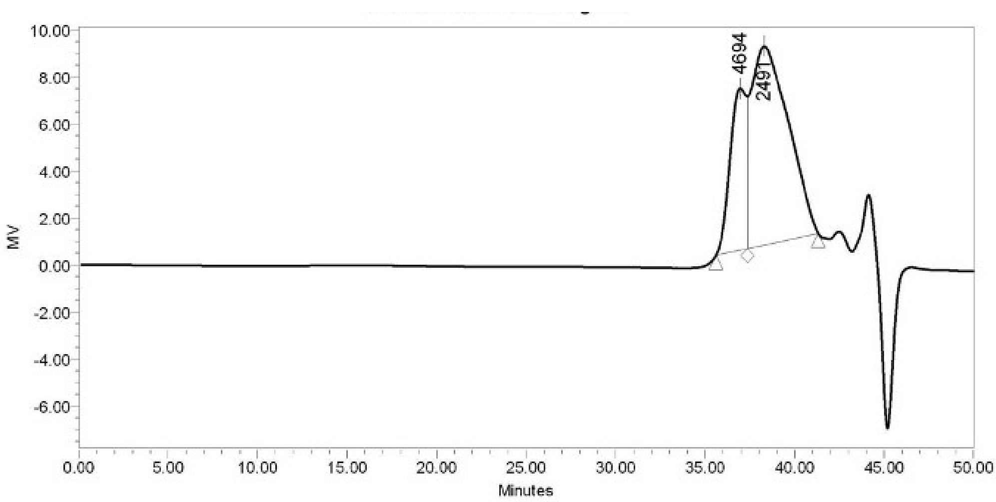
Figure S22 GPC trace of purified product P(PA-*alt*-CHO) copolymer derived by the action of I_2 and CH_3OK ($I_2/CH_3OK/PA/CHO$ = 1:1:100:400), (entry 8, Table 1).



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Poly dispersity	MW Marker 1	MW Marker 2
1		12014	12691	11978	13510	14485		1.056373		
2		5579	5820	5877	6050	6265		1.043214		

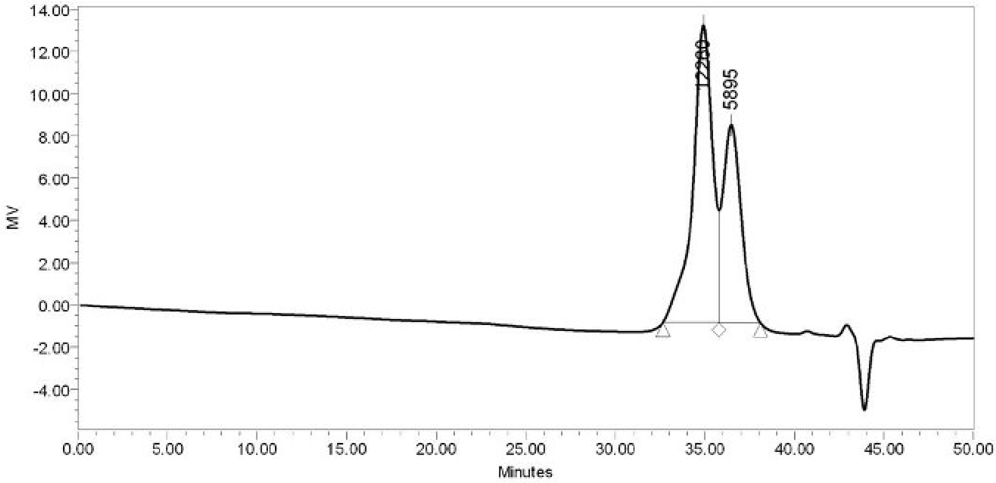
Figure S23 GPC trace of purified product P(PA-*alt*-CHO) copolymer derived by the action of I_2 and *i*PrOK (I_2/*i*PrOK /PA/CHO = 1:1:100:400), (entry 12, Table 1).



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Poly dispersity	MW Marker 1	MW Marker 2
1		4975	5126	4694	5292	5473		1.030294		
2		1808	2151	2491	2469	2730		1.189554		

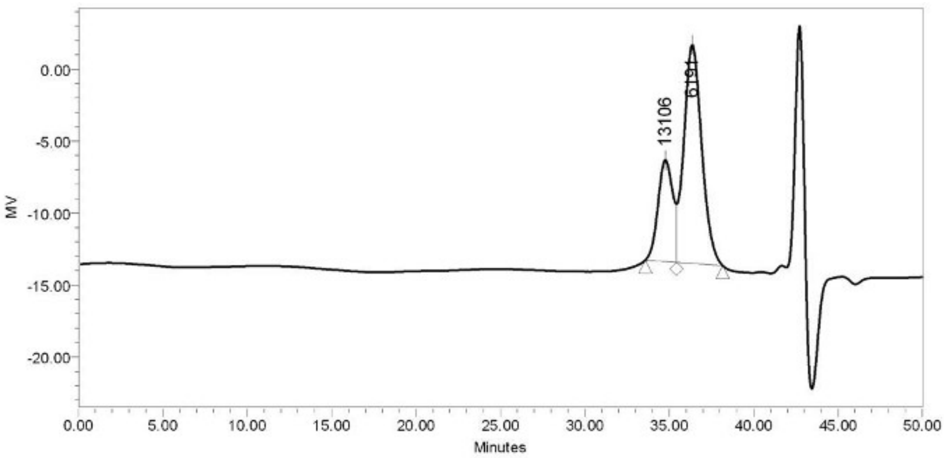
Figure S24 GPC trace of purified product P(PA-*alt*-CHO) copolymer derived by the action of I_2 and *t*BuOLi(I_2/*t*BuOLi/PA/CHO = 1:1:100:400), (entry 13, Table 1).



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Poly dispersity	MW Marker 1	MW Marker 2
1		12557	13556	12260	14873	16550		1.079515		
2		5518	5775	5895	6017	6239		1.046578		

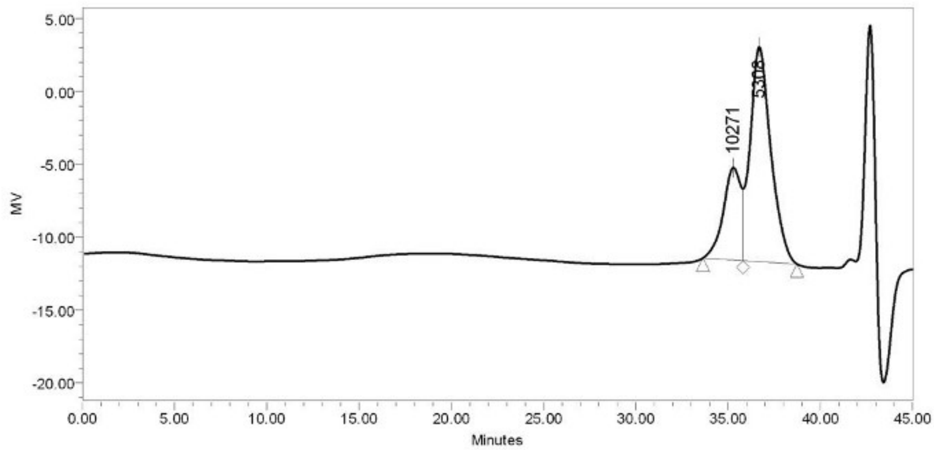
Figure S25 GPC trace of purified product of P(PA-*alt*-CHO) copolymer derived by the action of I_2 and *t*BuONa (I_2/*t*BuONa/PA/CHO = 1:1:100:400), (entry 14, Table 1).



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Poly dispersity	MW Marker 1	MW Marker 2
1		12913	13315	13106	13746	14201		1.031164		
2		5829	6155	6191	6472	6774		1.055935		

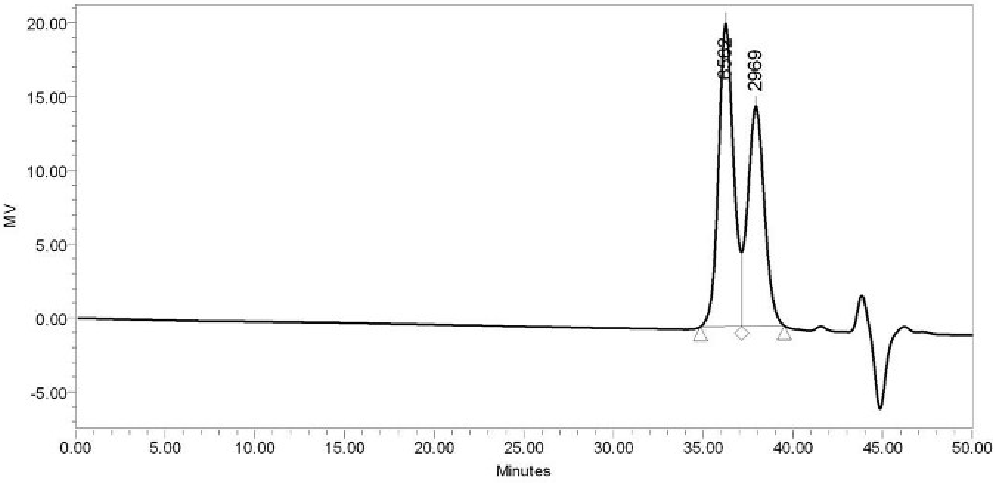
Figure S26 GPC trace of purified product P(PA-*alt*-CHO) copolymer derived by the action of I_2 and *t*BuOK (I_2/*t*BuOK/PA/CHO = 1:1:100:400), (entry15, Table 1).



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Poly dispersity	MW Marker 1	MW Marker 2
1		10725	11175	10271	11706	12317		1.042002		
2		4823	5142	5308	5443	5720		1.066224		

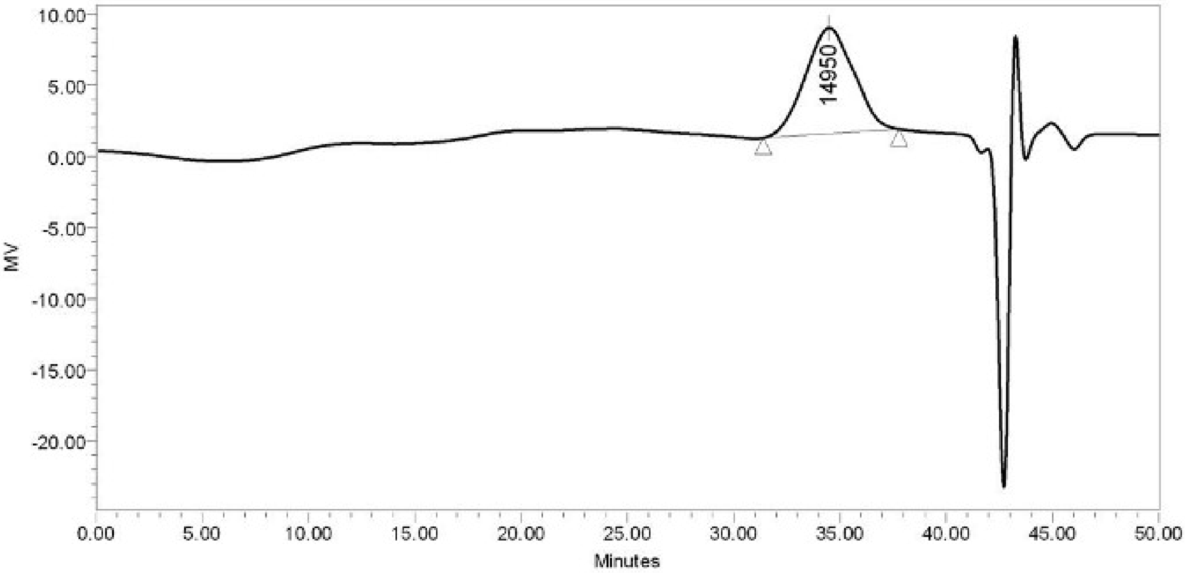
Figure S27 GPC trace of purified product P(PA-*alt*-CHO) copolymer derived by the action of I_2/*t*BuOK (I_2/*t*BuOK/PA/CHO = 1:1:250:800), (entry 20, Table 1).



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Poly dispersity	MW Marker 1	MW Marker 2
1		6336	6557	6562	6788	7030		1.034745		
2		2858	2977	2969	3091	3201		1.041374		

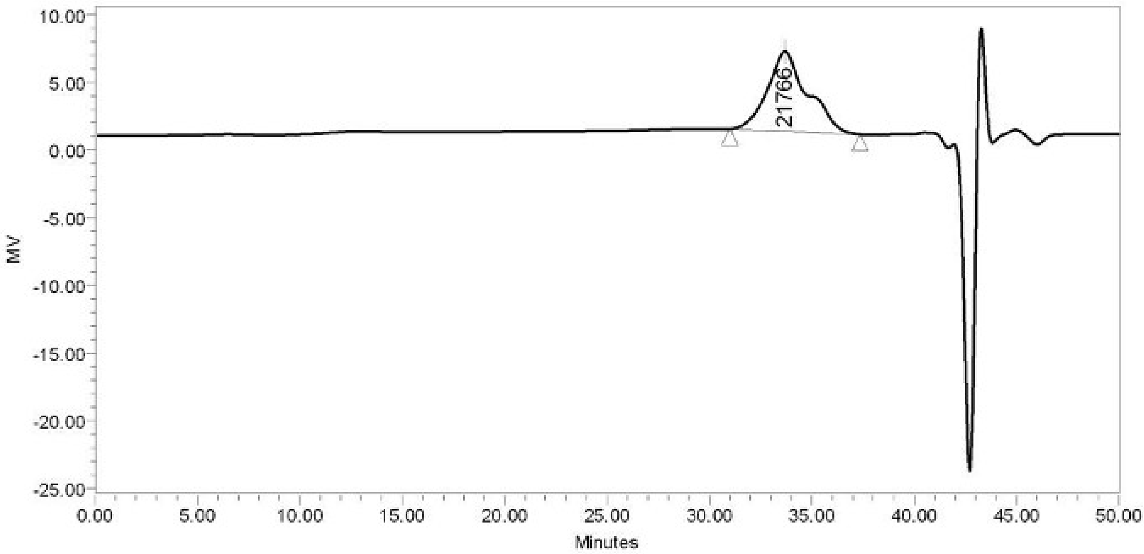
Figure S28 GPC trace of purified product P(PA-*alt*-CHO) copolymer derived by the action of KI (KI/PA/CHO = 1:100:300), (entry 24, Table 1).



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Poly dispersity	MW Marker 1	MW Marker 2
1		13016	16498	14950	20649	25194		1.267589		

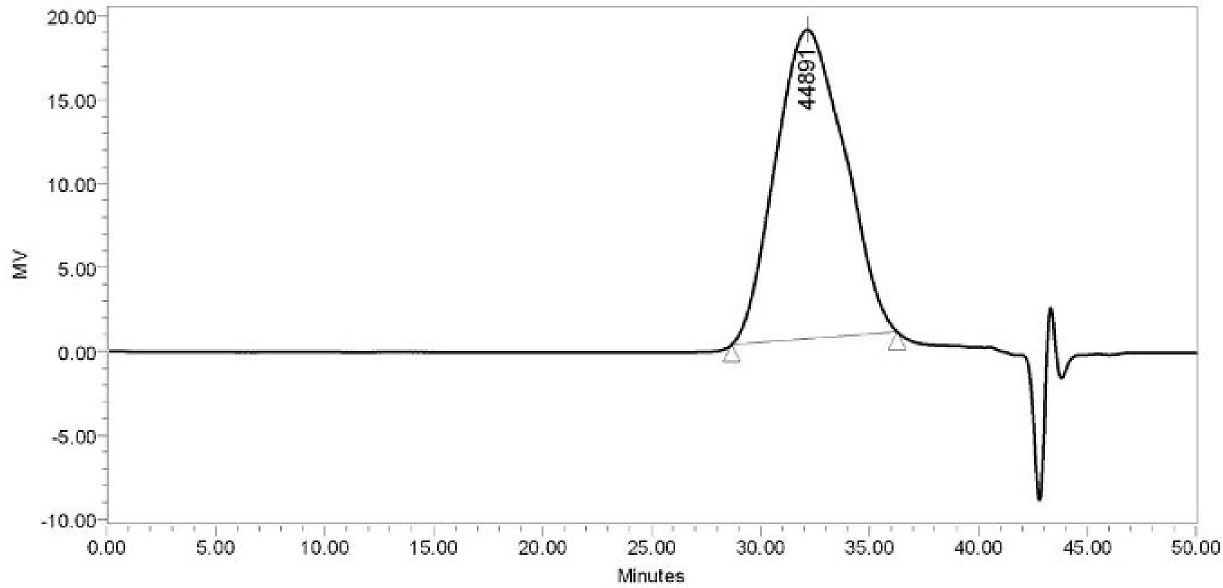
Figure S29 GPC trace of purified product P(PA-*alt*- *t*BGE) copolymer derived by the action of I_2 and *t*BuOK (I_2/*t*BuOK/PA/*t*BGE = 1:1:100:400), (entry 1, Table 2).



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		17159	21593	21766	26406	31379		1.258380		

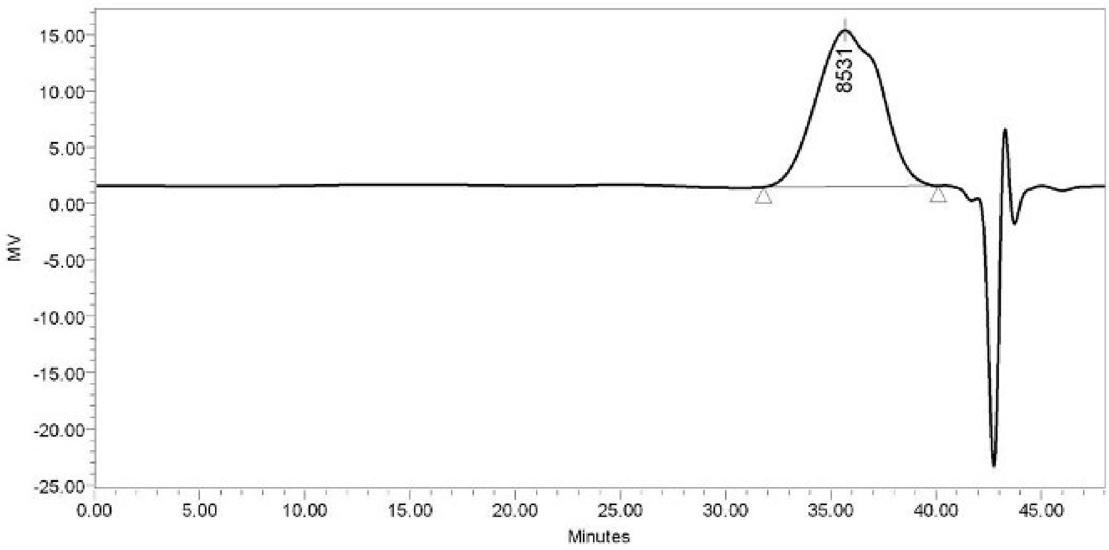
Figure S30 GPC trace of purified product P(PA-*alt*- *t*BGE) copolymer derived by the action of I_2 and *t*BuOK (I_2/*t*BuOK /PA/*t*BGE = 1:1:250:800), (entry 2, Table 2).



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		32989	49958	44891	71228	93004		1.514397		

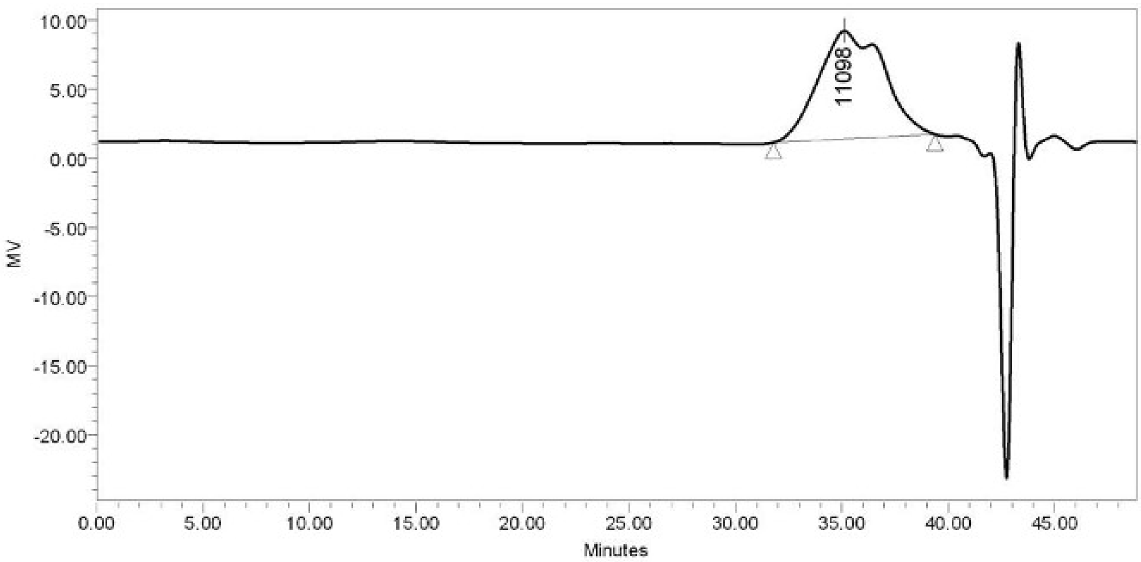
Figure S31 GPC trace of purified product P(PA-*alt*- *t*BGE) copolymer derived by the action of I_2 and *t*BuOK (I_2/*t*BuOK /PA/*t*BGE = 1:1:500:1200), (entry 3, Table 2).



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		6440	9423	8531	13441	18024		1.463186		

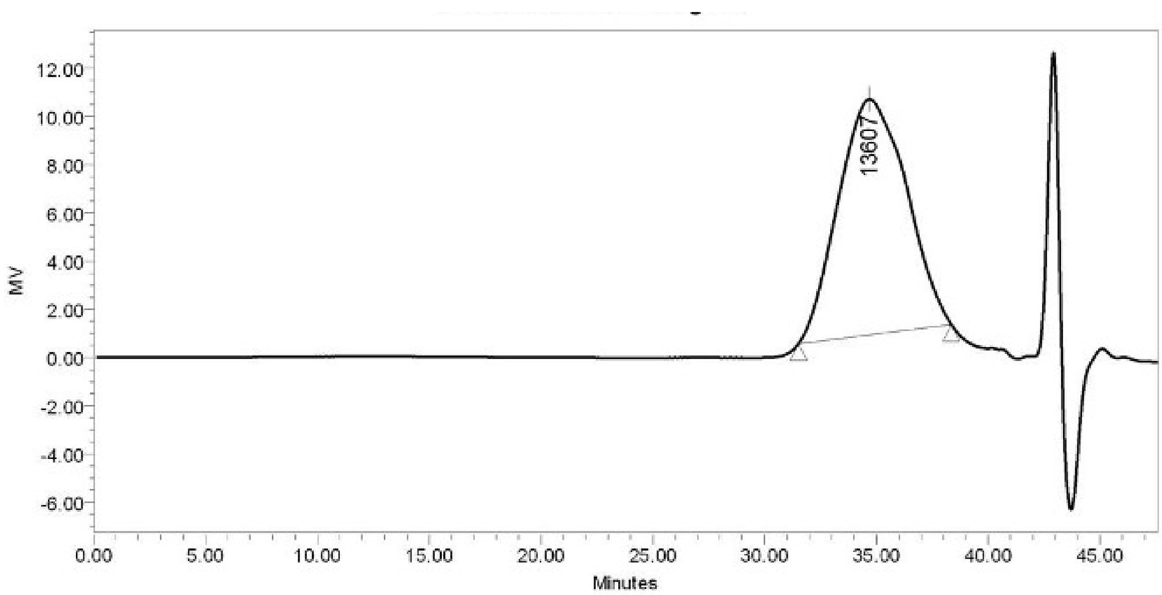
Figure S32 GPC trace of purified product P(PA-*alt*-PGE) copolymer derived by the action of I_2 and *t*BuOK (I_2/*t*BuOK /PA/PGE = 1:1:100:400), (entry 4, Table 2).



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		7565	11176	11098	15793	20682		1.477361		

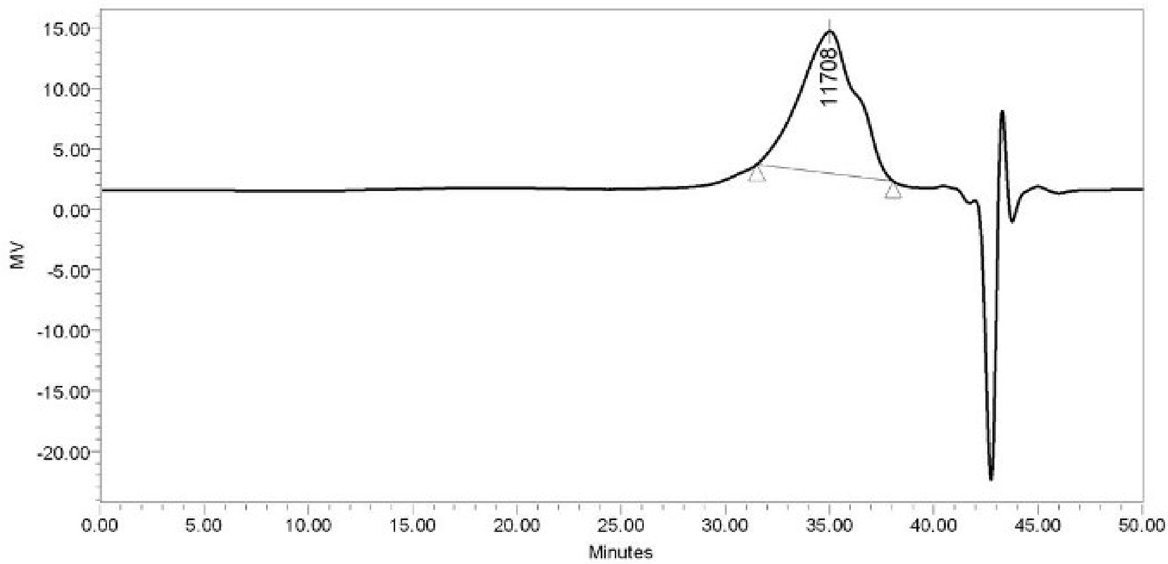
Figure S33 GPC trace of purified product P(PA-*alt*-PGE) copolymer derived by the action of I_2 and *t*BuOK (I_2/*t*BuOK /PA/PGE = 1:1:250:800), (entry 5, Table 2).



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Poly dispersity	MW Marker 1	MW Marker 2
1		10366	14989	13607	20706	26493		1.446044		

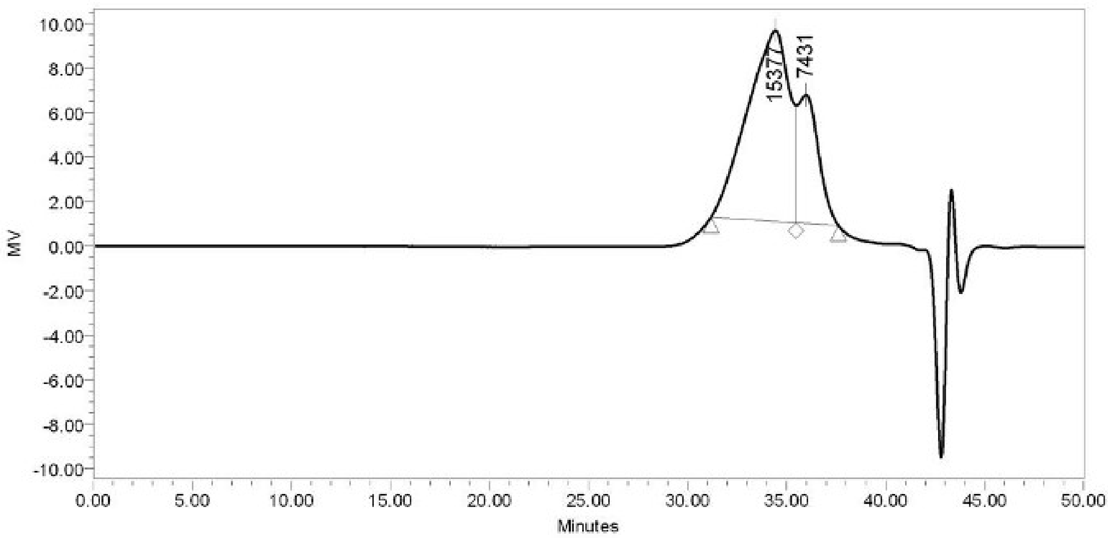
Figure S34 GPC trace of purified product of P(PA-*alt*-PGE) copolymer derived by the action of I_2 and *t*BuOK (I_2/*t*BuOK/PA/PGE = 1:1:500:1200), (entry 6, Table 2).



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Poly dispersity	MW Marker 1	MW Marker 2
1		10406	14488	11708	20019	26203		1.392364		

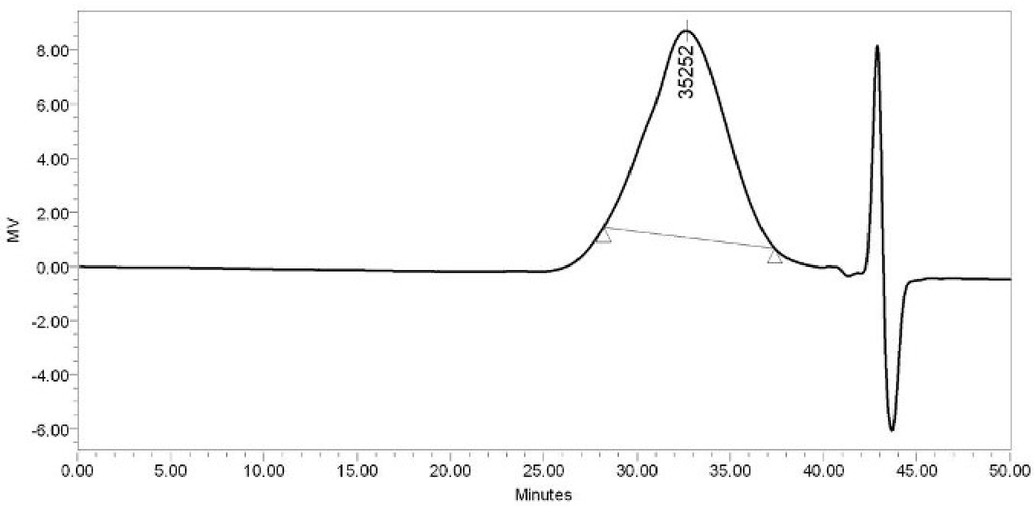
Figure S35 GPC trace of purified product P(PA-*alt*-AGE) copolymer derived by the action of I_2 and *t*BuOK (I_2/*t*BuOK/PA/AGE = 1:1:100:400), (entry 7, Table 2).



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		17891	21696	15377	26858	32785		1.212674		
2		6680	6984	7431	7264	7515		1.045599		

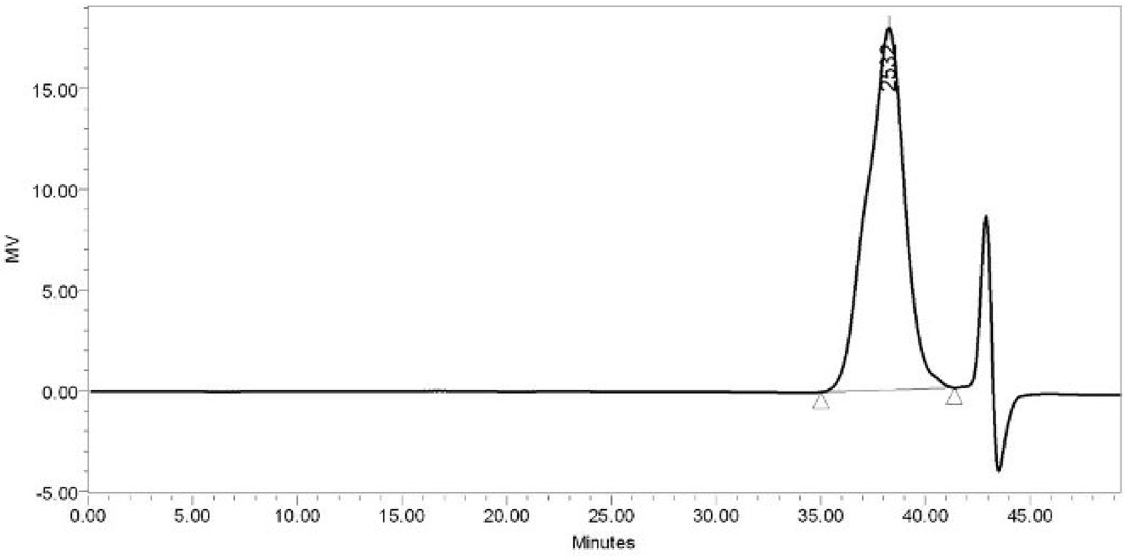
Figure S36 GPC trace of purified product P(PA-*alt*-AGE) copolymer derived by the action of I_2 and *t*BuOK (I_2/*t*BuOK/PA/AGE = 1:1:250:800), (entry 8, Table 2).



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		24824	48110	35252	85033	124271		1.938040		

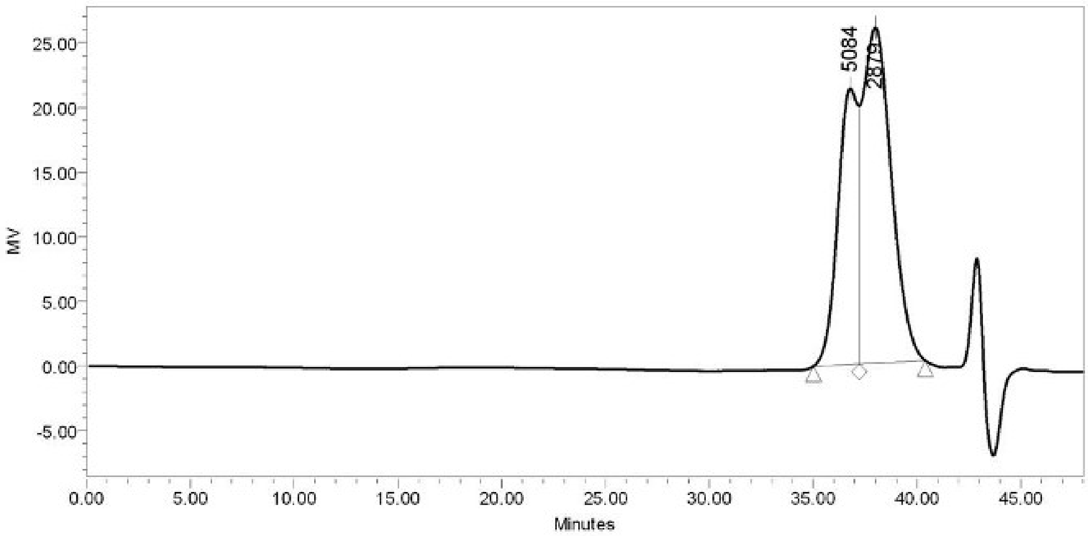
Figure S37 GPC trace of purified product P(PA-*alt*-AGE) copolymer derived by the action of I_2 and *t*BuOK (I_2/*t*BuOK/PA/AGE = 1:1:500:1200), (entry 9, Table 2).



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Poly dispersity	MW Marker 1	MW Marker 2
1		2536	3006	2532	3557	4179		1.185228		

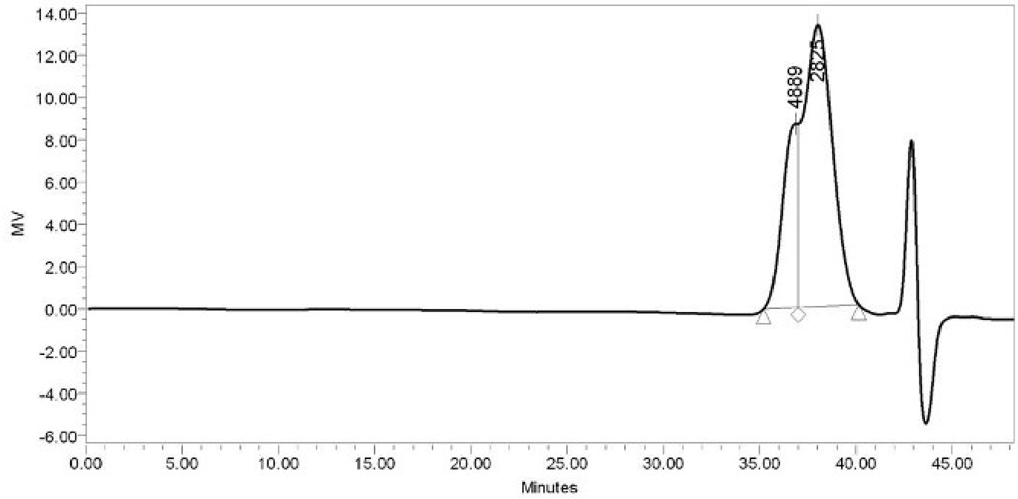
Figure S38 GPC trace of purified product P(PA-*alt*-SO) copolymer derived by the action of I_2 and *t*BuOK (I_2/*t*BuOK/PA/SO = 1:1:100:400), (entry 10, Table 2).



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Poly dispersity	MW Marker 1	MW Marker 2
1		5438	5645	5084	5885	6159		1.037966		
2		2532	2748	2879	2942	3111		1.085162		

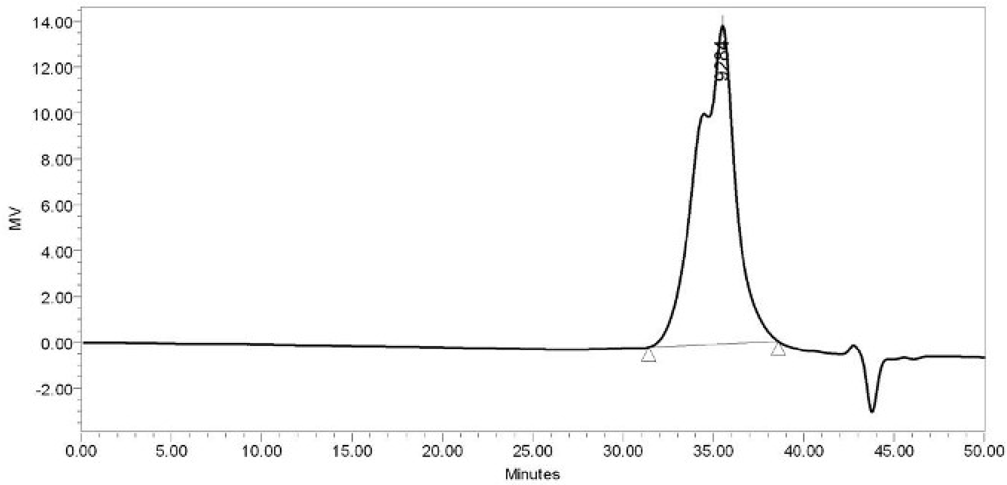
Figure S39 GPC trace of purified product P(PA-*alt*-SO) copolymer derived by the action of I_2 and *t*BuOK (I_2/*t*BuOK/PA/SO = 1:1:250:800), Table (entry 11, Table 2).



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Poly dispersity	MW Marker 1	MW Marker 2
1		5756	5919	4889	6105	6314		1.028316		
2		2616	2863	2825	3099	3313		1.094261		

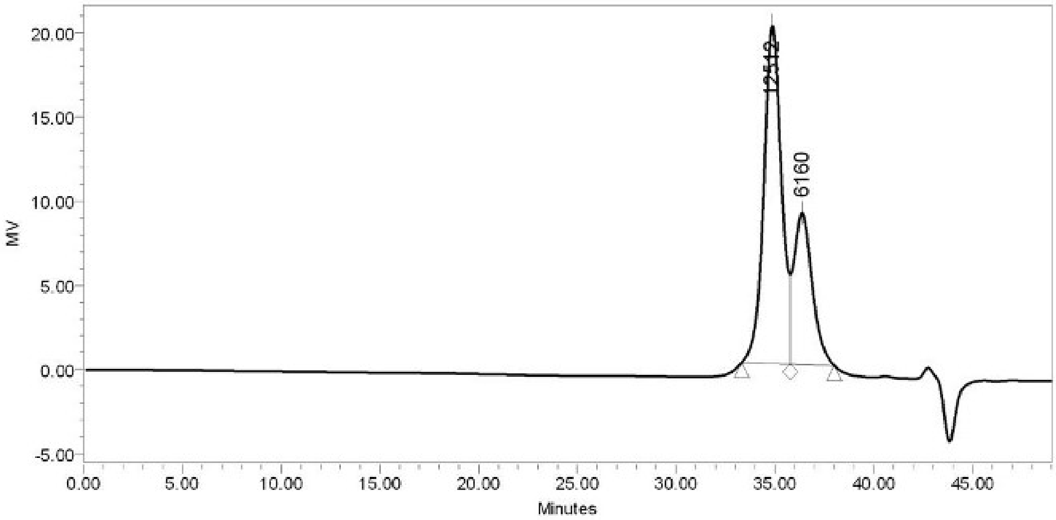
Figure S40 GPC trace of purified product P(PA-*alt*-SO) copolymer derived by the action of I_2 and *t*BuOK (I_2/*t*BuOK/PA/SO = 1:1:500:1200), (entry 12, Table 2).



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Poly dispersity	MW Marker 1	MW Marker 2
1		10030	13083	9284	17035	21762		1.304315		

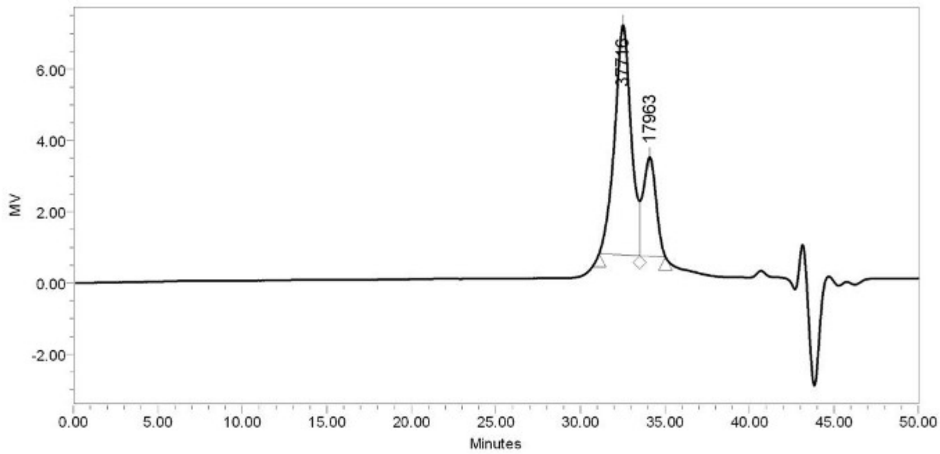
Figure S41 GPC trace of purified product P(PA-*alt*-PO) copolymer derived by the action of I_2 and *t*BuOK (I_2/*t*BuOK/PA/PO = 1:1:100:400), (entry 13, Table 2).



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		12177	12672	12512	13213	13802		1.040690		
2		5749	5989	6160	6210	6411		1.041783		

Figure S42 GPC trace of purified product P(PA-*alt*-PO) copolymer derived by the action of I_2 and *t*BuOK (I_2/*t*BuOK/PA/PO = 1:1:250:800), (entry 14, Table 2).



GPC Results

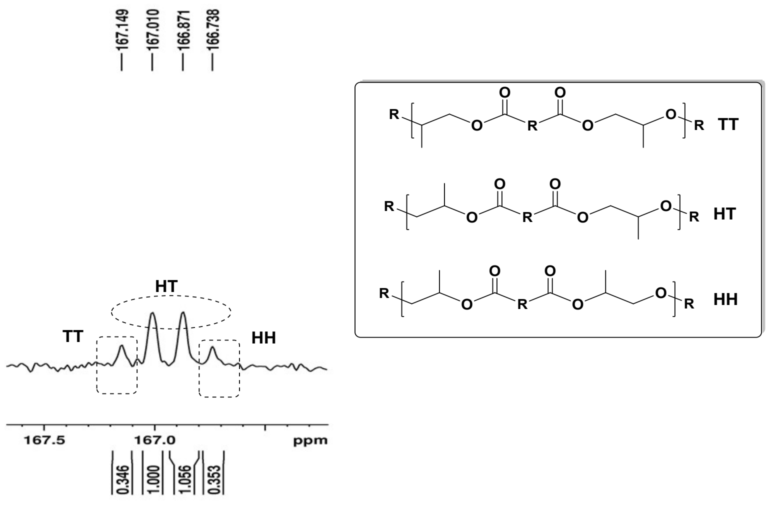
	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		37147	38959	37716	40907	42969		1.048774		
2		17805	18227	17963	18644	19049		1.023713		

Figure S43 GPC trace of purified product P(PA-*alt*-PO) copolymer derived by the action of I_2 and *t*BuOK (I_2/*t*BuOK/PA/PO = 1:1:500:1200), (entry 15, Table 2).

Table S1 ROAC of phthalic anhydride with cyclohexane oxide at various temperature and time using most active I_2/*t*BuOK catalyst.

Entry	Catalysts [a]	PA/CHO	T(°C)	t (h^{-1})	Conv. (%)[b]	%ester[c]	*M*n [d] (kDa)	PDI [d]
1	I_2:*t*BuOK	100:400	25	24	--	--	--	--
2	I_2:*t*BuOK	100:400	50	24	48	95	--	--
3	I_2:*t*BuOK	100:400	90	0.5	20	99	--	--
4	I_2:tBuOK	100:400	90	1	40	99	4.10(68)/1.90 (32) [e]	1.05/1.04
5	I_2:*t*BuOK	100:400	90	2	85	95	6.65(68)/3.0 (32) [e]	1.01/1.05
6	I_2:*t*BuOK	100:400	90	2.5	99	95	11.35(69)/5.07(31) [f]	1.02/1.05

[a] reaction conditions: I_2:tBuOK (1:1), solvent free. [*b*]Monomer conversion determined by ^{1}H NMR spectroscopy, [*c*] Calculated by ^{1}H NMR spectroscopy. [*d*] *M*n (GPC) measured by GPC at 40 °C in THF relative to polystyrene standards. [*e*] Bimodal distribution.



(PO-*alt*-PA)$_n$ ^{13}C - HH, HT TT

Figure S44 Regiostructures of polyesters: tail-to-tail (TT), head-to-tail (HT), and head-to-head (HH) junctions, P(PO-*alt*-PA)polymer.

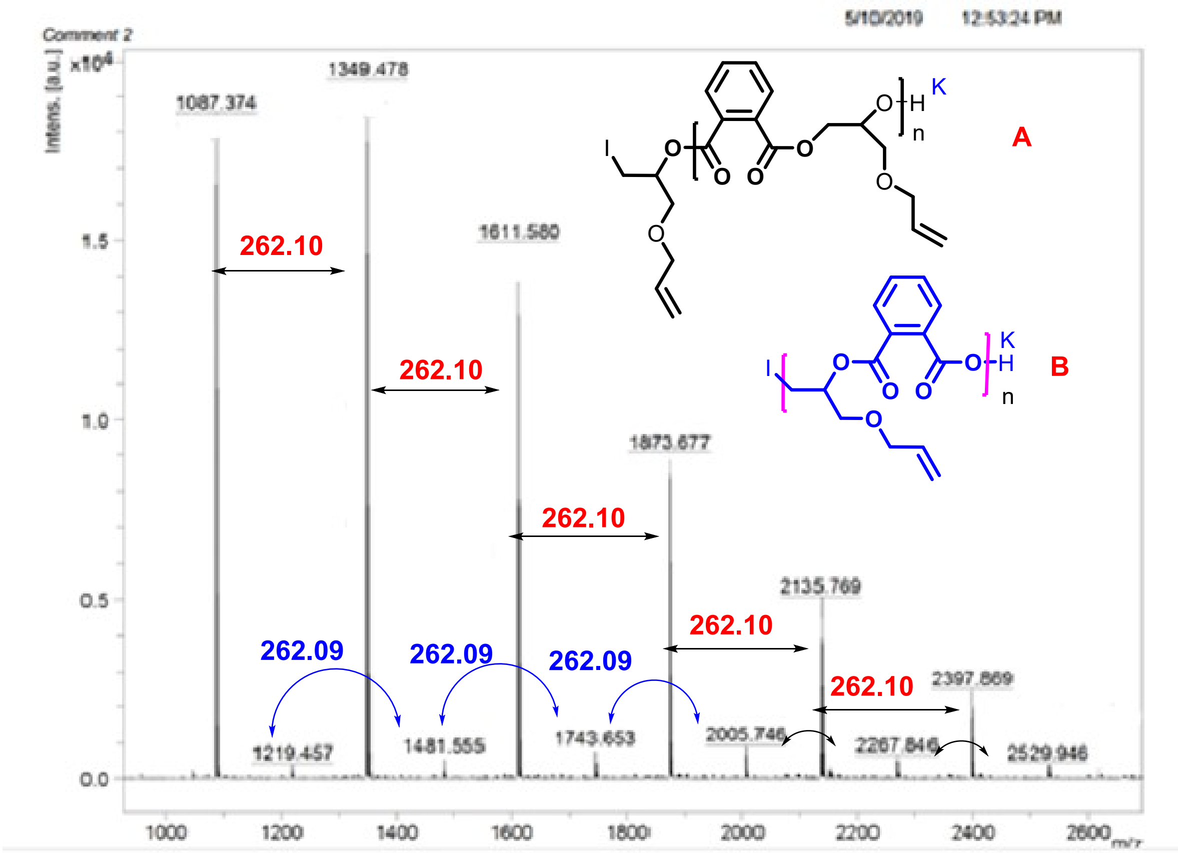


Figure S45 MALDI-TOF MS spectrum of the short P(PA-*alt*-AGE) precursor synthesized by the catalysis of I_2/*t*BuOK. The two (A and B) series shown as m/z = [126.90 (I) + 114.14 (AGE) + (262.1 × n) (PA + AGE) + 39.09 (K^+) +1.01 (H^+)] (n = 3 – 8) for A; m/z = [126.90 (I) + (262.1 × n) (PA + AGE) + 39.09 (K^+) + 1.01 (H^+)] (n = 4 – 9) for B. (n = number of repeating units). For example: distribution A= 1087.374 (experimental value) and 1088.408 (n= 3.08; calculated value). For distribution B = 1219.457 (experimental value) and 1220.642 (n= 4.02; calculated value).

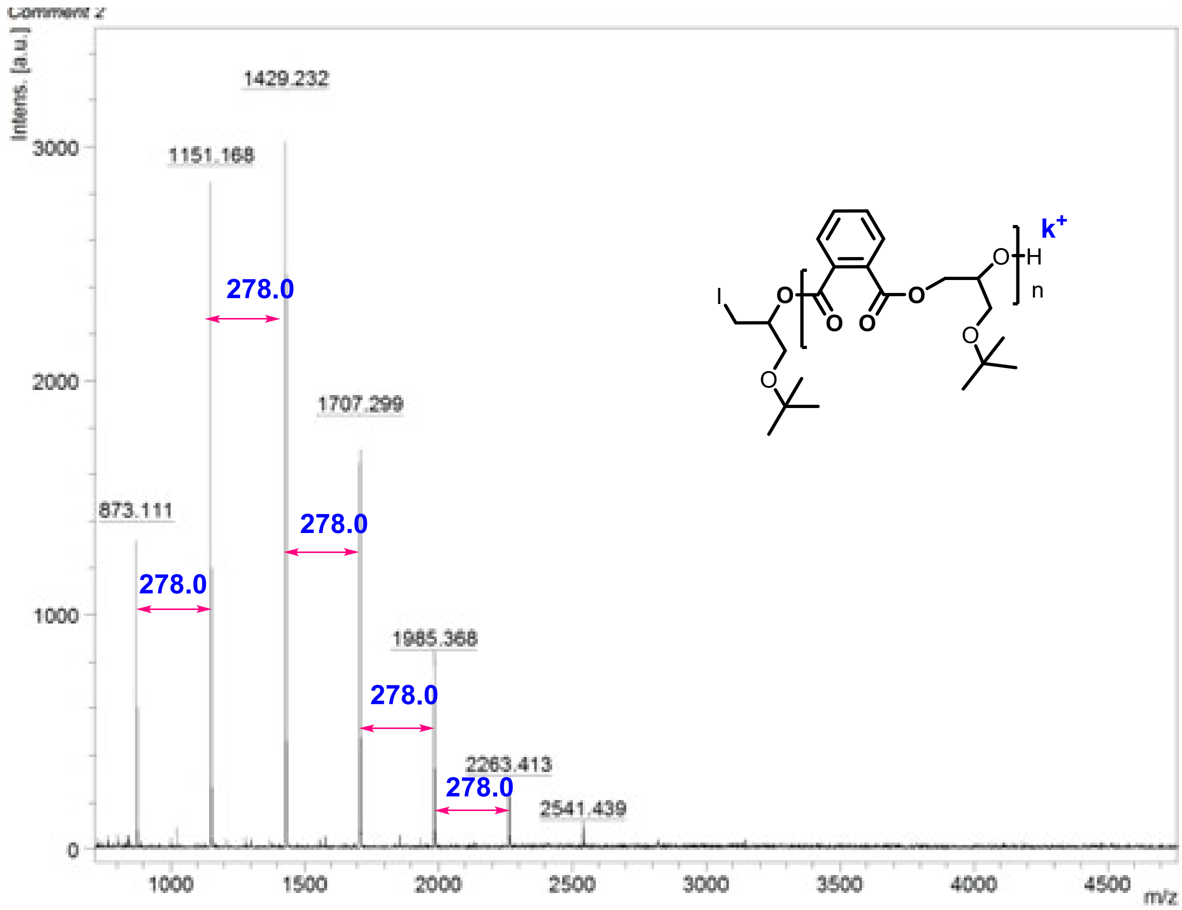


Figure S46 MALDI-TOF MS spectrum of the short P(PA-*alt*-*t*BGE) precursor synthesized by the catalysis of I_2/*t*BuOK. m/z = [126.90 (I) + 130.18 (*t*BGE) + (278.30 × n) (PA + *t*BGE) + 39.09 (K^+) + 1.01 (H+)] (n = 2–8). For example: 873.111 (experimental value) and 873.261 (n= 2.07; calculated value).

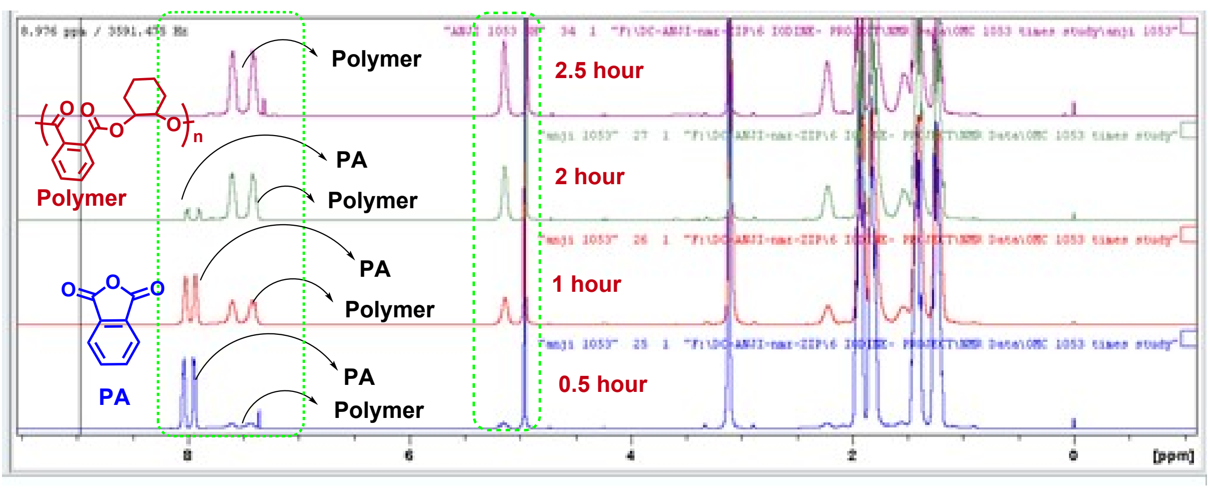


Figure S47 Overlap of [1]H NMR monitoring of copolymerization PA/CHO and catalysed by I_2/*t*BuOK catalyst system with the ratio I_2/*t*BuOK/PA/CHO = 1:1:100:400 (Entry 3 to 6, Table S1) with respect 0.5 h, 1 h, 2 h, and 2.5 h of reaction time.

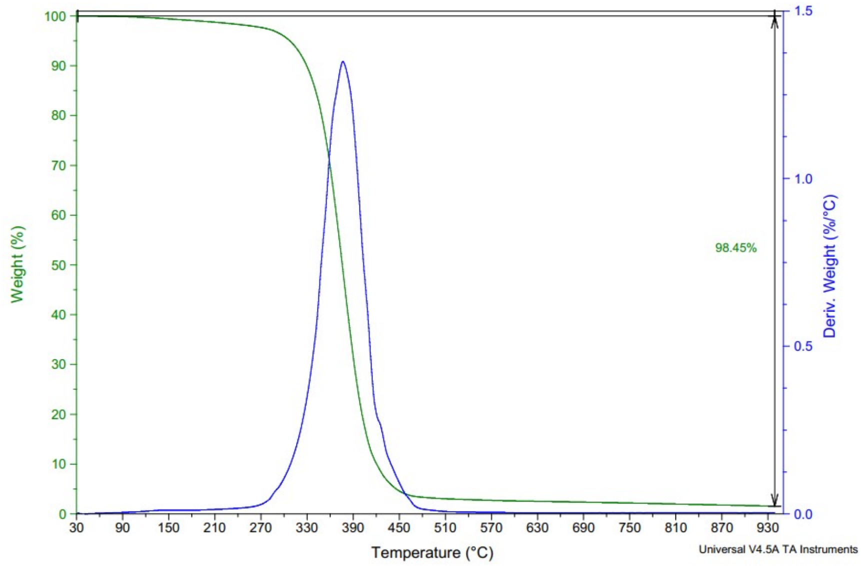


Figure S48 TGA and derivative thermogravimetry (DTG) curves of of P(PA-*alt*-AGE) copolymer derived by the action of I_2/*t*BuOK (I_2/*t*BuOK/PA/AGE = 1:1:100:400).

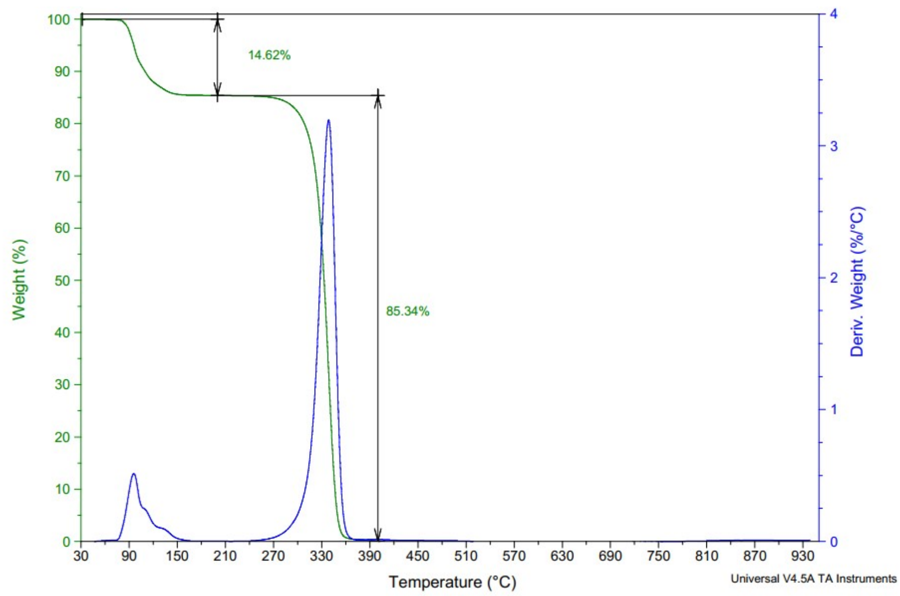


Figure S49 TGA and derivative thermogravimetry (DTG) curves of P(PA-*alt*-CHO) copolymer derived by the action of I_2/*t*BuOK (I_2/*t*BuOK/PA/CHO = 1:1:500:1200).

References

1 Y. Takeda, S. Okumura, S. Tone, I. Sasaki and S. Minakata, *Organic Letters*, 2012, **14**, 4874-4877.

2 D. D. Tanner, G. C. Gidley, N. Das, J. E. Rowe and A. Potter, *Journal of the American Chemical Society*, 1984, **106**, 5261-5267.