Electronic Supplementary Material (ESI) for Green Chemistry.
This journal is © The Royal Society of Chemistry 2019

Supporting Information

Fully Alternating Sustainable Polyesters from Epoxides and Cyclic Anhydrides：Economical and Metal-free Dual Catalysis

Experimental Procedures

Materials

All chemicals were used as received unless otherwise stated. Cyclohexane oxide (CHO), propene oxide (PO) and 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU) were refluxed over CaH for 24 h and vacuum-distilled prio to use. Phthalic anhydride (*J&K*, 98%), maleic anhydride (TCI, >99%) and succinic anhydride (*J&K*, 99%) were purified by sublimation. Triclocarban (TCI, 98%)，N,N'-diphenylurea (TCI,98%)，N,N'-dicycl- ohexylurea (TCI, 98%)，1-cyclohexyl-3-phenyl-urea (Fuyuan Technology company, 98%), 1-cyclohexyl-3-phenyl-thiourea (*J&K*, 98%), bis(triphenylphosphine)iminium chloride([PPN]Cl) (Alfa, 97%), tetrabutylammonium bromide (NBu4Br) (Alfa, 98%) and 4-dimethylaminopyridine (DMAP) (Alfa, 99%) were used as received.

Measurements

^{1}H NMR and ^{13}C NMR spectra were obtained on a Bruker DRX-500 MHz NMR spectrometer using $CDCl_3$ or DMSO-d_6 as solvent. Matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF MS) were recorded on Bruker ultrafleXtreme type. The polymer sample in THF (10 mg/mL), *trans*-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) in

THF as matrix (10 mg/mL) and sodium trifluoroacetate in methanol (1 mg/mL) were mixed in a 10:1:1 volume ratio, and then 1 μL of mixed solution was spotted onto the sample plate before being air-dried. Molecular weight determinations were carried out using a waters gel permeation chromatography (GPC) system with chloroform as eluent. The GPC system was calibrated by a series of polystyrene standards with polydispersity of 1.02. The glass-transition temperatures (T_g) were measured by a differential scanning calorimeter (DSC, Netzsch Model 204). The samples were firstly heated at a heating rate of 10 ^{o}C/min and then cooled at a cooling rate of 10 ^{o}C/ min by liquid nitrogen, followed by second heating.

General Procedure of Polymerization

Polymerizations were performed in a 25 mL vial using an external heating bath. The vial was charged with a predetermined amount of (thio)urea (0.05mmol, 1 equiv), organic base (0.05mmol, 1 equiv), epoxide (10mmol, 200 equiv) and anhydride (5mmol, 100 equiv), which were kept stirring for 5 min at room temperature in an N_2-filled glovebox. The vial was sealed, taken out of glovebox, and then immersed in the heating bath under the predetermined temperature. After equilibration at the desired polymerization temperature, the polymerization started. After a desired period of time, the vial was removed from heat block and a 0.2 mL of aliquot was taken from the reaction mixture and prepared for ^{1}H NMR analysis. Then the mixture was dissolved in $CHCl_3$ and precipitated into 10-fold excess of methanol or hexane, filtered, washed with methanol or hexane to remove unreacted monomer, and dried in a vacuum oven at room temperature to a constant weight.

Table S1. Copolymerization of CHO with PA Catalyzed by U1/PPNCl under different conditions.[a]

entry	LA/LB/ CHO/PA	t /min	PA conv./%[b]	ester /%[c]	Mn kDa[d]	PDI[d]
1	1:1:500:100	15	100	98	9.4	1.21
2	1:1:200:100	15	100	99	8.9	1.24
3	1:1:100:100	15	63	98	5.3	1.28
4[e]	1:1:100:100	60	84	98	4.6	1.26
5[f]	1:1:200:100	60	95	99	5.2	1.29
6	1:1:500:250	40	100	98	15.9	1.28
7[g]	1:1:200:-	180	CHO:0.8%			

[a] The copolymerizations were carried out at 110 °C in bulk, unless otherwise mentioned. [b] PA conversion was determined by ^{1}H NMR. [c] Ester linkage was determined via ^{1}H NMR by integrating ester and ether signals. [d] M_n and PDI were determined by GPC. [e] Performed in xylene, with a PA concentration of 5 mol/L. [f] At 80 ^{o}C. [g] Homopolymerization of CHO.

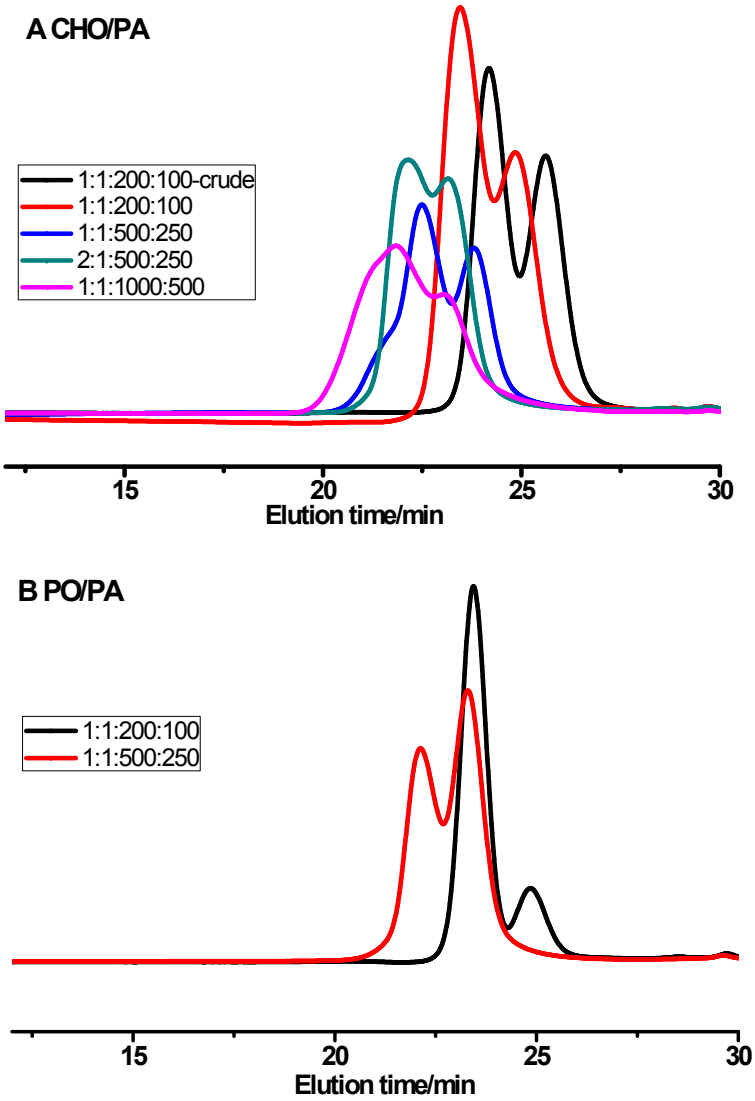


Figure S1 Representative GPC curves of resultant poly(CHO-*alt*-PA) A: a) 1:1:200:100-crude, M_n = 8.9 kDa (Table S1 entry 2); b) 1:1:200:100, M_n =13.0 kDa (Table 1 entry 11); c) 1:1:500:250, M_n =22.5 kDa (Table 1 entry 12); d) 2:1:500:250, M_n =26.2 kDa (Table 1 entry 13); e) 1:1:1000:500, M_n =34.6 kDa (Table 1 entry 14); poly(PO-*alt*-PA) B: a) 1:1:200:100, M_n = 14.1 kDa (Table 2 entry 1); b) 1:1:500:250, M_n =23.5 kDa (Table 2 entry 2);

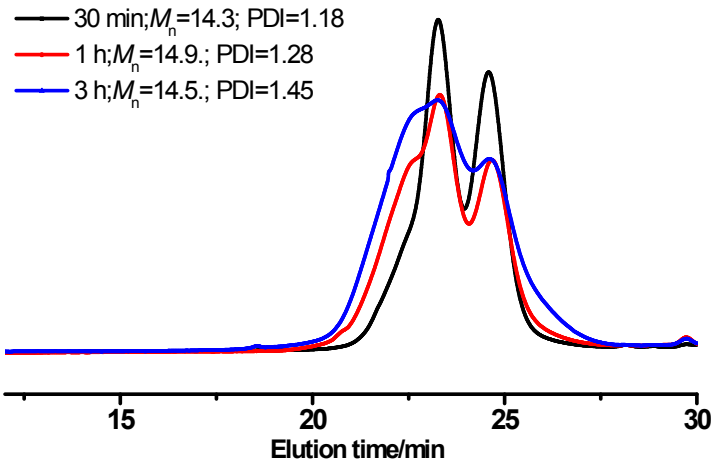
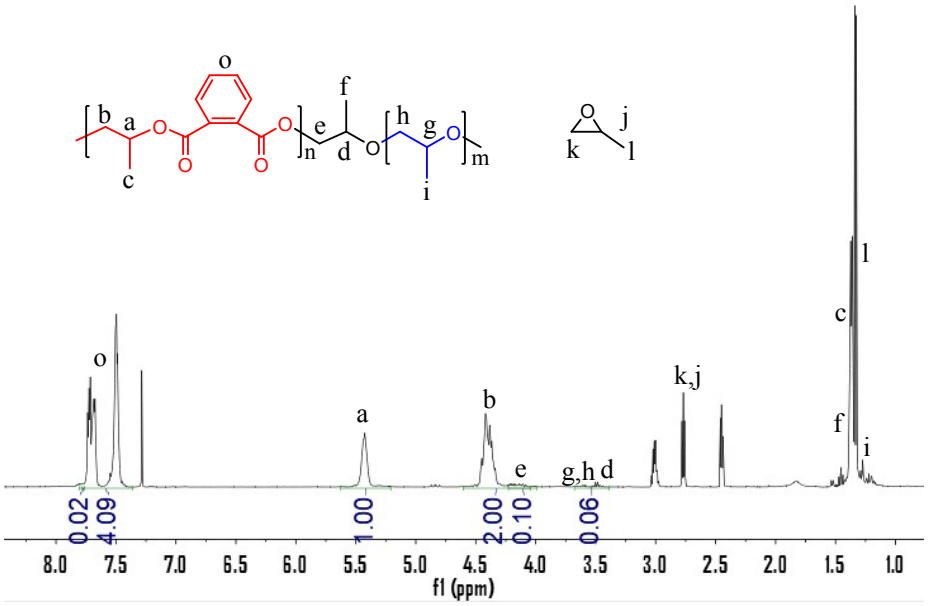


Figure S2 GPC curves of resultant poly(CHO-*alt*-PA) performed at U1/PPNCl/ CHO/PA = 1:1:200:100 in bulk at different reaction time.



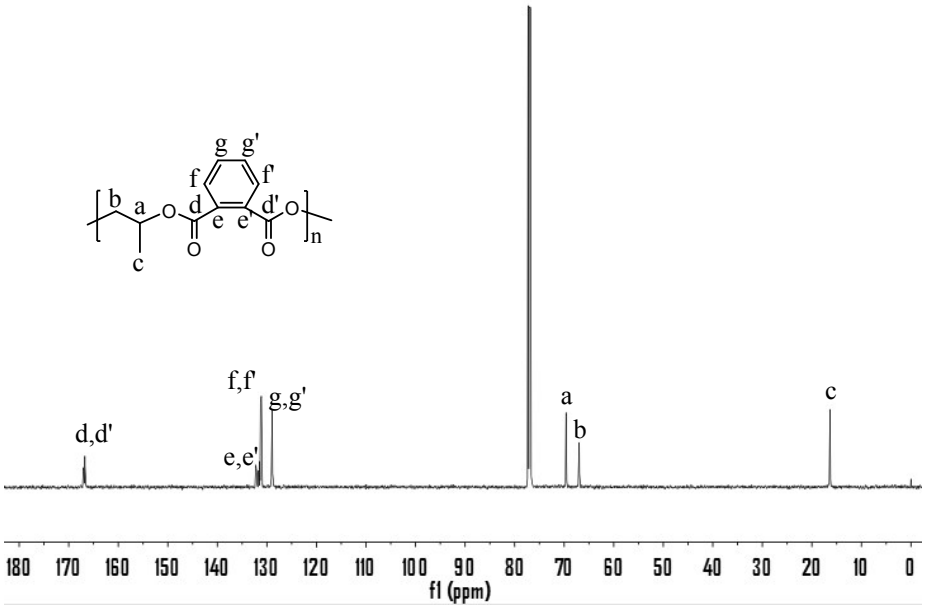
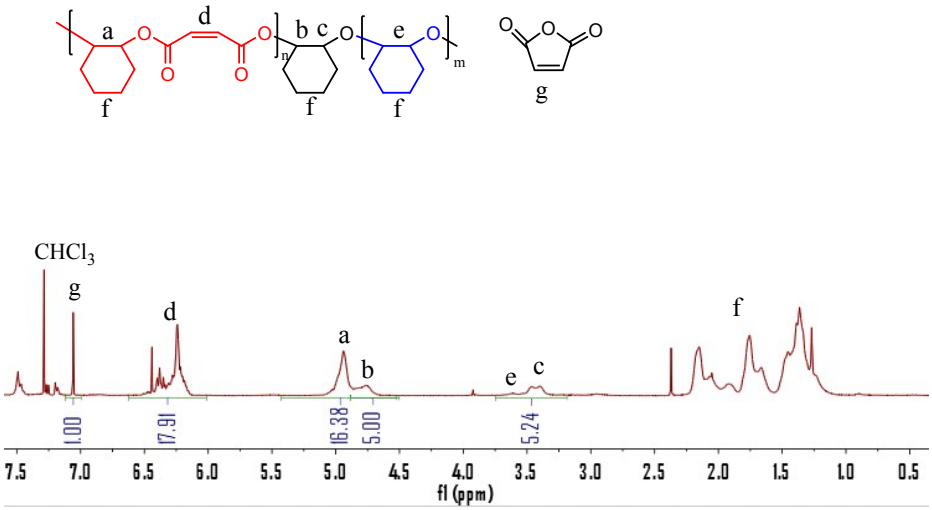


Figure S3 ^{1}H NMR and ^{13}C NMR spectrum and ^{13}C NMR spectrum of the poly(PO-*alt*-PA) in $CDCl_3$.



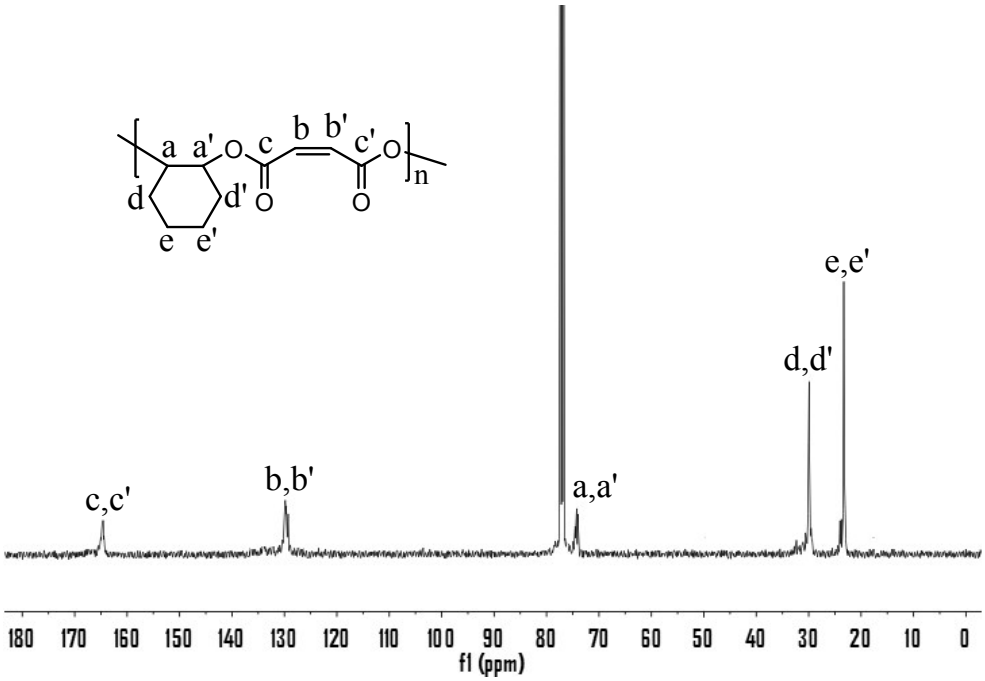
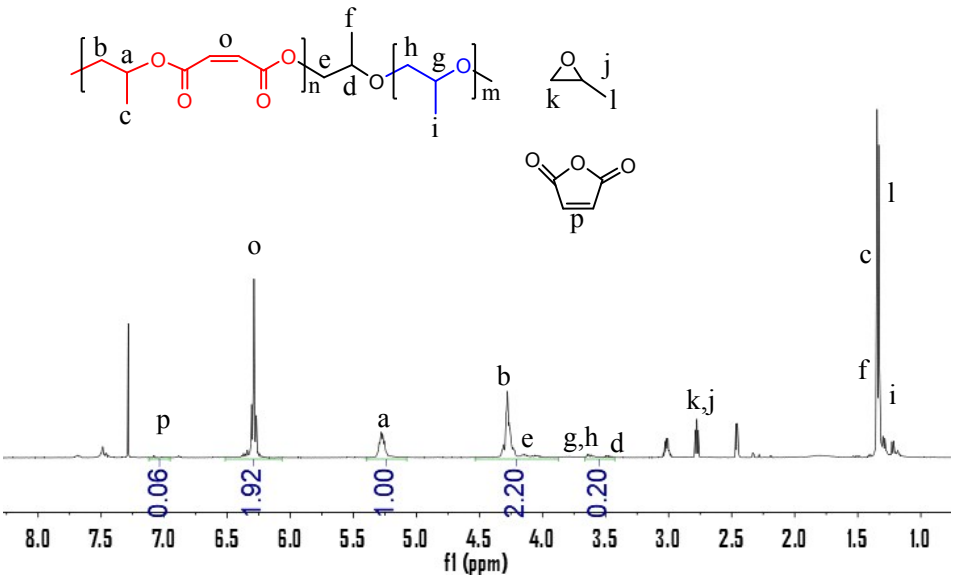


Figure S4 ^{1}H NMR and ^{13}C NMR spectrum of the poly(CHO-*alt*-MA) produced in xylene with 2% maleic acid in $CDCl_3$.



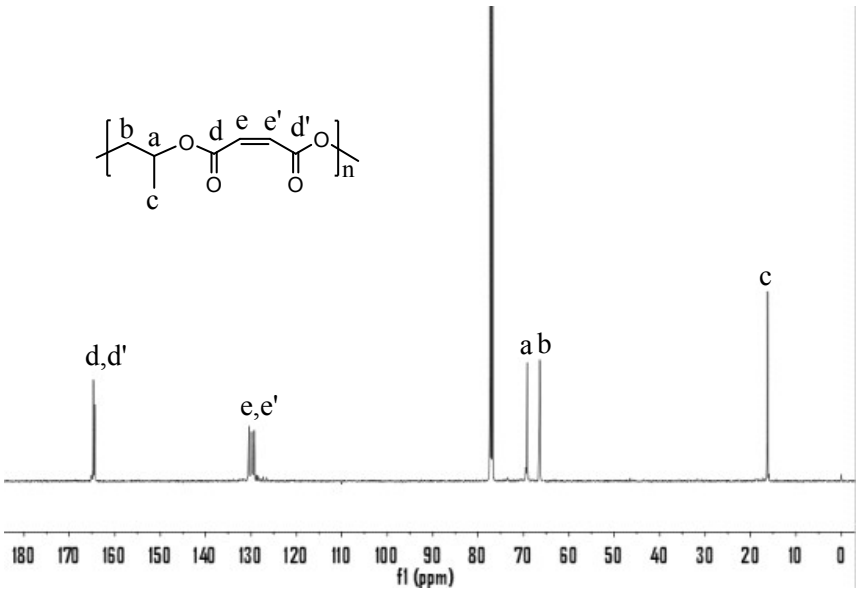
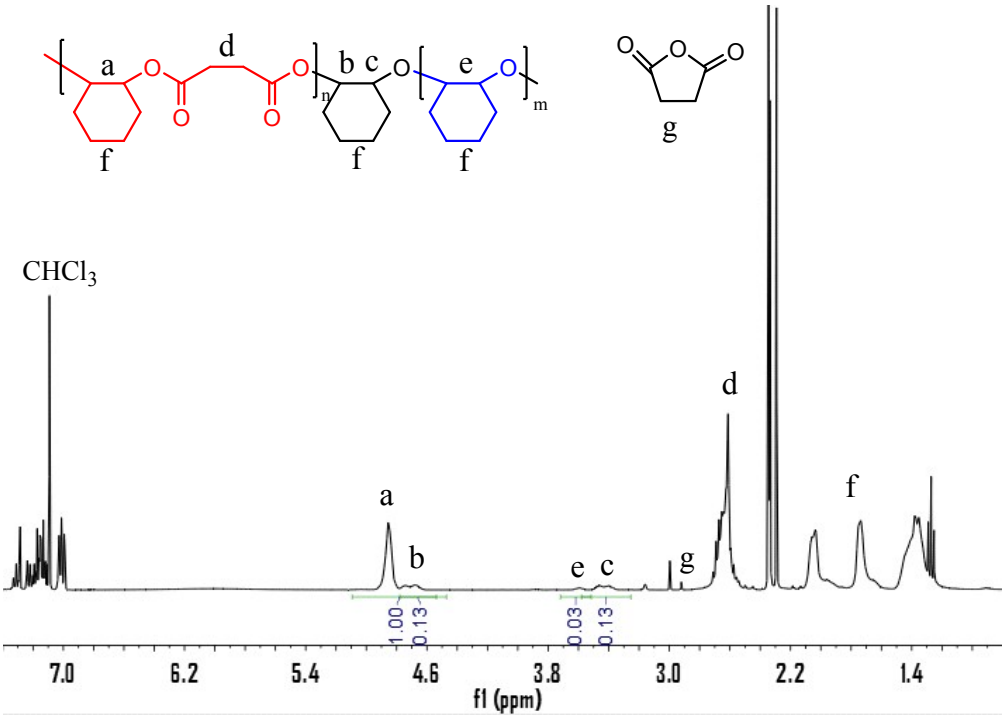


Figure S5 ^{1}H NMR and ^{13}C NMR spectrum and ^{13}C NMR spectrum of the poly(PO-*alt*-MA) in $CDCl_3$.



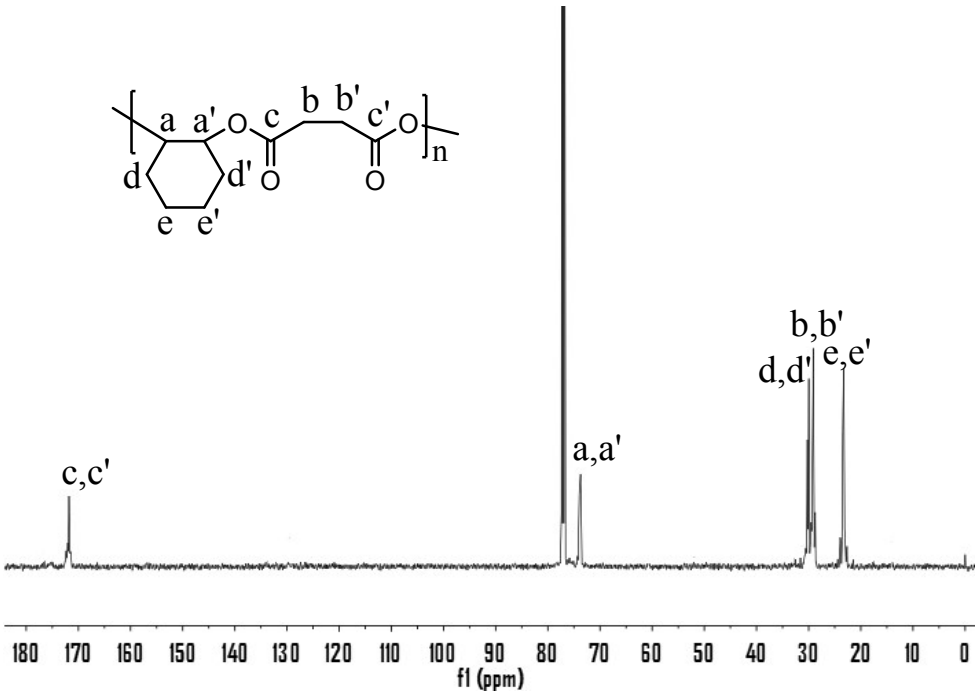
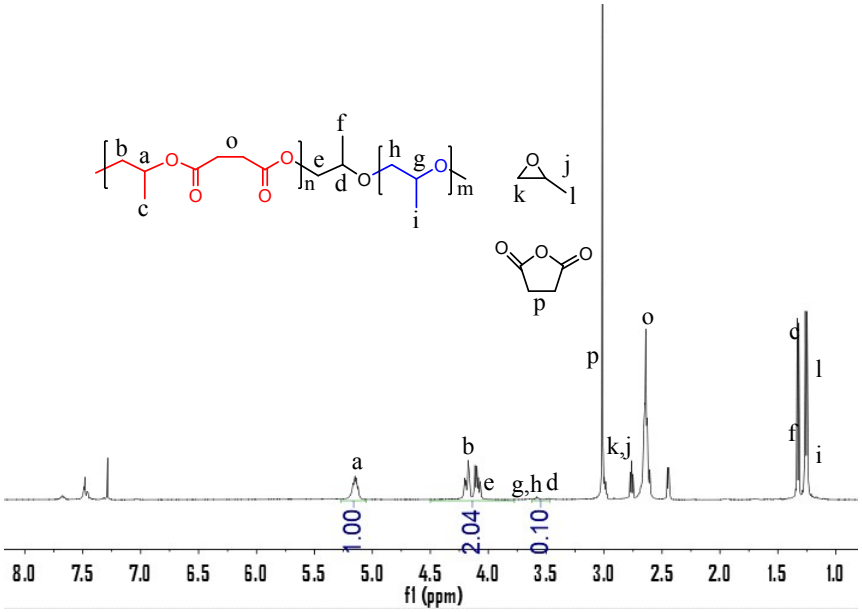


Figure S6 ^{1}H NMR and ^{13}C NMR spectrum and ^{13}C NMR spectrum of the poly(CHO-*alt*-SA) in $CDCl_3$.



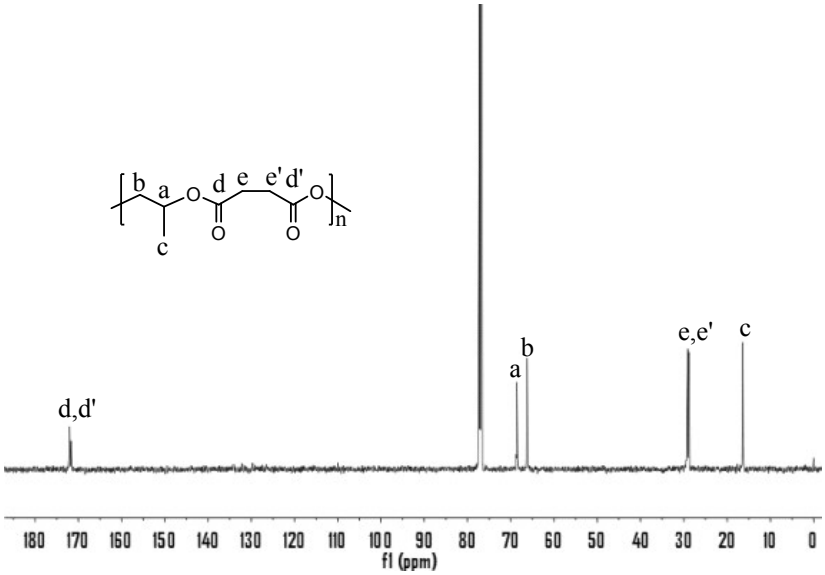
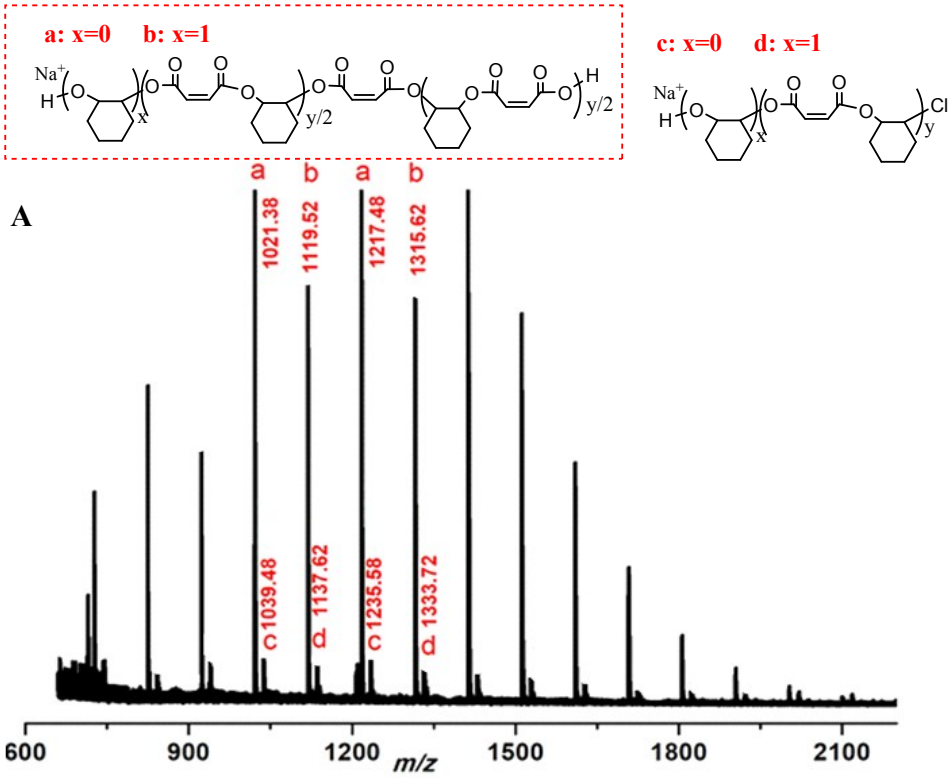


Figure S7 ^{1}H NMR and ^{13}C NMR spectrum and ^{13}C NMR spectrum of the poly(PO-*alt*-SA) in $CDCl_3$.



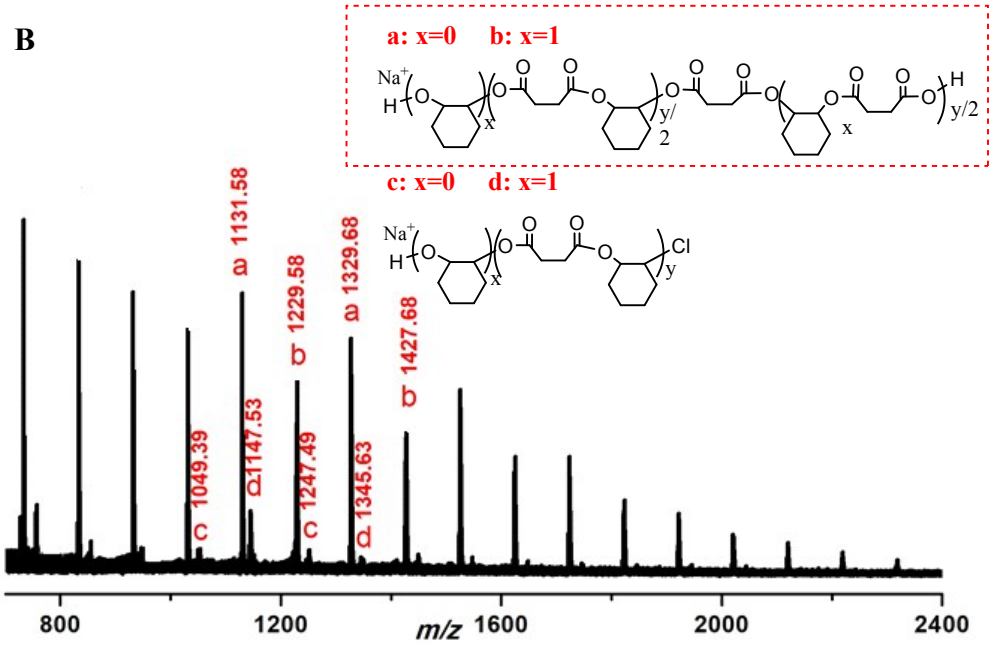


Figure S8 MALDI-TOF mass spectra of poly(CHO-*alt*-MA) produced in xylene with 2% maleic acid (A); poly(CHO-*alt*-SA) produced in xylene with 2% succinic acid (B).

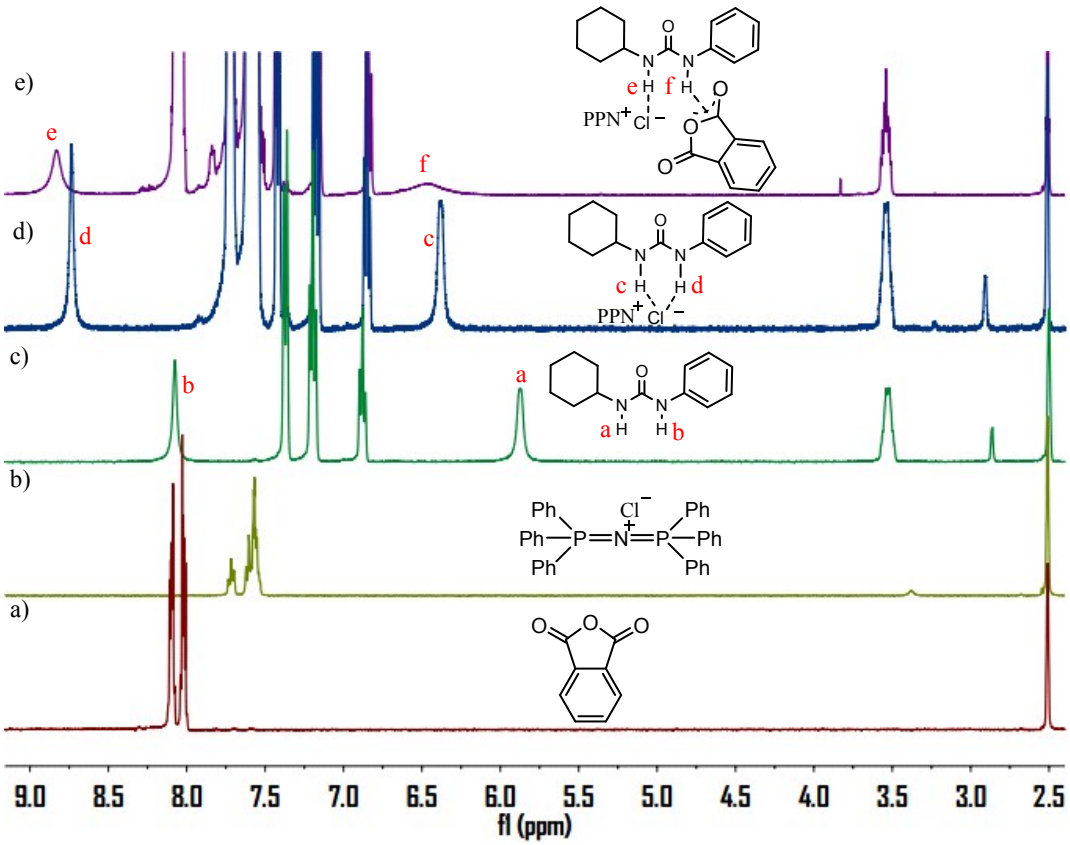


Figure S9 ^{1}H NMR spectra of a) PA; b) PPNCl; c)U2; d) U2/PPNCl (1:1); e)

U2/PPNCl/ PA (1:1:2) in DMSO-d_6 at 110 °C.

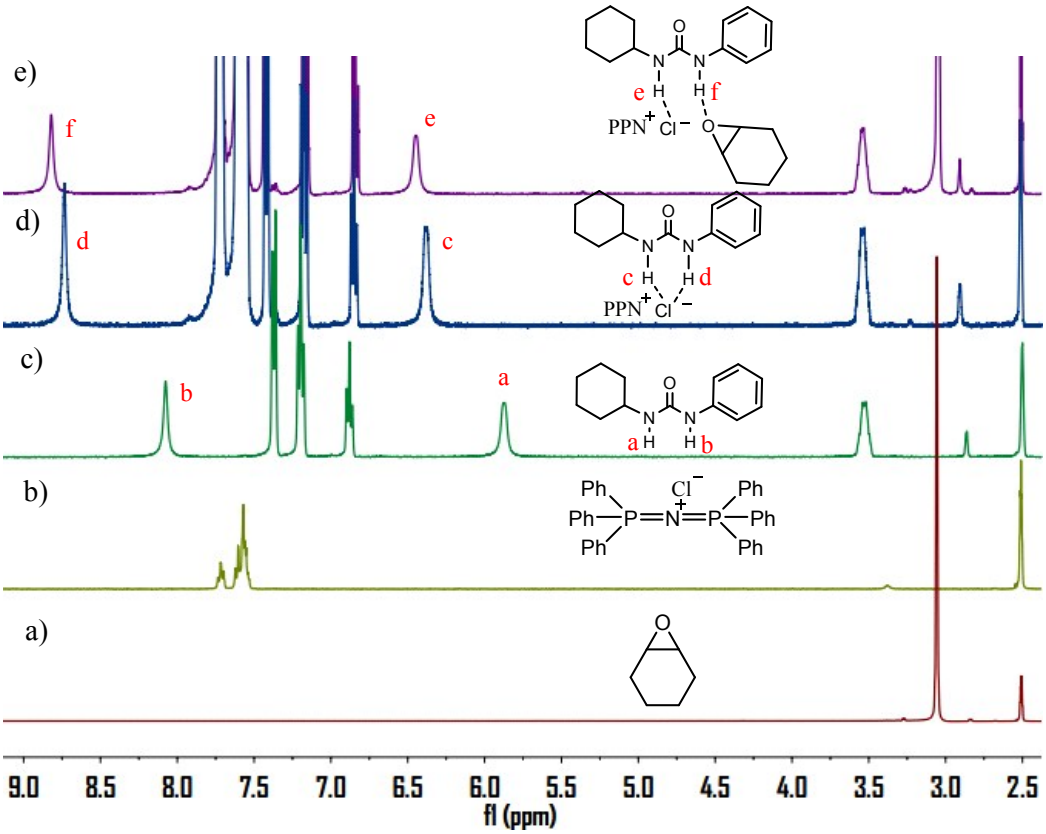


Figure S10 ^{1}H NMR spectra of a) CHO; b) PPNCl; c)U2; d) U2/PPNCl (1:1); e) U2/PPNCl/ CHO (1:1:2) in DMSO-d_6 at 110 °C.

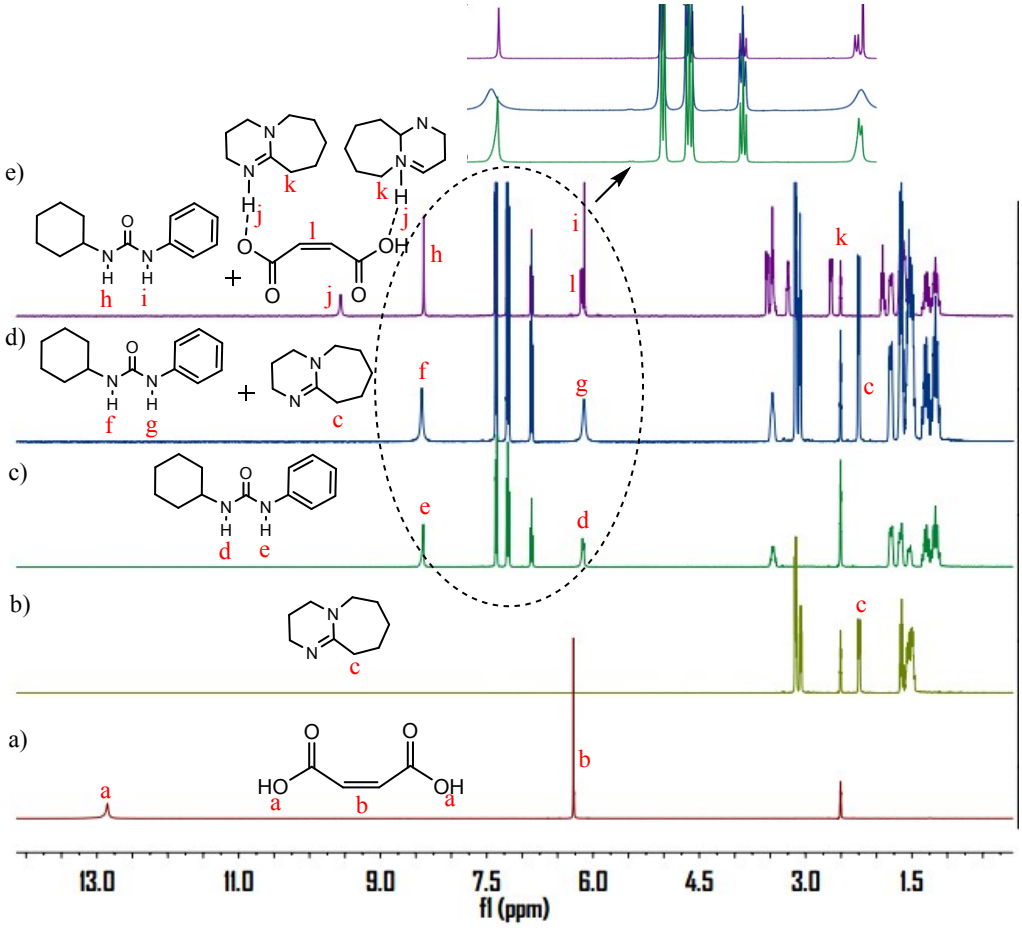


Figure S11 ^{1}H NMR spectra of a) maleic acid; b) DBU; c) U2; d) U2/DBU (1:2); e) U2/DBU/maleic acid (1:2:1) in DMSO-d_6.