SUPPLEMENTARY INFORMATION

Borane catalyzed polymerization and depolymerization reactions controlled by Lewis acid strength

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Experimental Procedures

General experimental conditions. Unless otherwise stated, all experimental procedures were completed using an MBraun Labmaster glove box or standard Schlenk techniques under a nitrogen atmosphere. Cyclohexene oxide, vinyl cyclohexene oxide, limonene oxide and poly(propylene carbonate) were purchased from Sigma Aldrich. All epoxides were dried over CaH_2 and distilled under vacuum prior to use. Bis(triphenylphosphine)iminium chloride (PPNCl), phthalic anhydride and cis-4-cyclohexene-1,2-dicarboxylic anhydride was purchased from Alfa Aesar. Anhydrides were recrystallized from chloroform prior to use. All solvents were dried and degassed using an MBraun Manual Solvent Purification system. Triphenylborane was purchased from Strem Chemicals and used as received. Caution should be taken when operating high pressure equipment.

Instrumentation. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer at 25 °C. All NMR spectra were obtained in $CDCl_3$ purchased from Cambridge Isotope Laboratories, Inc. ^{1}H and ^{13}C NMR spectra were referenced using the residual proton and ^{13}C resonances of the solvent. All cyclization and copolymerization reactions were carried out in a 100 mL stainless steel reactor vessel (Parr Instrument Company) equipped with a silicon sensor (SiComp), mechanical stirrer and a heating mantel. For kinetic measurements, the Si sensor was connected to a ReactIR 15 base unit (Mettler-Toledo) through a DS silver-halide Fiber-to-Sentinel conduit. The vessel was baked at 100 °C under vacuum overnight prior to any experiment. Gel permeation chromatography (GPC) analysis was performed on a set-up consisting of a miniDawn TREOS light scattering detector, a Viscostar-II viscometer, and an Optilab T-rEX differential refractive index detector (Wyatt Technology) connected to an Agilent Infinity 1260 HPLC system equipped with two Phenogel 103 Å 300 × 4.60 mm columns with THF as eluent. Samples were prepared in THF at a concentration of 4 mg mL^{-1}, filtered through a 0.2 μm syringe filter, and analyzed at a flow rate of 0.3 mL min^{-1} at 25 °C. The values of dn/dc were calculated online (columns detached) assuming 100% mass recovery using the Astra 6 software package (Wyatt Technologies). Glass transition temperatures (T_g) were obtained on a Mettler Toledo DSC Stare system equipped with a Julabo FT 100 immersion cooling system for low temperatures (-100 °C +20 °C). Samples were weighed into 40 μL aluminum pans and exposed to 3 heating cycles from 0 to 200 °C at a rate of 10 °C min^{-1}, with a hold time of 2 min at both 0 °C and 200 °C in each cycle. The reported Tg values were determined using data from the third heating cycle. Polymer end-group analysis was determined using a Bruker ultrafleXtreme MALDI TOF-TOF in positive-ion mode. Samples were prepared in a 1:3:20 sodium trifluoroacetate (NaTFA): 2,5-dihydroxybenzoic acid (DHB): sample ratio in a mixture of methanol and THF. 0.5 μL was spotted on the plate for analysis. Data was processed using Polymerix software

Ring-opening alternating copolymerization of epoxides and anhydrides. BPh_3 (5 mg, 2.1 x 10^{-3} mmol), PPNCl (11.6 mg, 2.0 x 10^{-2} mmol) and the appropriate anhydride (100 equivalents to BPh3) were combined in neat epoxide (1.00 g, 500 equivalents) and stirred under N_2 with heating for the desired time. NMR aliquots were taken and the bulk

sample was exposed to air, dissolved in dichloromethane and precipitated in cold acidified methanol. The solvent was decanted and product dried at 60 °C in a vacuum oven overnight.

Controlled block polyester synthesis. BPh_3 (5 mg, 2.1 x 10^{-3} mmol), PPNCl (11.6 mg, 2.0 x 10^{-2} mmol) and the appropriate anhydride (100 equivalents to BPh_3) were combined in neat epoxide (1.00 g, 500 equivalents) and stirred under N_2 with heating for the desired time. Once full consumption of anhydride was reached, the second anhydride was added and allowed to react. NMR aliquots were taken and the bulk sample was exposed to air, dissolved in dichloromethane and precipitated in cold acidified methanol. The solvent was decanted and product dried at 60 °C in a vacuum oven overnight.

One-pot block copolymerization of epoxides, anhydrides and CO_2. Appropriate amounts of BPh_3 (31 mg, 0.13 mmol) and PPNCl (73 mg, 0.13 mmol) and anhydride (5.2 mmol, 40 equivalents) were combined in 3 mL of dichloromethane and the solution was injected into the pressure vessel. The dichloromethane was removed under vacuum and cyclohexene oxide (2.5 g, 26 mmol) was injected into the pressure vessel. The vessel was then heated to 100 °C for 30 min allowing the alternating copolymerization of anhydride and epoxide to occur. The vessel was then cooled back to room temperature, pressurized to 40 bar CO_2 and heated to 60 °C for 24 hours. The vessel was then cooled, the mixture was dissolved in dichloromethane and polymer precipitated in cold acidified methanol.

Penta(fluorophenyl)borane catalyzed degradation experiments. 100 mg of polymer was combined with BCF (5.1 mg, 1.0 x 10^{-2} mmol, 5 mol%) in 3 mL of dichloromethane and sealed in a microwave vial inside a glovebox. The vial was taken out of the box and heated to 130 °C for 3 hours. The vial was then cooled, opened, a crude sample was taken for ^{1}H NMR analysis and the resulting mixture was concentrated to 1 mL and added to cold acidified methanol to precipitate any remaining polymer.

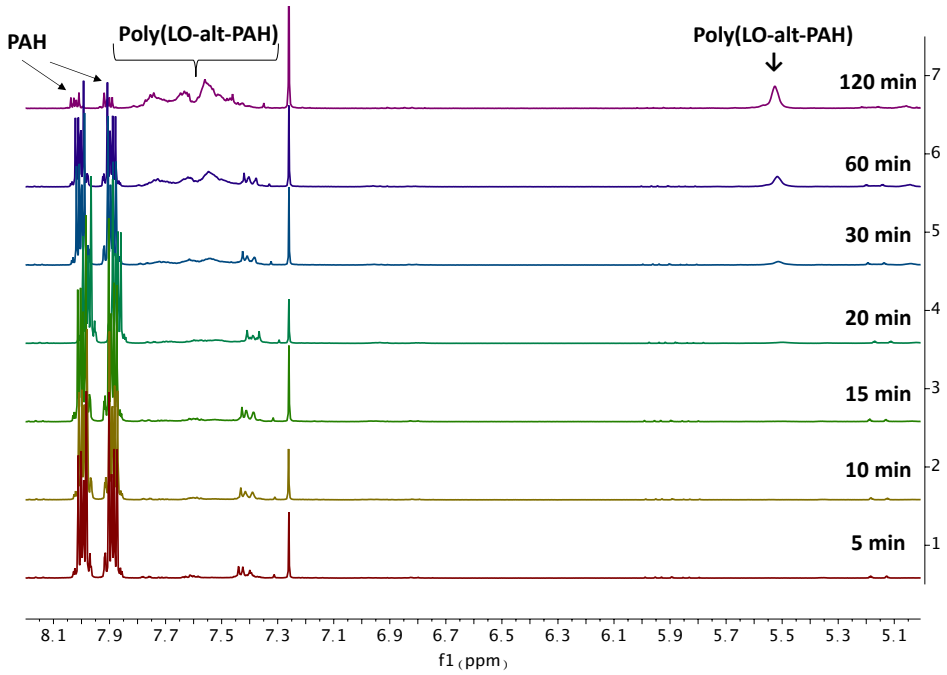

Figure S1. Stacked ^{1}H NMR (300 MHz, 298 K, $CDCl_3$) spectra of alternating ring-opening polymerization of LO and PAH (Table 1, entry 1)

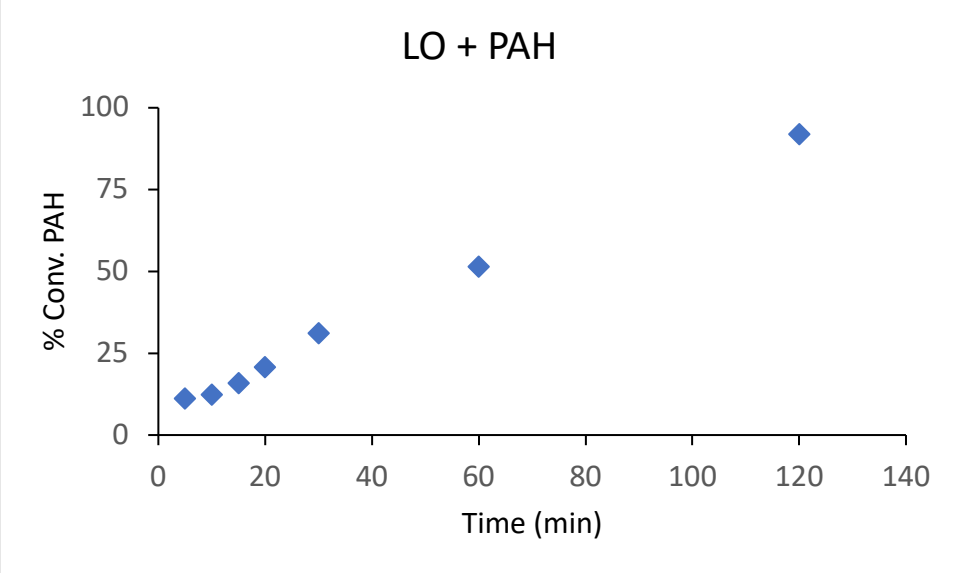

Figure S2. Conversion vs. time plot of alternating ring-opening polymerization of LO and PAH (Table 1, entry 1)

Table S1. Anhydride conversion and GPC data for alternating ring-opening polymerization of LO and PAH (Table 1, entry 1)

Aliquot Time (min)	% Conv. PAH[a]	M_n (g/mol)[b]	$Đ$[b]
5	11.2	-	-
10	12.3	-	-
15	15.8	-	-
20	20.8	-	-
30	31.2	-	-
60	51.5	4 085	1.30
120	91.9	6 051	1.16

[a]Determined from ^{1}H NMR [b]Đ, dispersity = Mw/Mn. Determined in THF by GPC equipped with a multiangle light-scattering detector. GPC data not obtained for lower conversions due to inability to isolate material

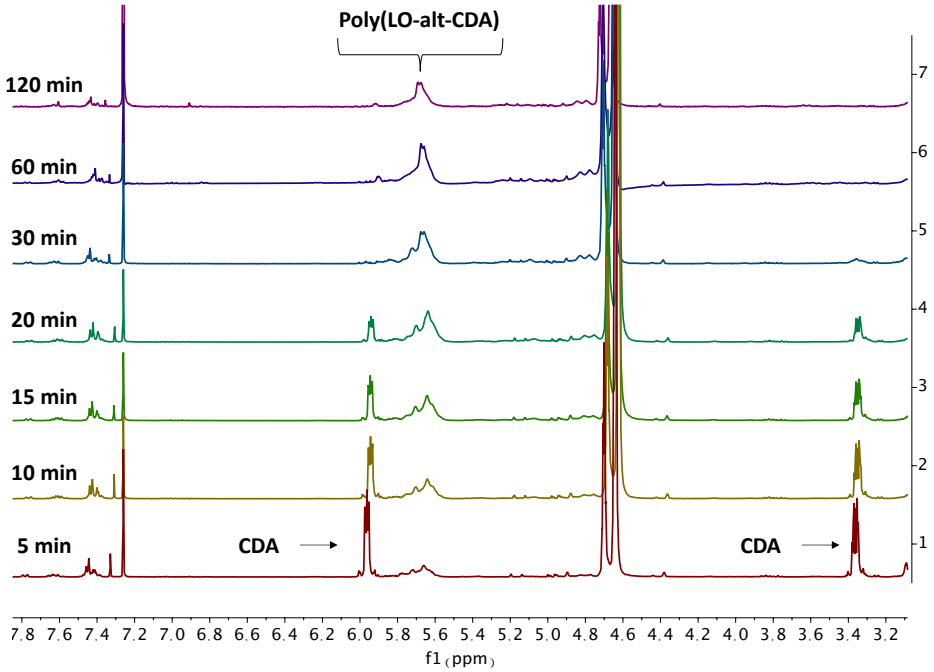

Figure S3. Stacked ^{1}H NMR (300 MHz, 298 K, $CDCl_3$) spectra of alternating ring-opening polymerization of LO and CDA (Table 1, entry 2)

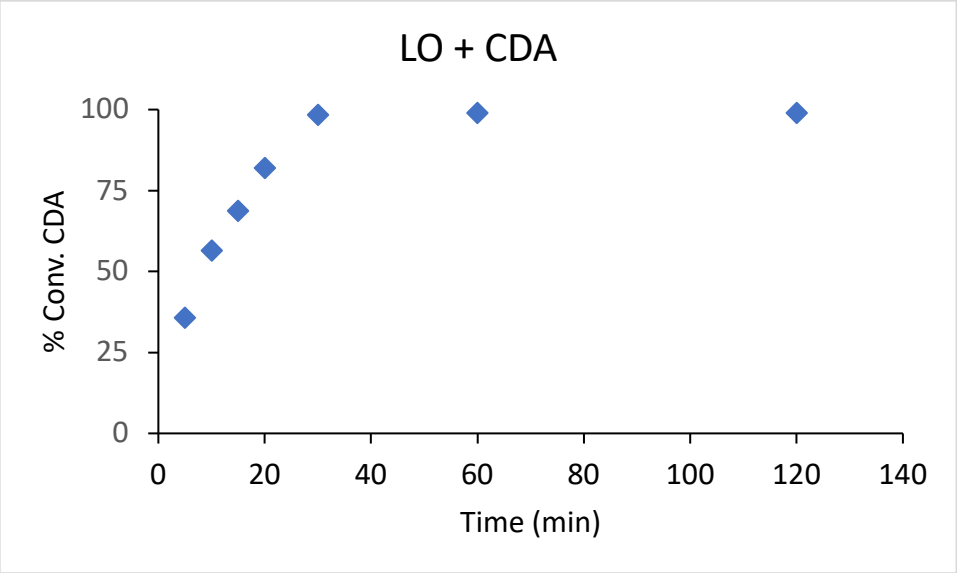

Figure S4. Conversion vs. time plot of alternating ring-opening polymerization of LO and CDA (Table 1, entry 2)

Table S2. Anhydride conversion and GPC data for alternating ring-opening polymerization of LO and CDA (Table 1, entry 2)

Aliquot Time (min)	% Conv. CDA[a]	M_n (g/mol)[b]	$Đ$[b]
5	35.7	420	1.05
10	56.5	717	1.04
15	68.7	852	1.04
20	81.9	937	1.03
30	98.4	924	1.06
60	99	1 118	1.08
120	99	2 437	1.09

[a]Determined from ^{1}H NMR [b]Đ, dispersity = Mw/Mn. Determined in THF by GPC equipped with a multiangle light-scattering detector.

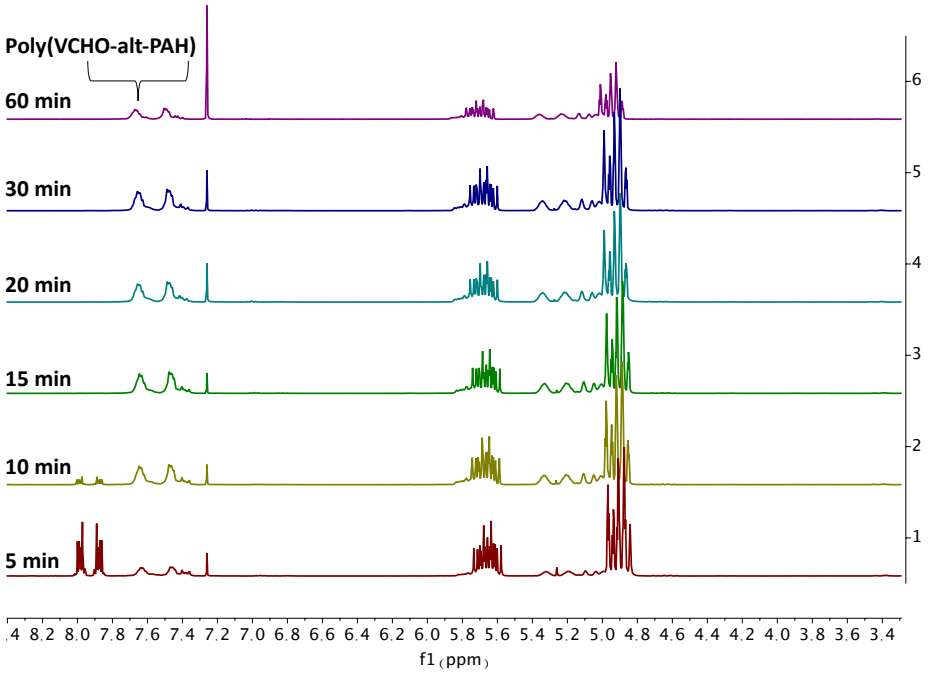

Figure S5. Stacked ^{1}H NMR (300 MHz, 298 K, $CDCl_3$) spectra of controlled alternating ring-opening polymerization of VCHO and PAH (Table 1, entry 3)

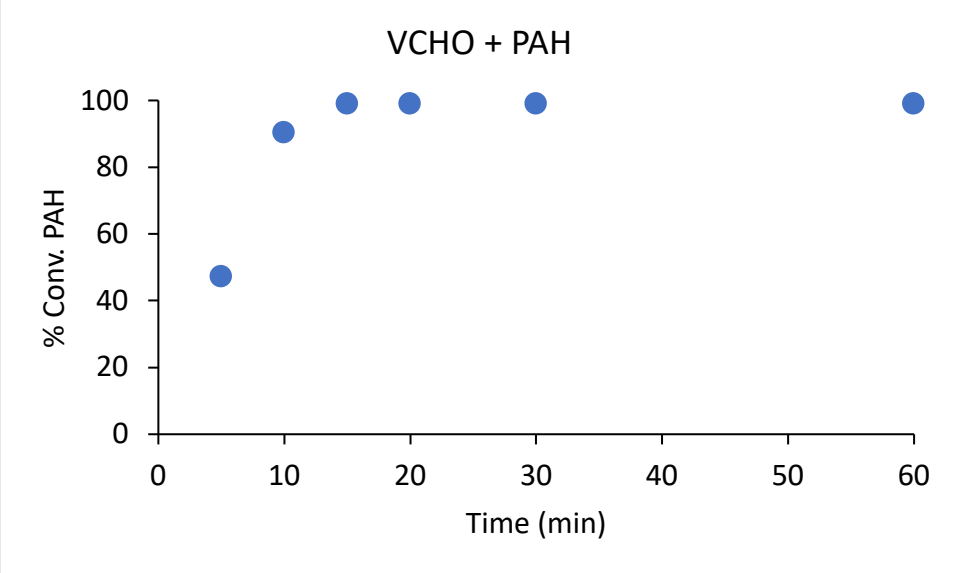

Figure S6. Conversion vs. time plot of controlled alternating ring-opening polymerization of VCHO and PAH (Table 1, entry 3)

Table S3. Anhydride conversion and GPC data for controlled alternating ring-opening polymerization of VCHO and PAH (Table 1, entry 3).

Aliquot Time (min)	% Conv. PAH[a]	M_n (g/mol)[b]	$Đ$[b]
5	47.2	9 964	1.12
10	90.5	17 140	1.14
15	99	20 290	1.14
20	99	20 680	1.17
30	99	20 260	1.17
60	99	20 260	1.17

[a]Determined from ^{1}H NMR [b]Đ, dispersity = Mw/Mn. Determined in THF by GPC equipped with a multiangle light-scattering detector.

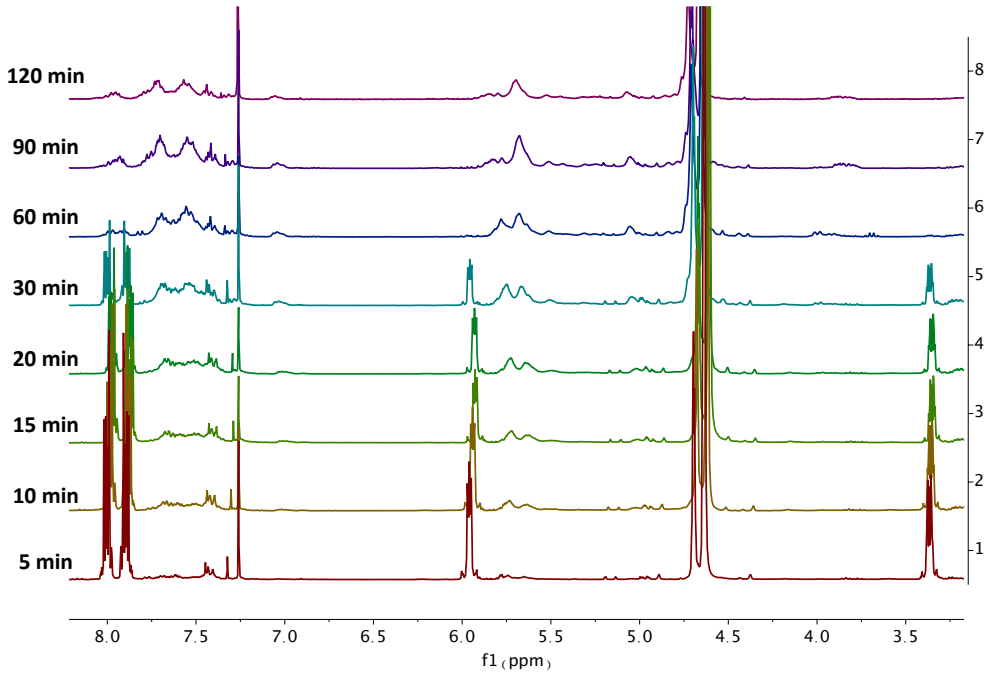

Figure S7. Stacked ^{1}H NMR (300 MHz, 298 K, $CDCl_3$) spectra of random alternating ring-opening polymerization of LO, PAH and CDA (Table 1, entry 7)

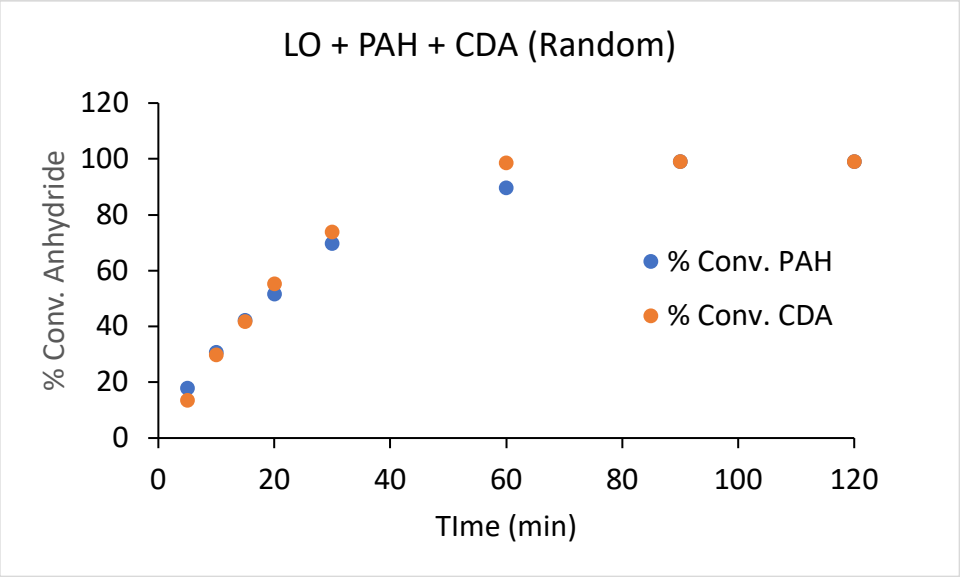

Figure S8. Conversion vs. time plot of random alternating ring-opening polymerization of LO and PAH (Table 1, entry 7)

Table S4. Anhydride conversion and GPC data for random alternating ring-opening polymerization of LO and PAH (Table 1, entry 7).

Aliquot Time (min)	% Conv. PAH[a]	% Conv. CDA[a]	M_n (g/mol)[b]	$Đ$[b]
5	17.9	13.6	626	1.04
10	30.8	29.7	568	1.03
15	42.2	41.8	790	1.03
20	51.5	55.2	825	1.05
30	69.6	73.8	881	1.06
60	89.7	98.5	1 737	1.75
90	99	99	1 737	1.75
120	99	99	1 737	1.75

[a]Determined from ^{1}H NMR [b]Đ, dispersity = Mw/Mn. Determined in THF by GPC equipped with a multiangle light-scattering detector.

Figure S9. 2D DOSY NMR spectra (500 MHz, 298 K, $CDCl_3$) of random alternating ring-opening polymerization of LO, PAH and CDA (Table 1, entry 7).

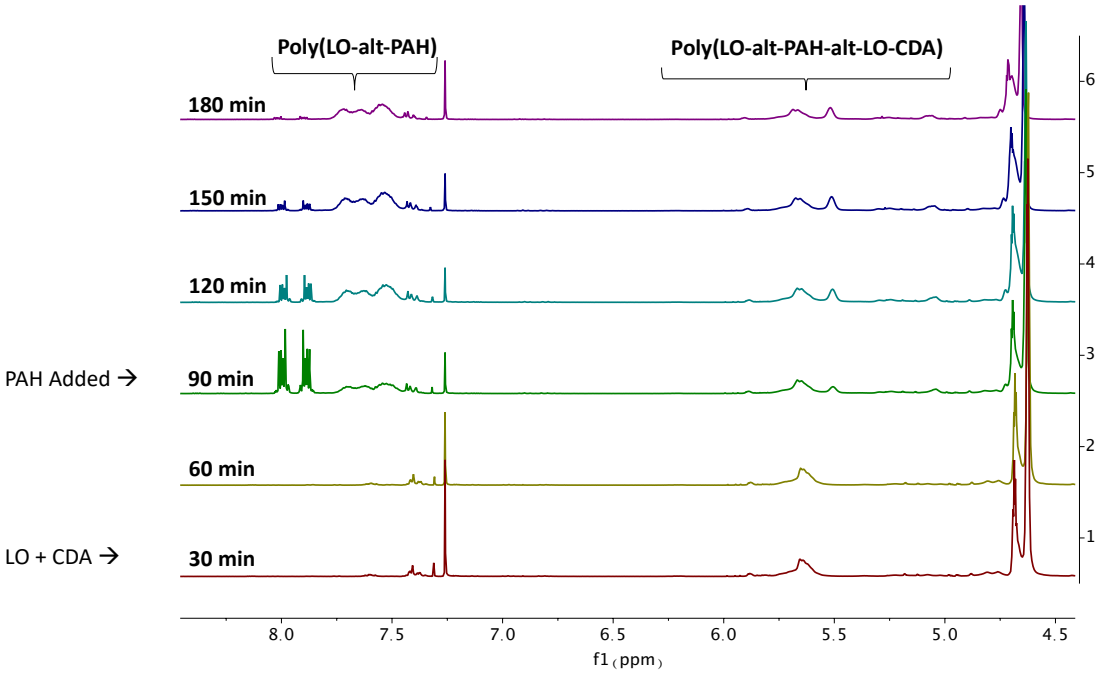

Figure S10. Stacked ^{1}H NMR (300 MHz, 298 K, $CDCl_3$) spectra of controlled alternating ring-opening polymerization of LO, PAH and CDA (Table 1, entry 8)

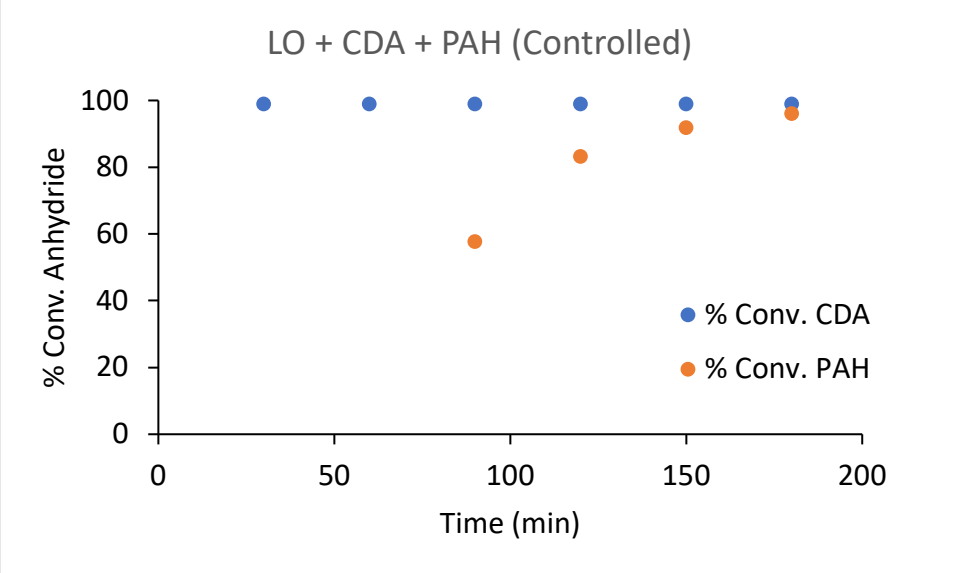

Figure S11. Conversion vs. time plot of controlled alternating ring-opening polymerization of LO and PAH (Table 1, entry 8)

Table S5. Anhydride conversion and GPC data for controlled alternating ring-opening polymerization of LO, PAH and CDA (Table 1, entry 8).

Aliquot Time (min)	% Conv. PAH[a]	% Conv. CDA[a]	M_n (g/mol)[b]	$Đ$[b]
30	-	99	880	1.1
60	-	99	920	1.1
90	58	99	1920	1.1
120	83	99	2120	1.1
150	92	99	2140	1.1
180	96	99	2100	1.2

[a]Determined from ^{1}H NMR [b]Đ, dispersity = Mw/Mn. Determined in THF by GPC equipped with a multiangle light-scattering detector.

Figure S12. 2D DOSY NMR spectra (500 MHz, 298 K, $CDCl_3$) of controlled alternating ring-opening polymerization of LO, PAH and CDA (Table 1, entry 8).

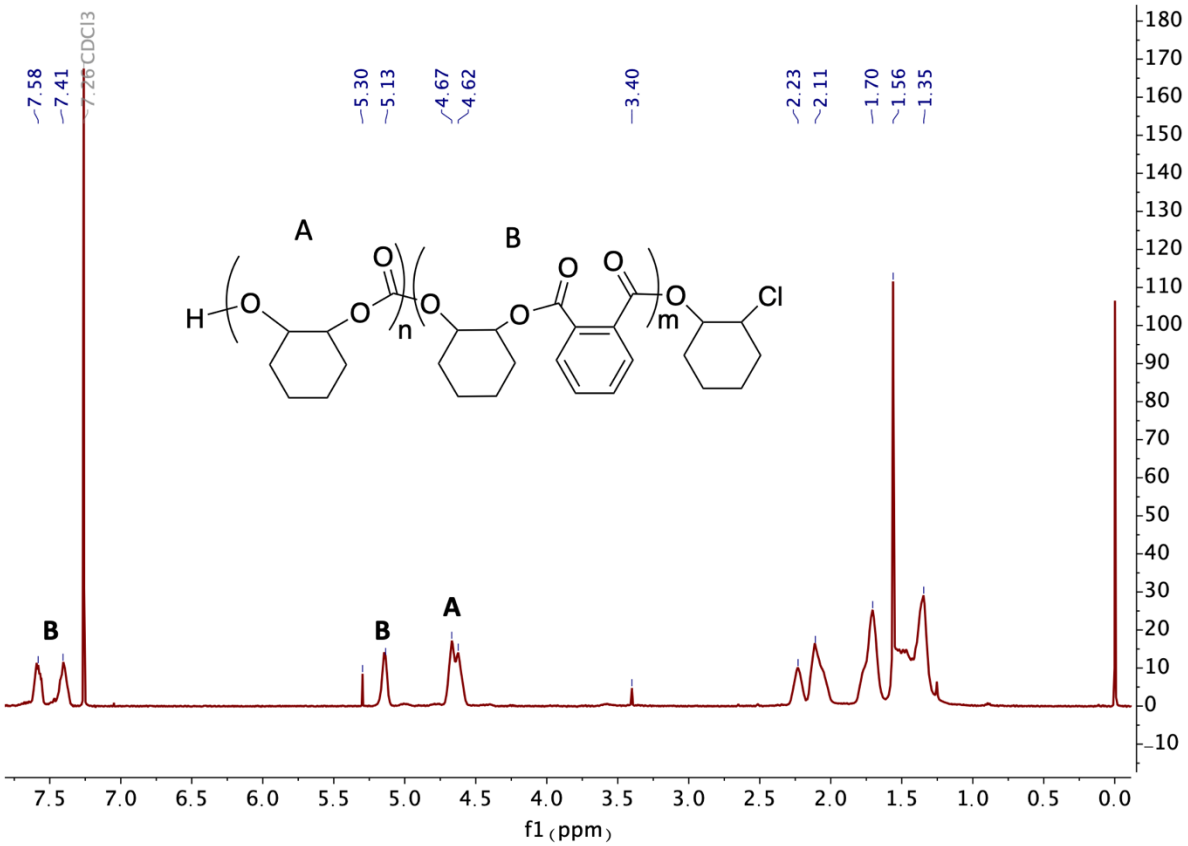

Figure S13. ^{1}H NMR (300 MHz, 298 K, $CDCl_3$) spectra of poly(CHC)-alt(CHO-PAH) block copolymer.

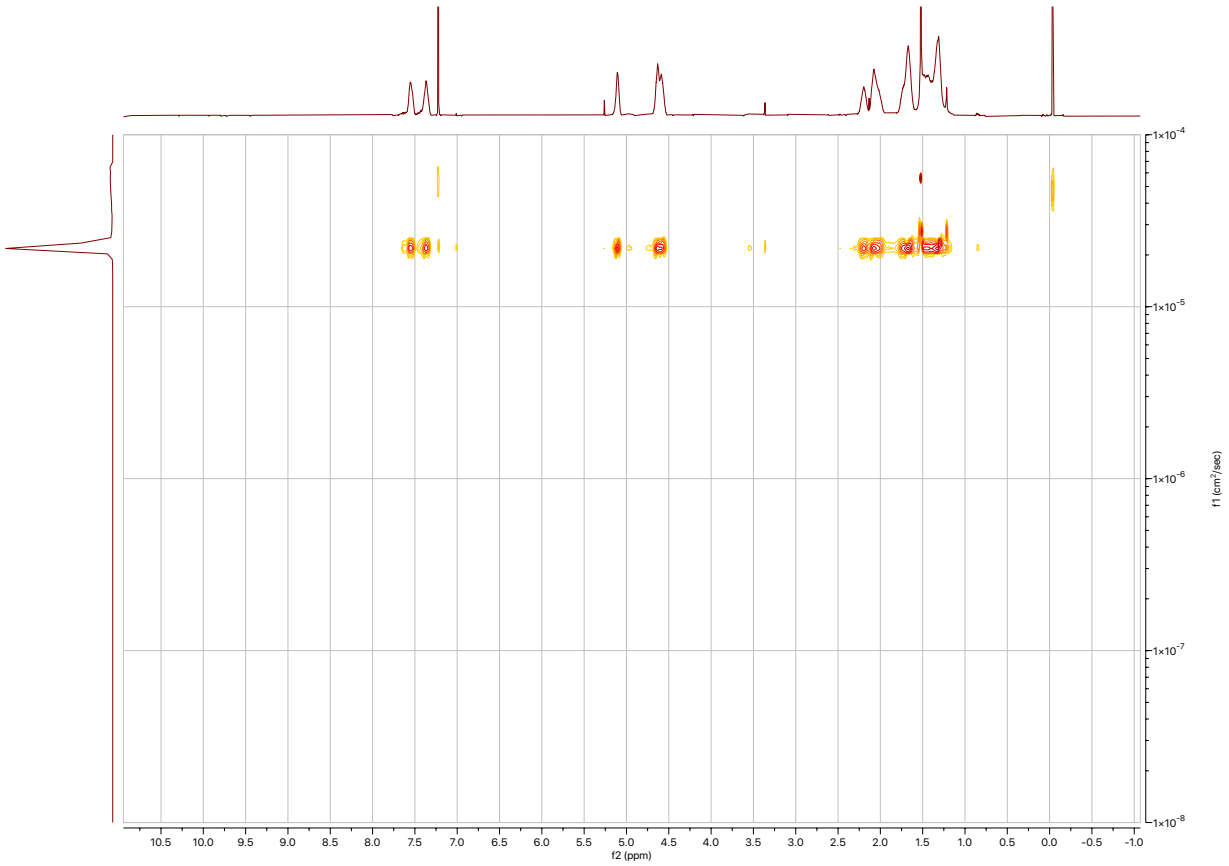

Figure S14. 2D DOSY NMR spectra (500 MHz, 298 K, $CDCl_3$) of poly(CHC)-alt(CHO-PAH) block copolymer.

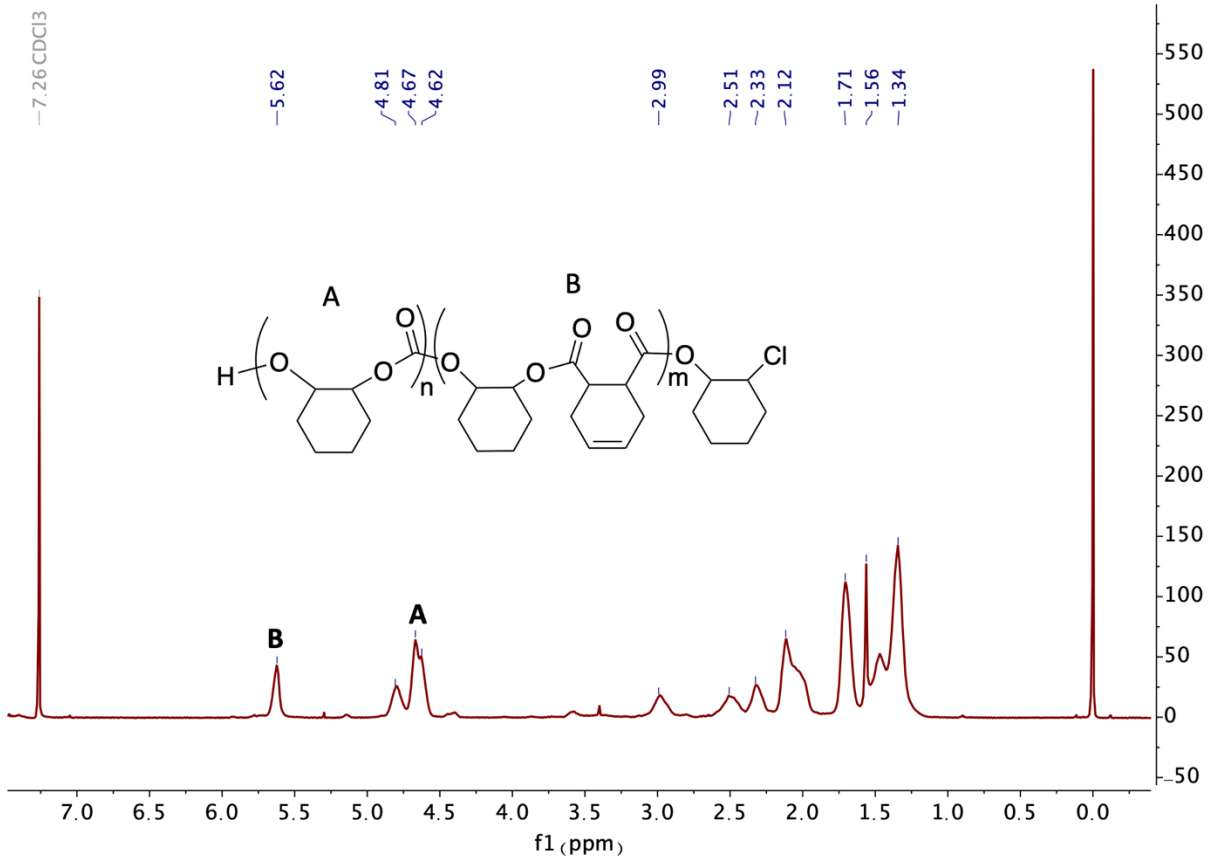

Figure S15. ^{1}H NMR (300 MHz, 298 K, $CDCl_3$) spectra of poly(CHC)-alt(CHO-CDA) block copolymer.

Figure S16. 2D DOSY NMR spectra (500 MHz, 298 K, $CDCl_3$) of poly(CHC)-alt(CHO-CDA) block copolymer.

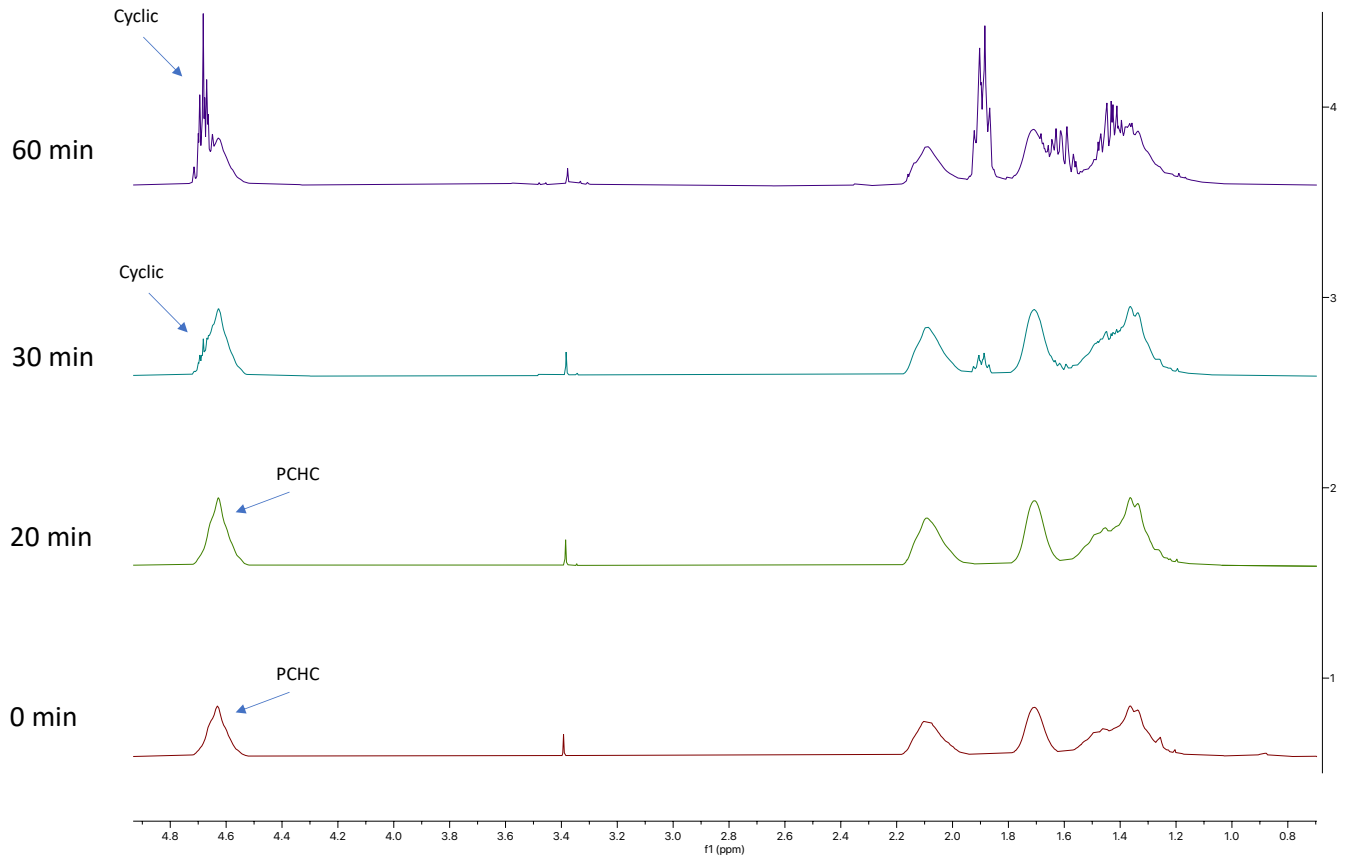

Figure S17. Stacked ^{1}H NMR (300 MHz, 298 K, $CDCl_3$) spectra of BCF catalyzed PCHC degradation experiments

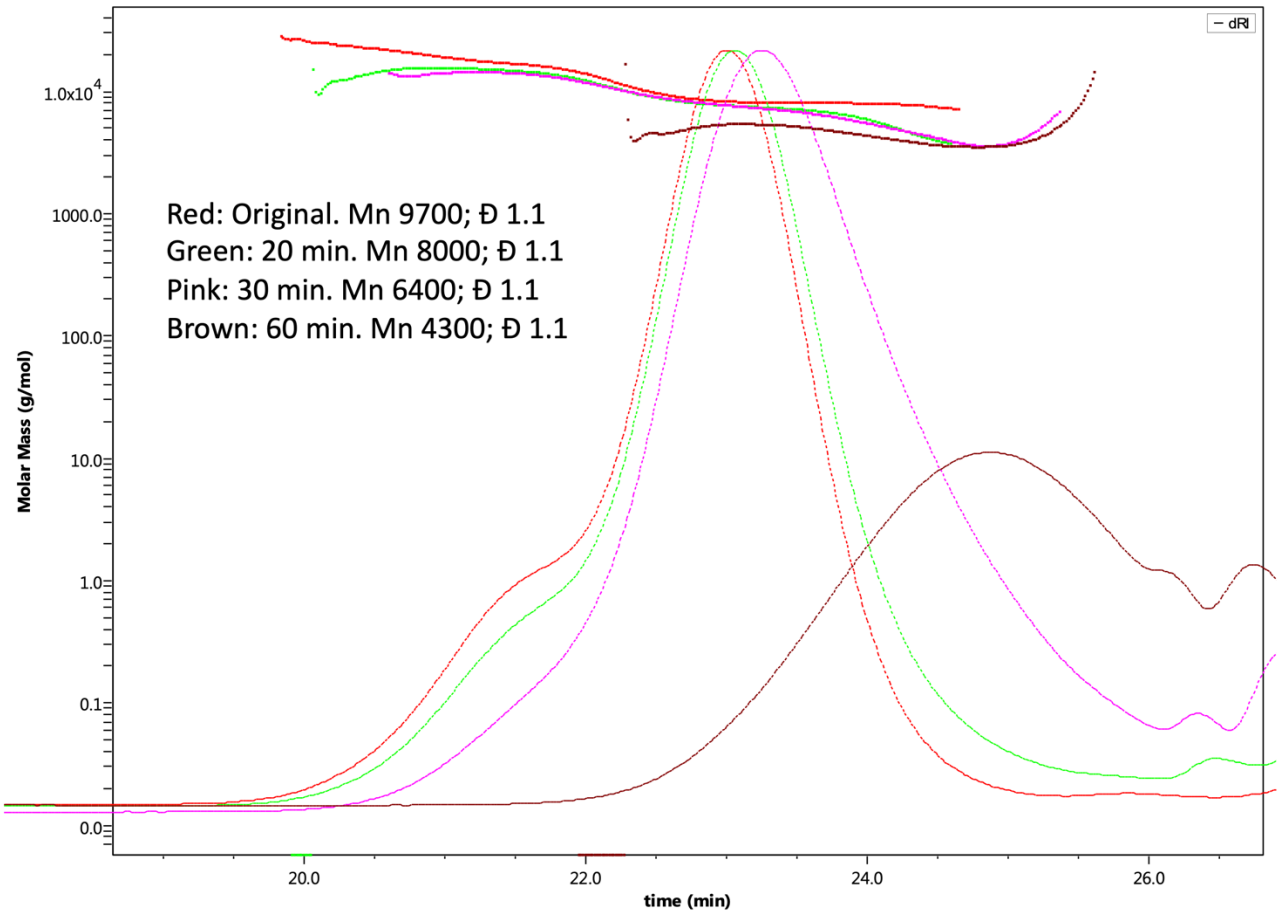

Figure S18. GPC overlay of polymer samples from BCF catalyzed PCHC degradation experiments.

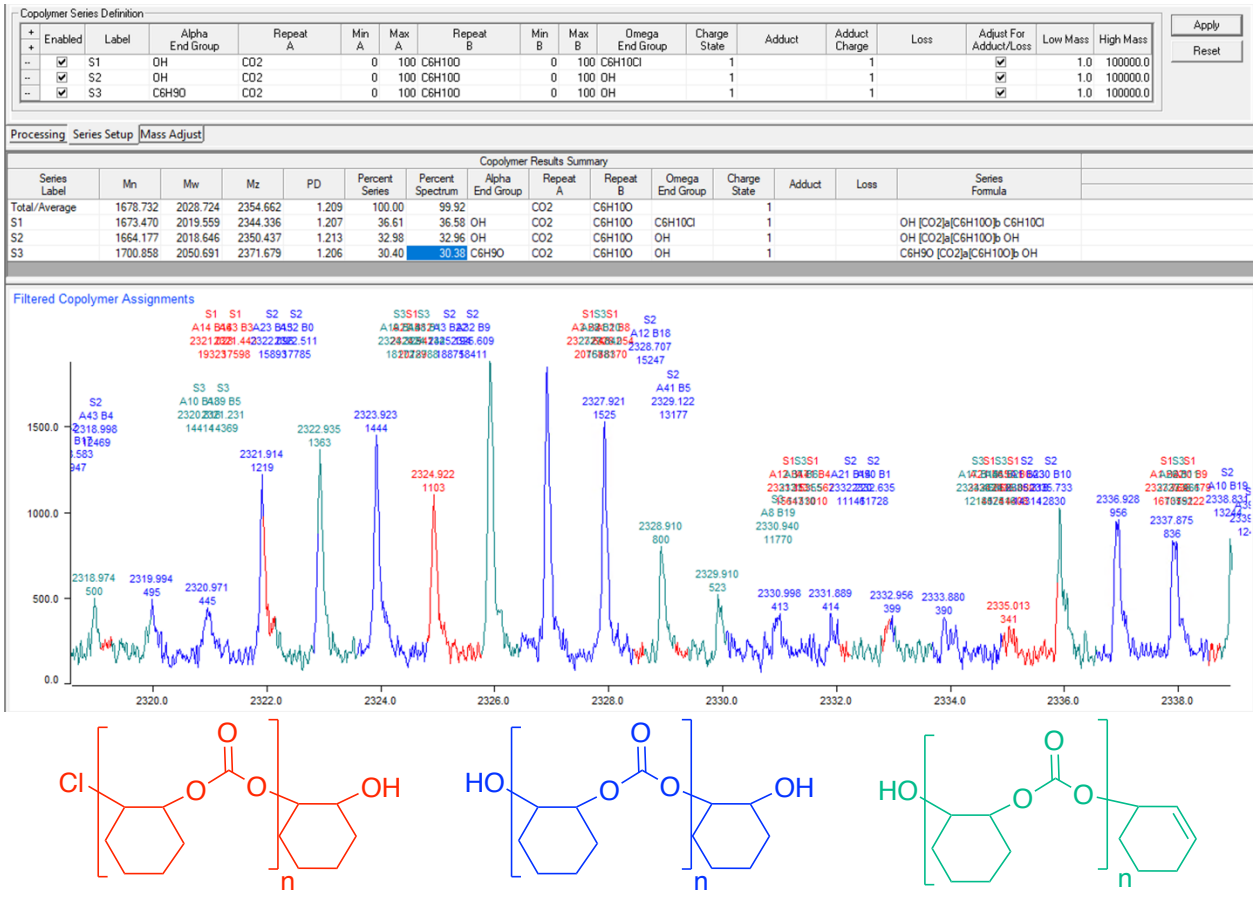

Figure S19. High molecular weight region of a representative MALDI-TOF spectrum of polycyclohexene carbonate used in degradation experiments and modeling of spectrum showing the three series of polymers (S1-S3) and their identified end group combinations [S1, red (36.58%); S2, blue (32.96%); S3, green (30.38%), this combination gives an overall 99.92% total spectrum match from *m/z* 1.00 to 100,000].