

# Electronic Supplementary Information for Understanding Differences in Rate versus Product Determining Steps to Enhance Sequence Control in Epoxide/Cyclic Anhydride Copolymers

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## 1. General Considerations

All polymerization reactions were set up on a benchtop under atmospheric conditions. Protio and deuterated chloroform were purchased from commercial suppliers and used as received. 1-Butene oxide (BO) and cyclohexene oxide (CHO) were dried over  $\text{CaH}_2$ , degassed by three freeze-pump-thaw cycles and vacuum transferred prior to use, unless stated otherwise. Carbic anhydride (CPMA) was recrystallized from hot 30:70 ethyl acetate/hexanes and dried under reduced pressure for 24 h prior to use. Phthalic anhydride (PA) was sublimed prior to use. Glutaric anhydride (GA) was purchased from commercial suppliers and used as received. Bis(triphenylphosphine)iminium chloride ([PPN]Cl) was recrystallized from  $\text{CH}_2\text{Cl}_2$ /hexanes and dried under reduced pressure for 24 h prior to use.

**Methods.**  $^1\text{H}$  NMR spectra were recorded on a Varian 400-MR 2-Channel, Varian Mercury 400 2-Channel, Varian VNMRS-500 2-Channel, and Varian VNMRS-600 3-Channel NMR spectrometers and referenced against residual protio solvent resonances.  $^1\text{H}$  NMR kinetics were recorded on a Varian VNMRS-600 3-Channel NMR spectrometer. Polymer molecular weights and dispersities were determined using a SEC-MALS instrument equipped with an Agilent 1260 Infinity II HPLC System and autosampler, 2 Agilent PolyPore columns (both 5 micron, 4.6 mm ID) in sequence, a Wyatt DAWN HELEOS-II light scattering detector, and a Wyatt Optilab T-rEX refractive index detector. The columns were eluted with HPLC grade THF at 30 °C at a flow rate of 0.3 mL/min, and polymer samples were dissolved in this solvent and filtered through a 0.2 micron PTFE membrane before dRI analyses.  $dn/dc$  values were calculated from the RI signal by using the 100% mass recovery method in the Astra software and a known sample concentration. The DSC measurements were made at a heating rate of 10 °C/min and  $\text{N}_2$  flow rate of 20 ml/min, and  $T_g$  values were obtained from the midpoint of the glass transition in the second heating curve. DSC traces were recorded using a Perkin-Elmer DSC 8000 and processed with Pyris software.

## 2. General Procedures for Polymerization

On the benchtop,  $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$  (1 equiv),  $[\text{PPN}]\text{Cl}$  (1 equiv), anhydride, epoxide and a stir bar were charged into a vial equipped with a Teflon-lined cap. For epoxide mixtures (Table S3),  $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$  (1 equiv, 3.3 mg, 0.011 mmol),  $[\text{PPN}]\text{Cl}$  (1 equiv, 6.2 mg, 0.011 mmol), carbic anhydride (400 equiv, 702.0 mg, 4.2 mmol), and a total of 2 mL of epoxides were added to the vial. For anhydride mixtures (Table S4),  $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$  (1 equiv, 3.0 mg, 0.0099 mmol),  $[\text{PPN}]\text{Cl}$  (1 equiv, 5.7 mg, 0.0099 mmol), cyclohexene oxide (2000 equiv, 2 mL, 19.7 mmol), and two anhydrides of choice (200 equiv. each, 1.97 mmol) were added to the vial. The vial was then taped with electrical tape, and placed inside a Chemglass high throughput tray that was preheated to 110 °C for at least 1 h. After the desired time, the vial was cooled to room temperature and the resulting mixture was dissolved in 1 mL of chloroform. Hexanes was then added in excess until the polymer started to precipitate out. The precipitate was allowed to settle, and the supernatant was pipette away. The isolated polymer was then dried under reduced pressure at 110 °C overnight. Conversions were calculated via analysis of crude  $^1\text{H}$  NMR spectra in  $\text{CDCl}_3$ .

### 2.1 General Procedure for Anhydride Reactivity Ratio Reactions

On the benchtop,  $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$  (1 equiv, 3.0 mg, 0.0099 mmol),  $[\text{PPN}]\text{Cl}$  (1 equiv, 5.7 mg, 0.0099 mmol), 2 anhydrides of choice (each 50 equiv, 0.49 mmol), cyclohexane oxide (500 equiv, 0.50 mL, 4.94 mmol) and a stir bar were charged into a vial equipped with a Teflon-lined cap and placed inside a Chemglass high throughput tray that was preheated to the desired reaction temperature (80 °C or 110 °C) for at least 1 h. Aliquots, which were then dissolved in  $\text{CDCl}_3$ , were then taken at selected times for each reaction to monitor monomer conversion by  $^1\text{H}$  NMR (Fig. 5 and Fig. S60).

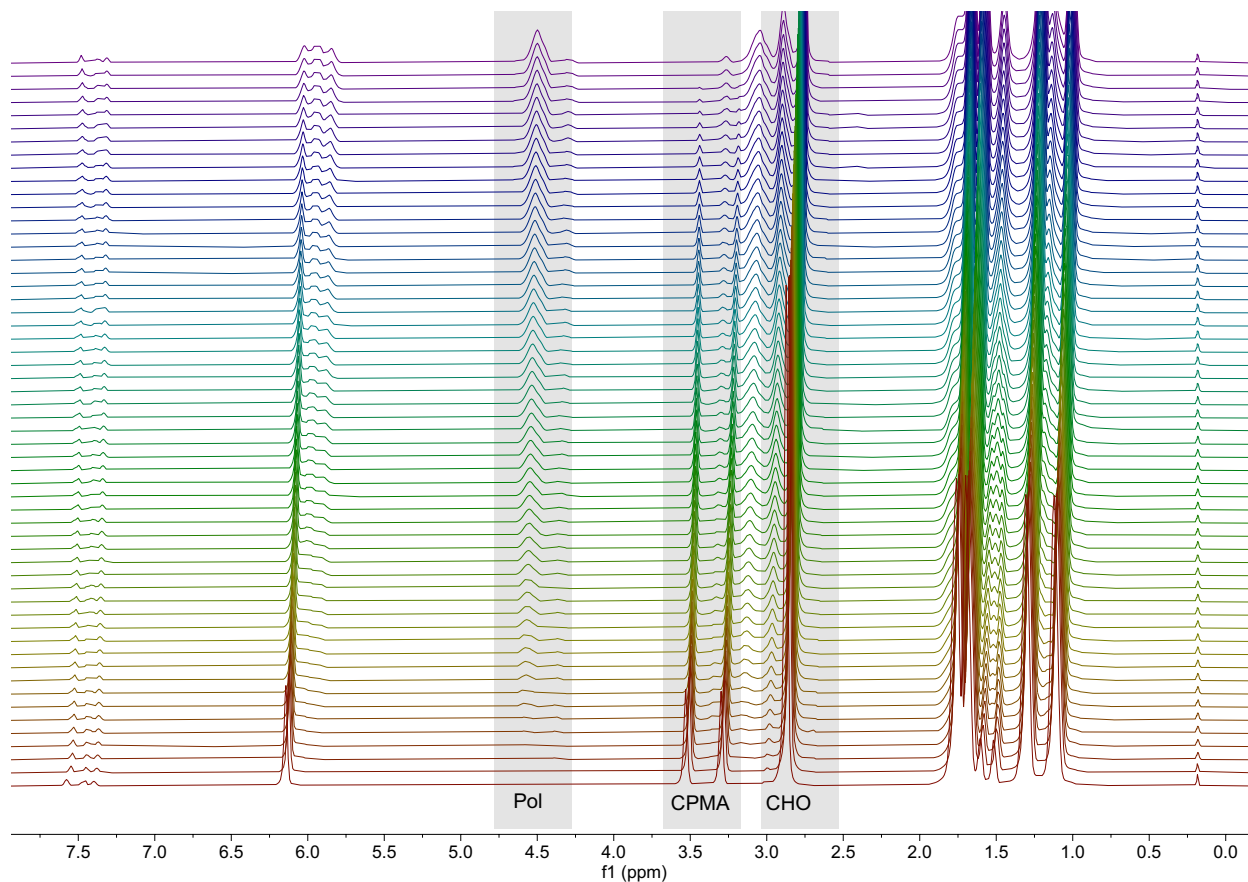
### 3. Kinetics Procedure

**3.1 <sup>1</sup>H NMR Kinetics Procedures.** A representative procedure for the kinetic studies is described and adopted from Tolman and coworkers.<sup>1</sup> Catalyst, cocatalyst, and anhydride were weighed into a glass vial with a Teflon coated cap on the benchtop. The epoxide was added via syringe and the vial was stirred at 60 °C for 5 minutes. In cases with lower epoxide concentrations, chlorobenzene was added to keep the total volume between 700 and 780 μL. The final volume of each homogenous solution was measured with a syringe, and the solution was immediately transferred to a oven-dried NMR tube containing a 15.7 mM capillary solution of p-C<sub>6</sub>H<sub>4</sub>(TMS)<sub>2</sub> in C<sub>6</sub>D<sub>6</sub>. The NMR tube was capped, the cap wrapped in electrical tape and the tube was transferred to a spectrometer. The temperature of the NMR spectrometer was calibrated to 110 °C using a pure ethylene glycol standard. An arrayed set of spectra were taken with no delay between each, with 8 scans and maximum gain. The arrayed experiment was allowed to proceed until >20% of anhydride was consumed unless otherwise noted. The obtained arrayed NMR data were phased and baseline corrected in Mestrenova before being integrated in the same program. The integrations were recorded and entered into an Excel spreadsheet. Absolute concentrations of epoxide and anhydride as a function of time were computed relative to the concentration of the internal standard.

**Table S1.** Experimental data for kinetic polymerization experiments.

Condition #	[YCl <sub>3</sub> ·6H <sub>2</sub> O] (M) <sup>a</sup>	[[PPN]Cl] (M) <sup>a</sup>	[CHO] (M) <sup>b</sup>	[CPMA] (M) <sup>b</sup>	Initial rate (M/s) <sup>c</sup>
1a	0.016	0.017	9.10	1.76	6.8x10 <sup>-4</sup>
1b	0.016	0.017	10.50	2.02	8.0x10 <sup>-4</sup>
1c	0.016	0.017	8.83	1.77	1.3x10 <sup>-3</sup>
1d	0.016	0.016	12.24	2.36	1.6x10 <sup>-3</sup>
2a	0.019	0.020	10.52	1.57	1.0x10 <sup>-3</sup>
3a	0.019	0.020	11.69	1.18	1.4x10 <sup>-3</sup>
4a	0.021	0.020	7.07	1.84	7.7x10 <sup>-4</sup>
5a	0.021	0.019	3.93	1.41	3.1x10 <sup>-4</sup>

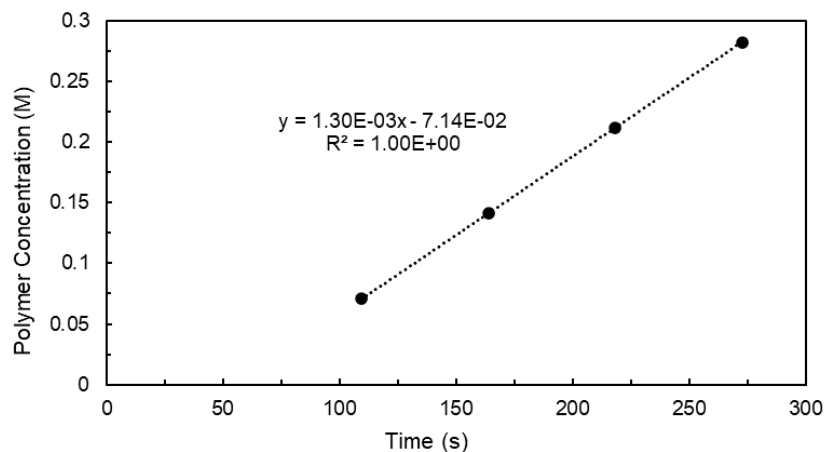
<sup>a</sup> Calculated concentrations from weight of material and final volumes of the reaction solution. <sup>b</sup> Observed concentration in <sup>1</sup>H NMR, calibrated with the internal standards. <sup>c</sup> Initial rates described in section 3.2.



**Fig. S1** Example of CHO/CPMA stack used for  $^1\text{H}$  NMR kinetics.

**3.2 Initial Rate Determination.** Reaction orders were determined by examining initial rates of reaction. Due to the varying times taken to set up each run, one particular time point could not be used for comparison between reactions. The concentration of polymer vs. time data was fit to a first order polynomial (Fig. S2). Using the linear fit, reaction times at 15% completion, determined by examining the amount of anhydride reacted, were compared. An order was determined for every combination of runs using eq 1, where the rate constant,  $k$ , and conditions with identical conditions cancel, and averaged. Table S2 shows a summary of the determined orders.

$$\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{k[\text{CHO}]_1^x [\text{CPMA}_1]^y [\text{Cat}_1]^z}{k[\text{CHO}_2]^x [\text{CPMA}_2]^y [\text{Cat}_2]^z} \quad (1)$$



**Figure S2** Example of plot used for to obtain an initial rate from kinetic studies.

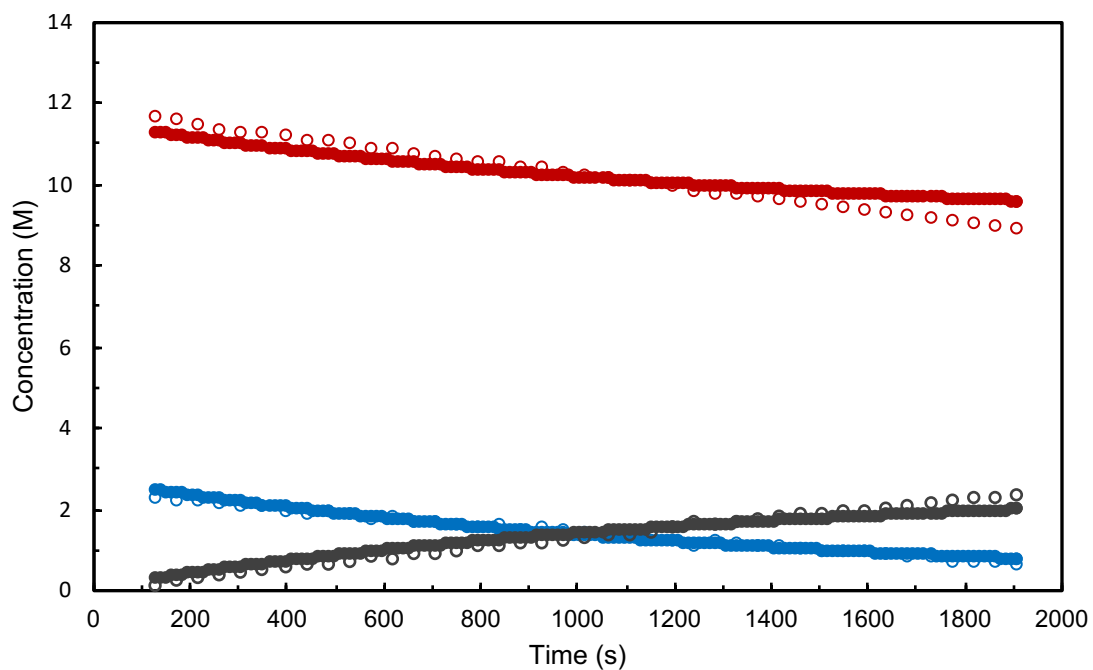
**Table S2.** Determined orders for CHO, CPMA, and Cat ( $YCl_3 \cdot 6H_2O/[PPN]Cl$  pair) using initial rates.

	CHO	CPMA
Reaction order	0.9 (4)	0.0 (6)

**3.3 COPASI Fitting Software.** The concentration vs time data obtained from the  $^1H$  NMR data were input into the global kinetics fitting program COPASI (version 4.30), and fit to eq 2 to obtain a  $k_{obs}$  value.<sup>2</sup>

$$Rate = k_{obs}[CHO] \quad (2)$$





**Fig. S3** COPASI fit for Table S1, Entry 1d. Colored circles represent experimental data, and the solid lines represent the fit data for each species.  $K_{\text{obs}} = 6.57 \times 10^{-5} \text{ (1) (M s}^{-1}\text{)}$

#### 4. Tabulated polymerization data

**Table S3.** Tabulated polymerization data for ROCOP of CHO, BO, and CPMA catalyzed by  $\text{YCl}_3 \cdot 6\text{H}_2\text{O}/[\text{PPN}]\text{Cl}$ .<sup>a</sup>

Entry #	$f_{\text{BO}}:f_{\text{CHO}}$	$F_{\text{BO}}:F_{\text{CHO}}$ (expt.)	% conversion <sup>d</sup>	% ester <sup>e</sup>	% epimer <sup>f</sup>	$^{\text{Exp}}M_n$ (kDa) <sup>g</sup>	$\bar{D}$ <sup>h</sup>	$T_g^f$ (°C)
1	2000:0	100:0	73	97	14	4.9	1.49	54
2	1600:400	79:21	85	>99	8	4.5	1.18	69
3	1200:800	65:35	81	>99	11	3.8	1.26	79
4	1000:1000	48:52	76	98	8	4.1	1.24	91
5	800:1200	37:63	79	99	5	3.7	1.27	99
6	400:1600	28:72	66	97	13	3.2	1.23	97
7	0:2000	0:100	60	98	9	3.1	1.23	116

<sup>a</sup>  $[\text{BO}+\text{CHO}]:[\text{CPMA}]:[\text{YCl}_3 \cdot 6\text{H}_2\text{O}]:[[\text{PPN}]\text{Cl}]$  was 1908 - 2091:400:1:1 at 110 °C for 4 hrs. <sup>b</sup> Ratios are in  $\mu\text{L}$  to keep a consistent volume, with 2 mL epoxide used. <sup>c</sup> Based on  $^1\text{H}$  NMR of the purified polymers, comparing polyester BO peaks to polyester CHO peaks. <sup>d</sup> Determined using  $^1\text{H}$  NMR spectra of crude reaction mixtures, comparing conversion of anhydride to polymer. <sup>e</sup> Based on  $^1\text{H}$  NMR of the purified polymers, comparing the polyether signal to the polyester signal. <sup>f</sup> Determined using  $^1\text{H}$  NMR spectra of purified polymers as described previously: epim (%) =  $\{2 \times A_{2.7} \text{ ppm} / (6.0-6.5)\} \times 100$ .<sup>3</sup> <sup>g</sup> Identified by gel permeation chromatography (GPC), using a Wyatt dRI detector calibrated with polystyrene standards. <sup>h</sup> Determined by differential scanning calorimetry (DSC).

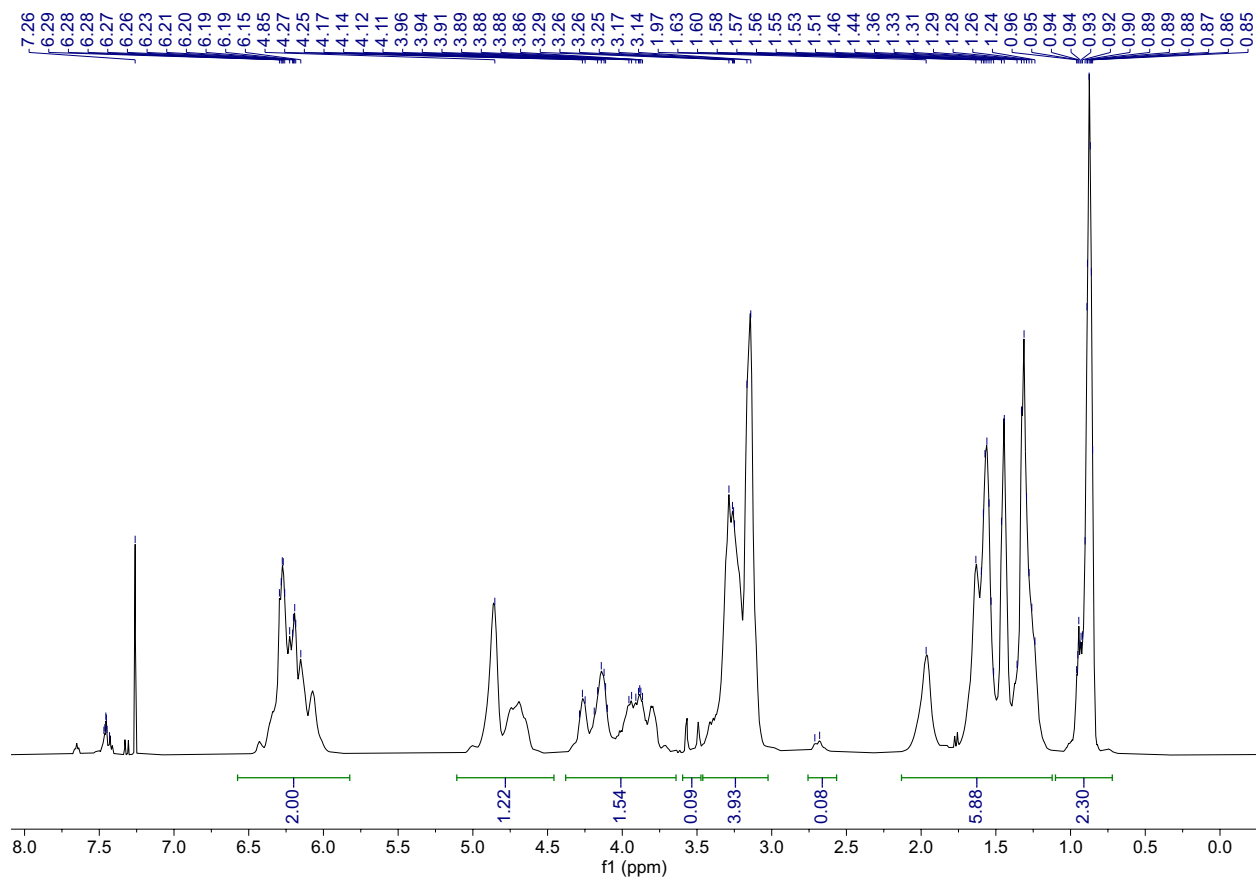
**Table S4.** Tabulated polymerization data for ROCOP of CHO, and multiple anhydrides, catalyzed by  $\text{YCl}_3 \cdot 6\text{H}_2\text{O}/[\text{PPN}]\text{Cl}$ .<sup>a</sup>

Entry #	Anhydride equiv.	% conversion <sup>b</sup>	% ester <sup>c</sup>	% epimer <sup>d</sup>	$^{\text{Exp}}M_n$ (kDa) <sup>e</sup>	$\bar{D}$ <sup>e</sup>	$T_g^f$ (°C)
1	300CPMA:100PA	66,>99	92	15	3.3	1.21	121
2	200CPMA:200PA	>99,>99	82	16	3.5	1.21	125
3	300CPMA:100GA	83,>99	90	25	2.2	1.43	87
4	200CPMA:200GA	>99,>99	83	27	2.2	1.57	60
5	100CPMA:300GA	>99,>99	71	50	2.1	1.63	34
6	200PA:200GA	>99,>99	74	-	1.6	1.56	55

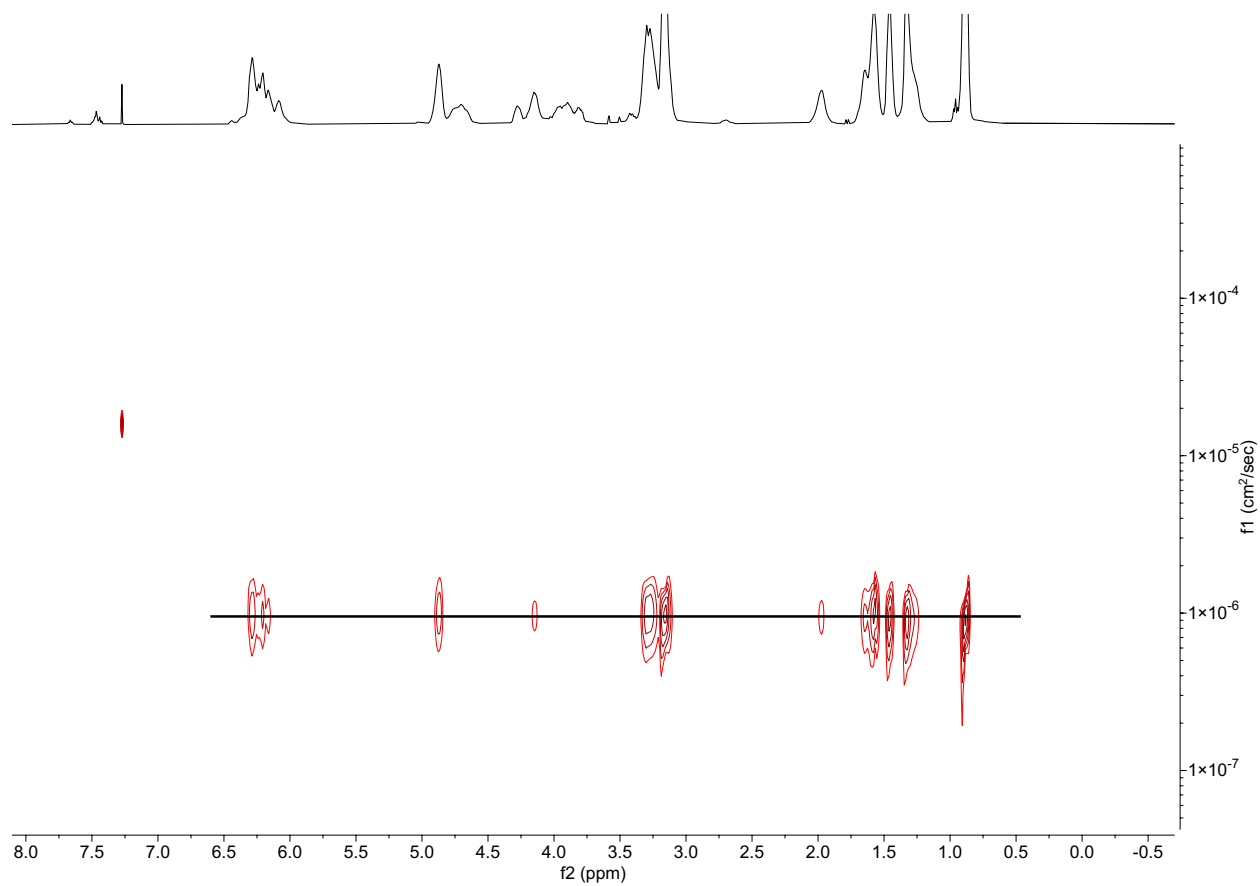
<sup>a</sup>  $[\text{CHO}]:[\text{Anhydride A} + \text{Anhydride B}]:[\text{YCl}_3 \cdot 6\text{H}_2\text{O}]:[[\text{PPN}]\text{Cl}]$  was 2000:400:1:1 at 110 °C for 4 hrs. <sup>b</sup> Determined using  $^1\text{H}$  NMR spectra of crude reaction mixtures, comparing conversion of anhydride to polymer. <sup>c</sup> Based on  $^1\text{H}$  NMR of the purified polymers, comparing polyester BO peaks to polyester CHO peaks. <sup>d</sup> Based on  $^1\text{H}$  NMR of the purified polymers, comparing the polyether signal to the polyester signal. <sup>e</sup> Determined using  $^1\text{H}$  NMR spectra of purified polymers as described previously: epim (%) =  $\{2 \times A_{2.7} \text{ ppm} / (6.0-6.5)\} \times 100$ .<sup>3</sup> <sup>f</sup> Identified by gel permeation chromatography (GPC), using a Wyatt dRI detector calibrated with polystyrene standards. <sup>g</sup> Determined by differential scanning calorimetry (DSC).

## 5. $^1\text{H}$ NMR Spectra of Isolated Polymers and Reaction Mixtures

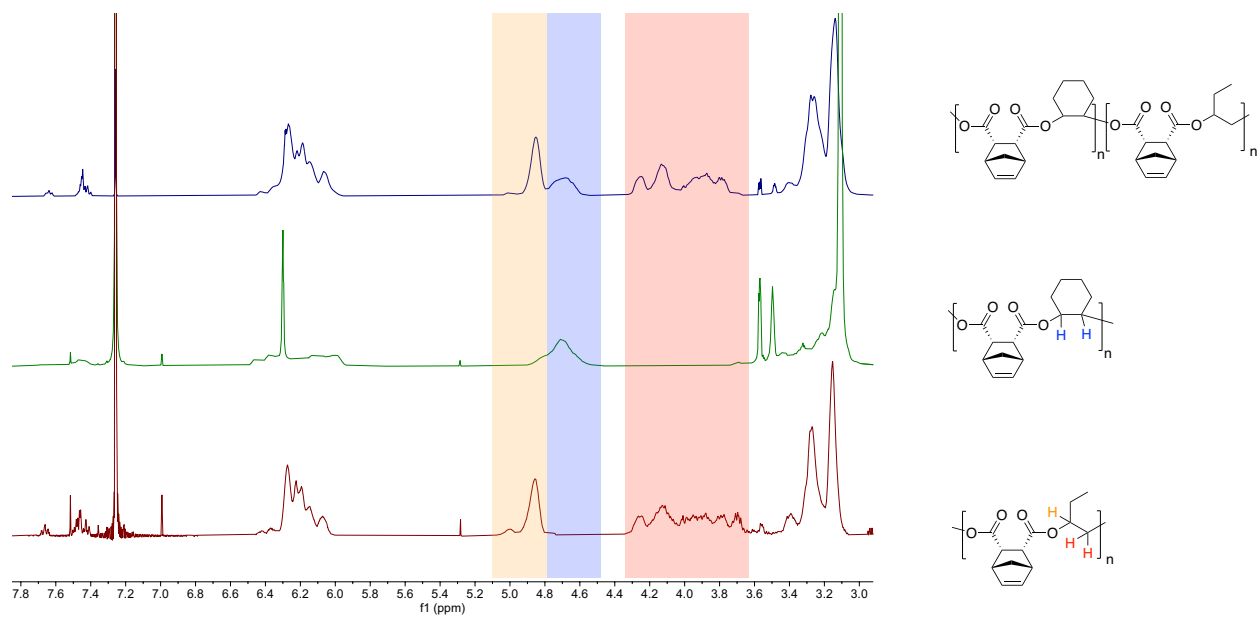
### 5.1 $^1\text{H}$ NMR Spectra from Polymerization Reactions



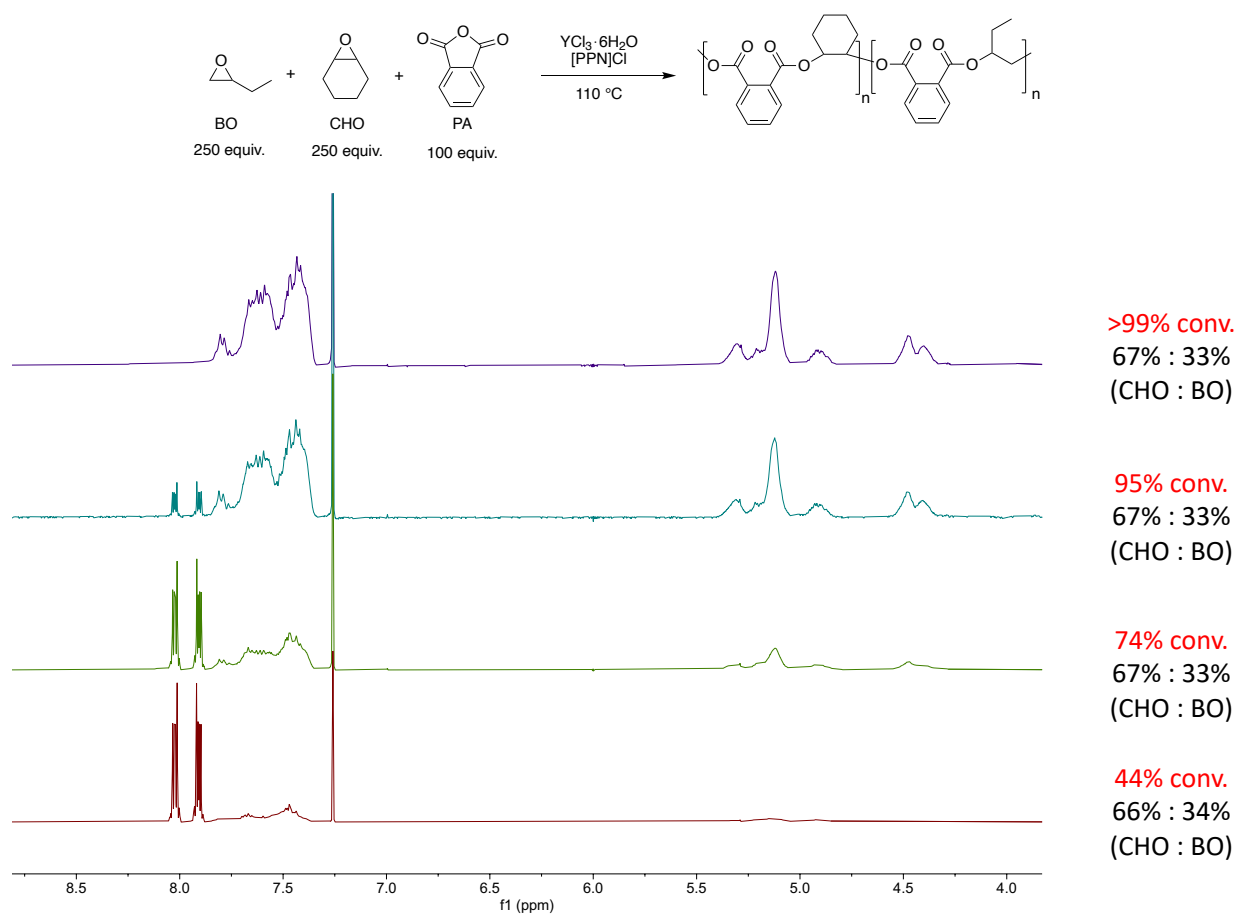
**Fig. S4**  $^1\text{H}$  NMR spectrum of CHO/CPMA-*r*-BO/CPMA in  $\text{CDCl}_3$  (Table 2, Entry 1). Resonances  $> 7.26$  ppm assignable to [PPN] phenyl groups (from the [PPN]Cl).



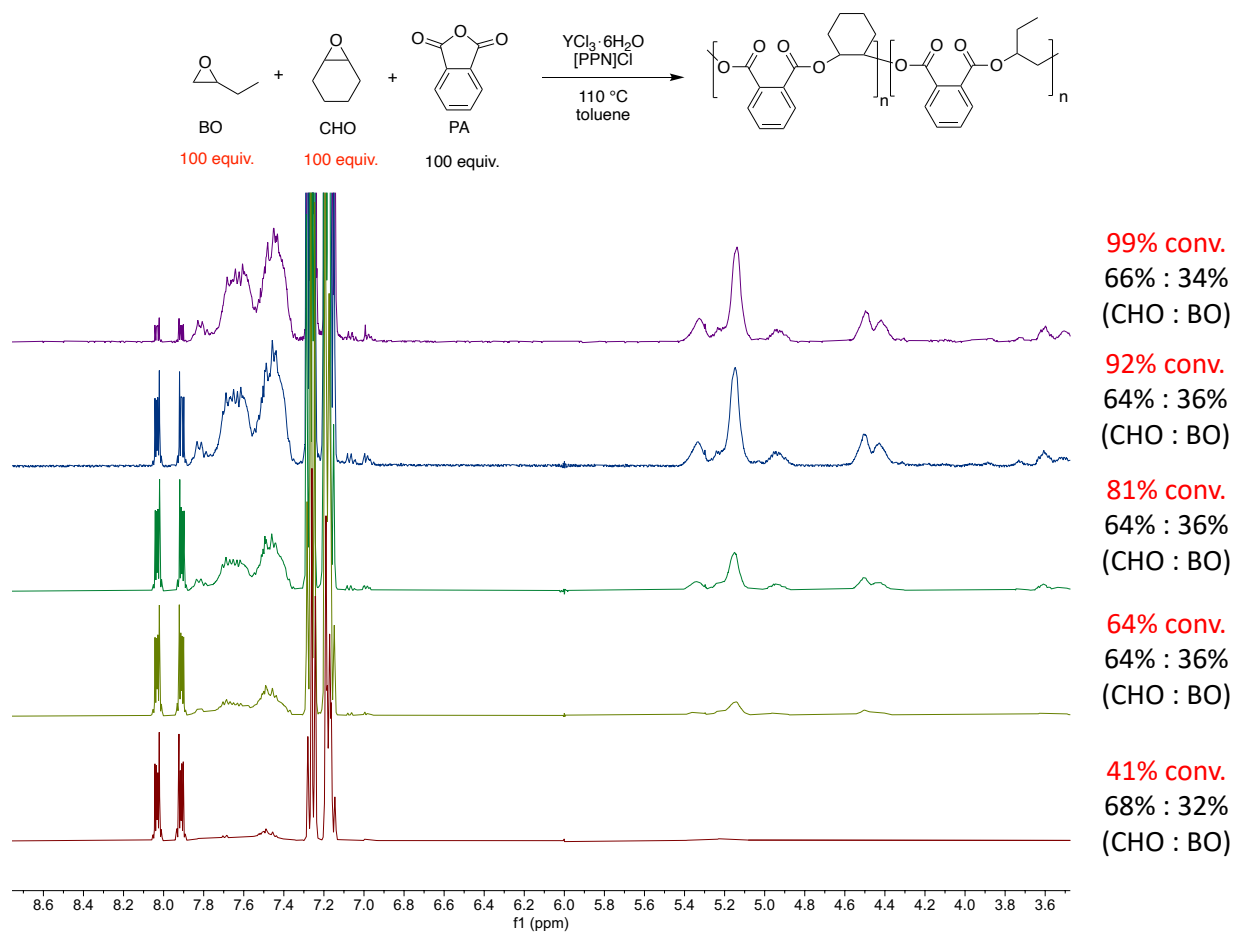
**Fig. S5**  $^1\text{H}$  DOSY NMR spectrum of CHO/CPMA-*r*-BO/CPMA in  $\text{CDCl}_3$  (Table 2, Entry 1).



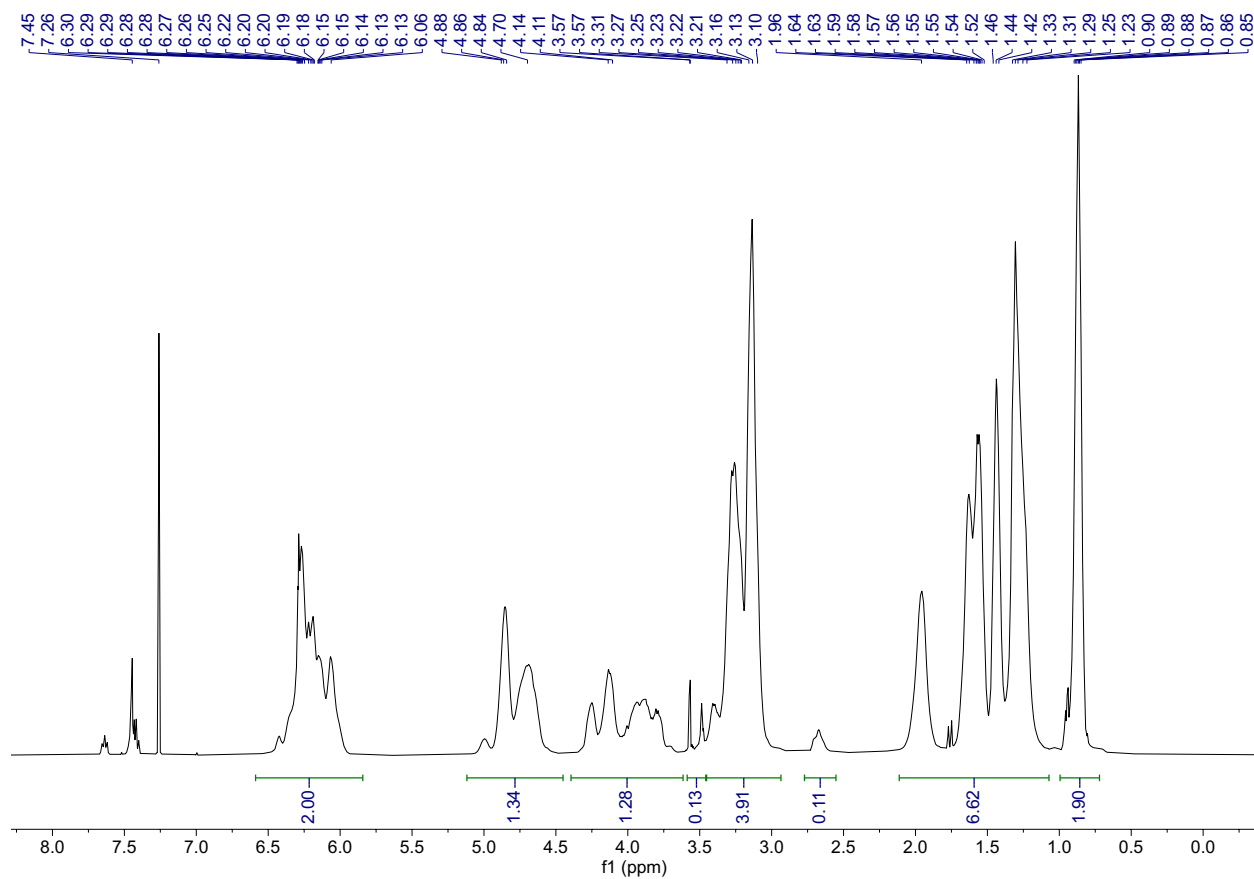
**Fig. S6**  $^1\text{H}$  NMR spectrum stack of BO/CPMA, CHO/CPMA, and CHO/CPMA-*r*-BO/CPMA in  $\text{CDCl}_3$  (Table 2, Entry 1).



**Fig. S7**  $^1\text{H}$  NMR spectrum stack of timepoints for CHO/PA-*r*-BO/PA in  $\text{CDCl}_3$ . % conversion of PA is in red.

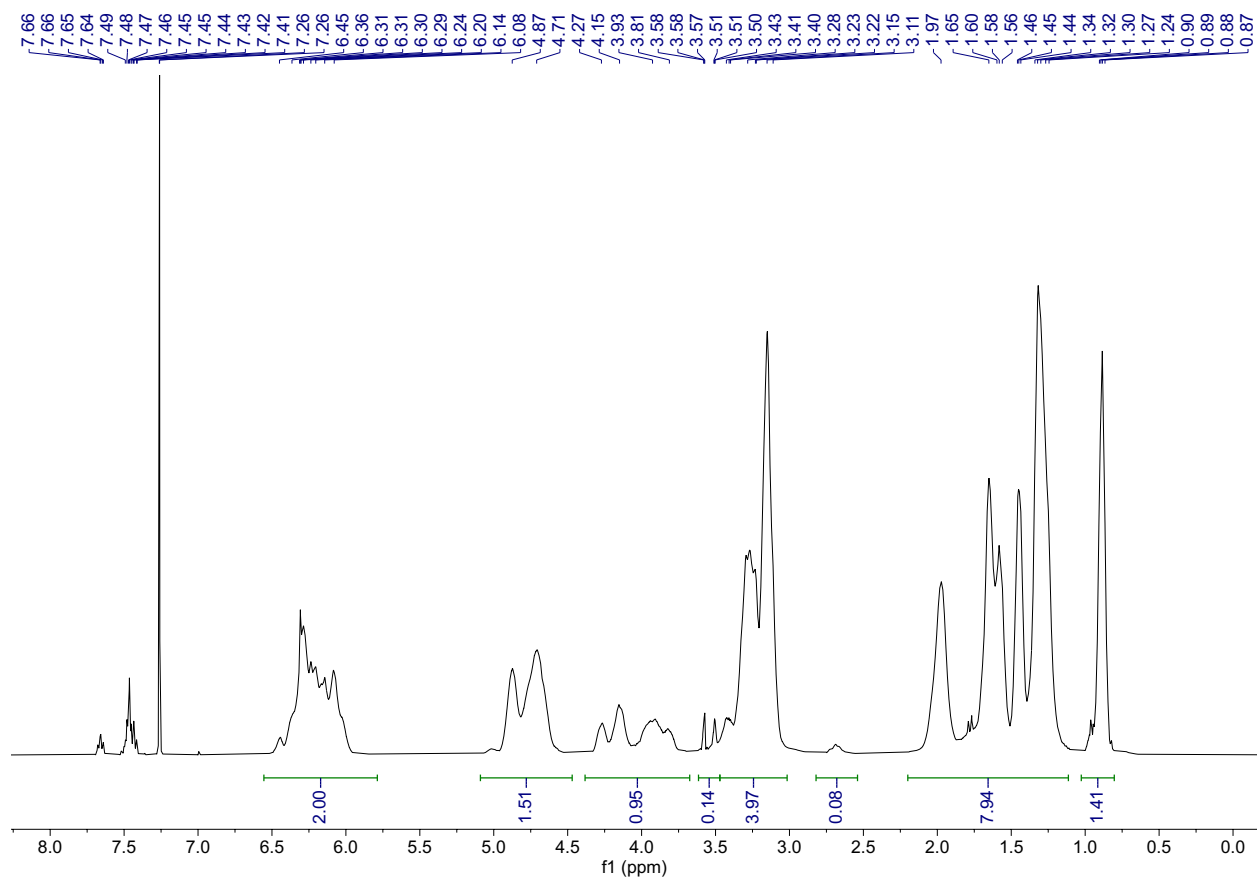


**Fig. S8**  $^1\text{H}$  NMR spectrum stack of timepoints for CHO/PA-*r*-BO/PA in  $\text{CDCl}_3$ . % conversion of PA is in red.

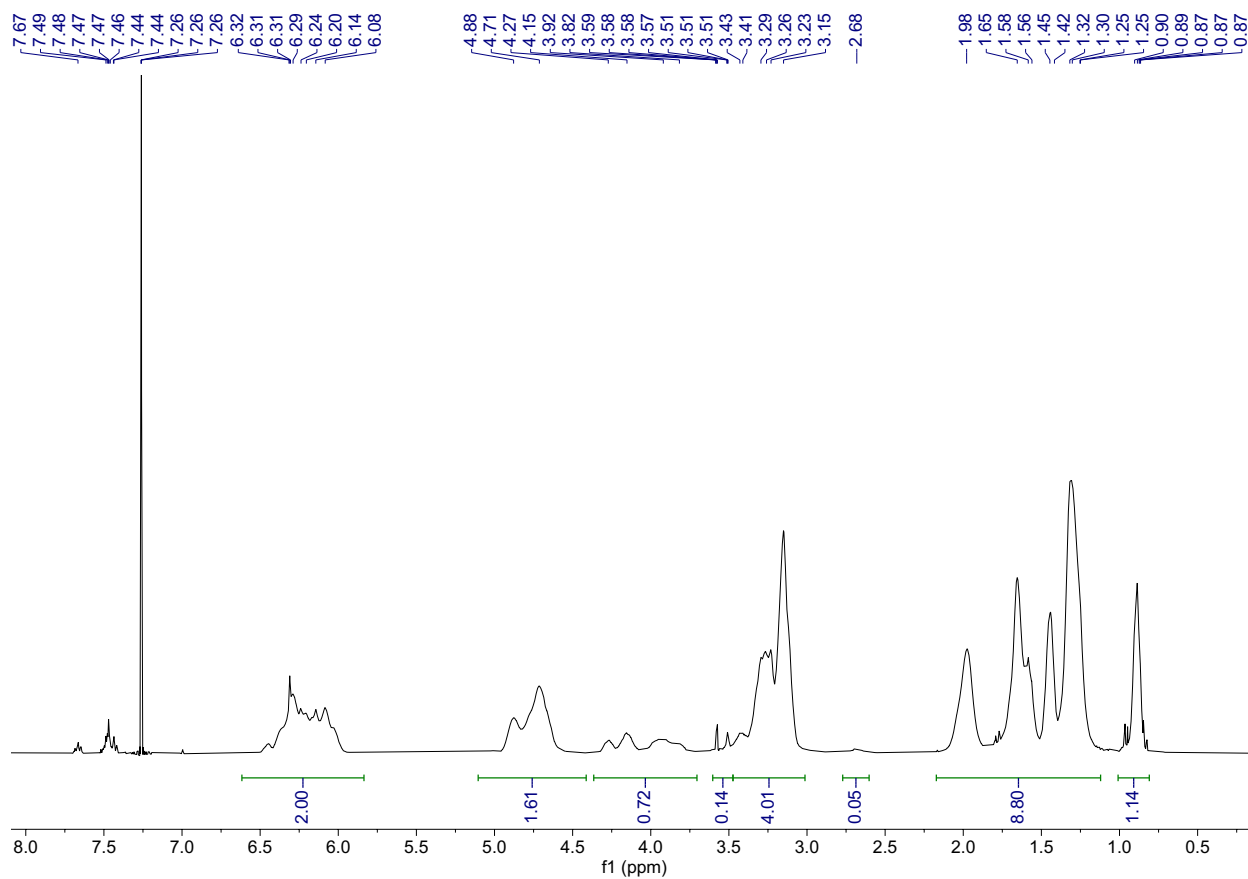


**Fig. S9**  $^1\text{H}$  NMR spectrum of CHO/CPMA-*r*-BO/CPMA in  $\text{CDCl}_3$  (Table 2, Entry 2). Resonances  $> 7.26$  ppm assignable to [PPN] phenyl groups.

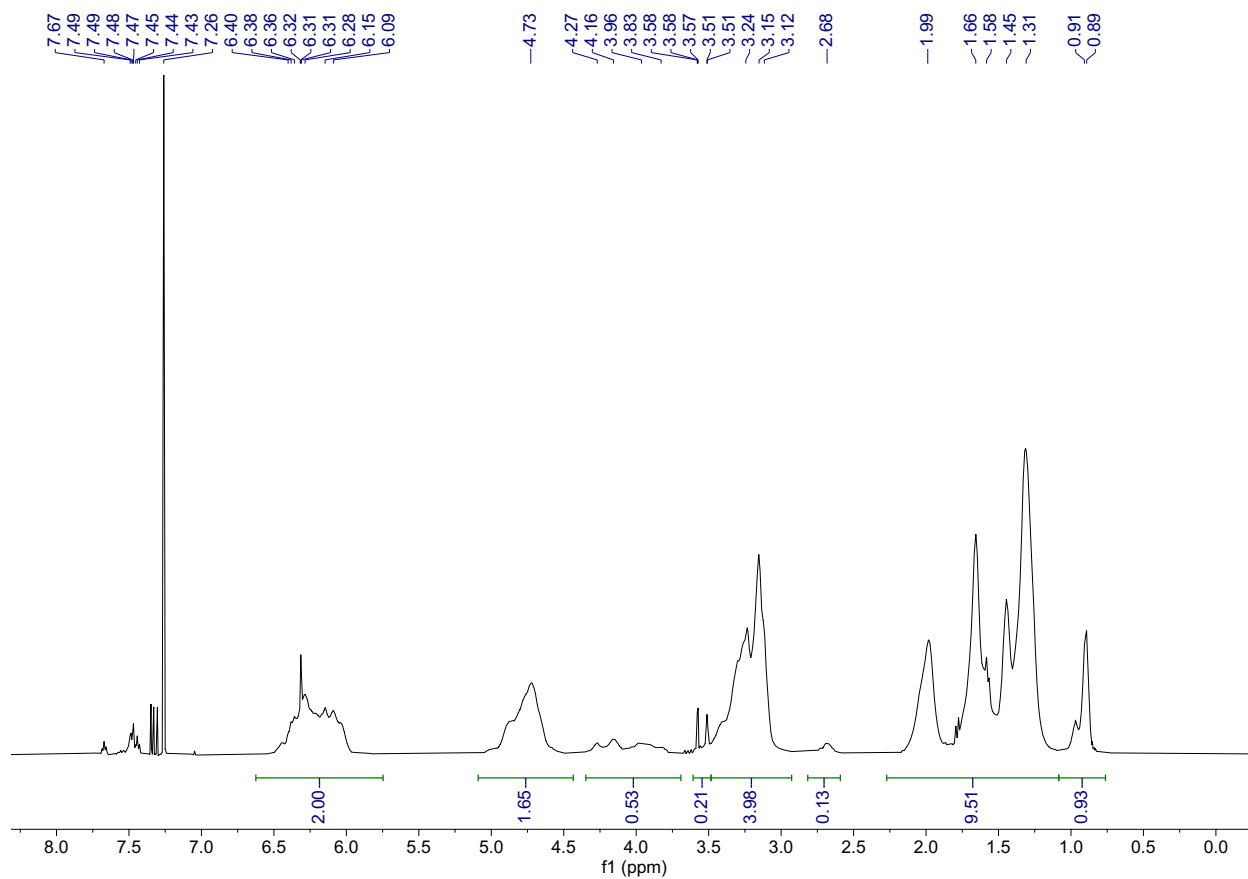




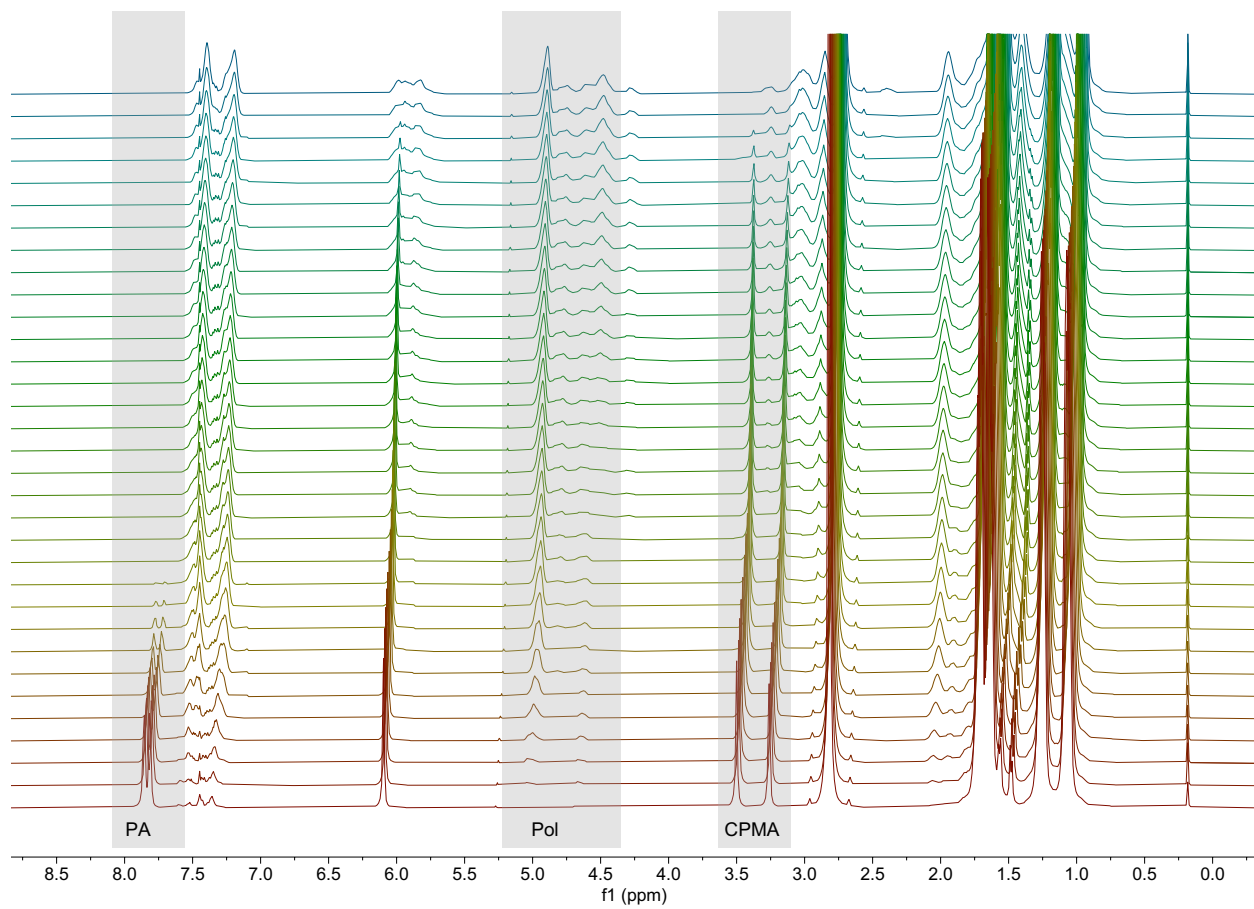
**Fig. S10**  $^1\text{H}$  NMR spectrum of CHO/CPMA-*r*-BO/CPMA in  $\text{CDCl}_3$  (Table 2, Entry 3). Resonances  $> 7.26$  ppm assignable to PPN phenyl groups.



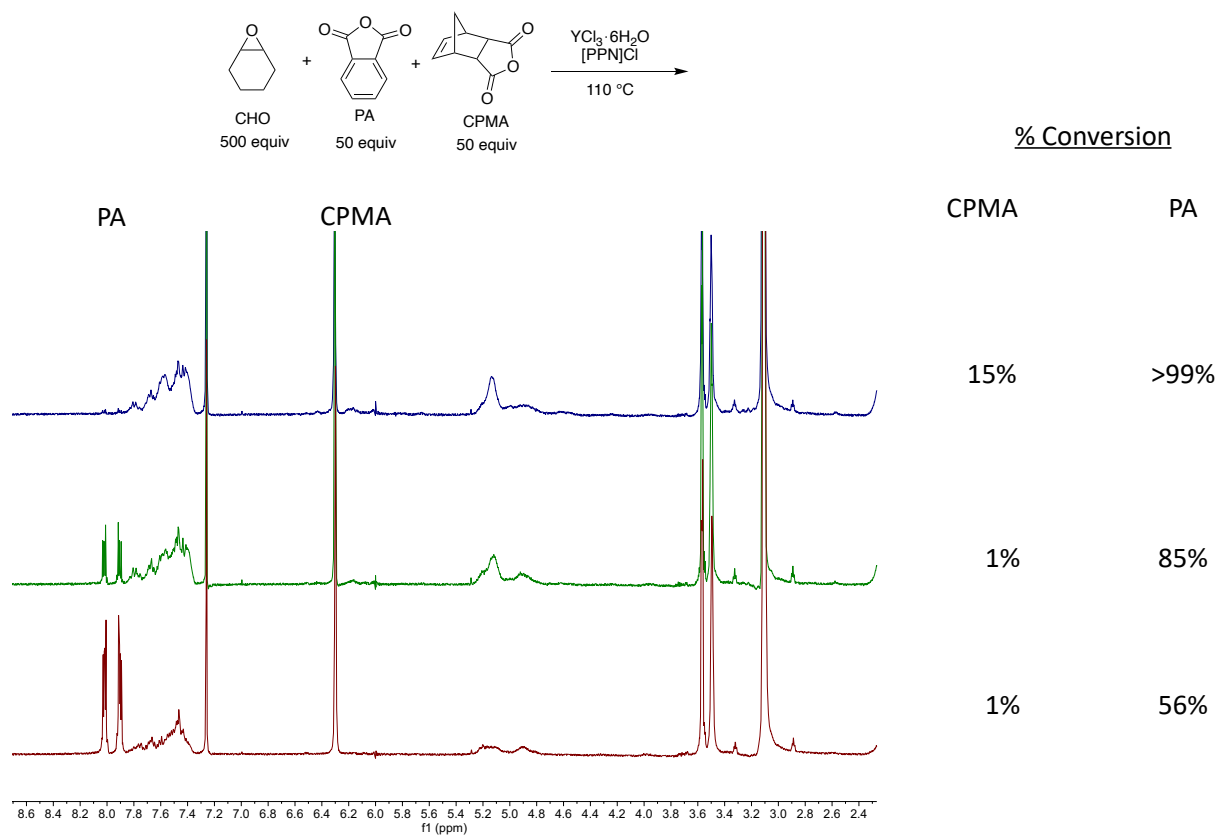
**Fig. S11**  $^1\text{H}$  NMR spectrum of CHO/CPMA-*r*-BO/CPMA in  $\text{CDCl}_3$  (Table 2, Entry 4). Resonances  $> 7.26$  ppm assignable to PPN phenyl groups.



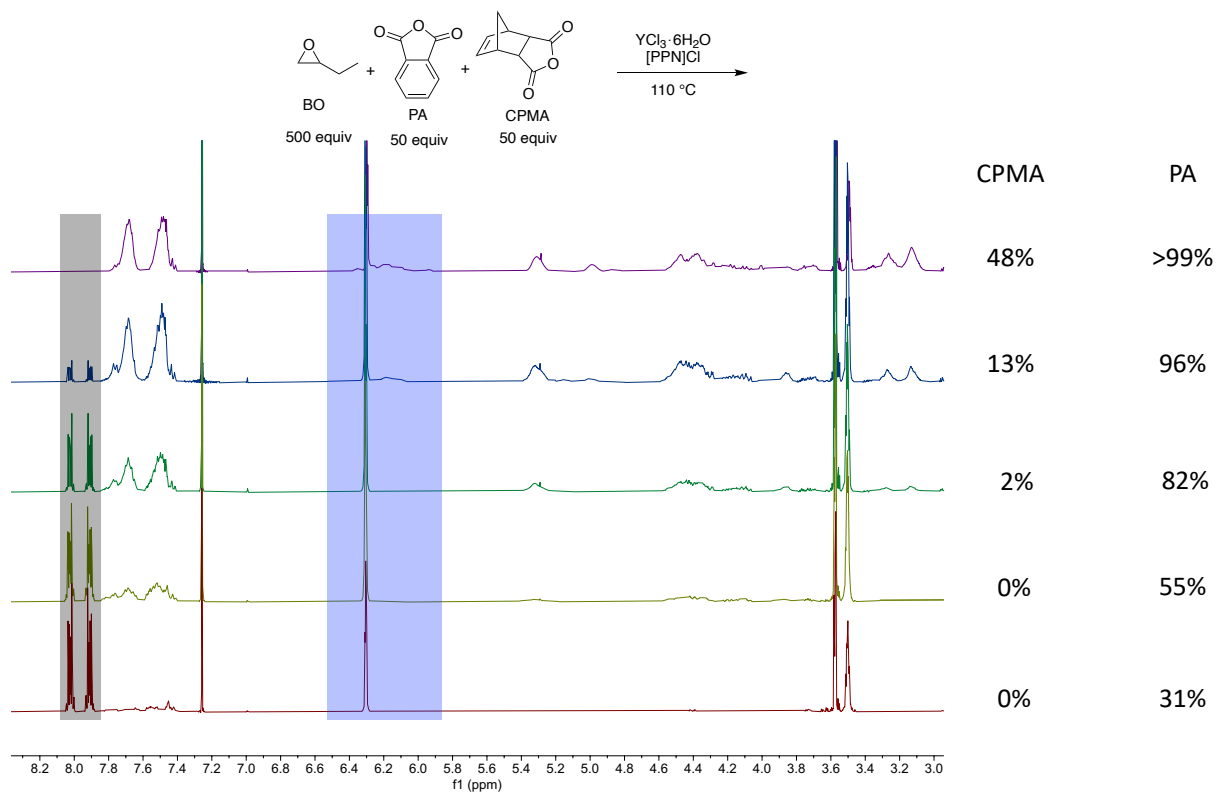
**Fig. S12**  $^1\text{H}$  NMR spectrum of CHO/CPMA-*r*-BO/CPMA in  $\text{CDCl}_3$  (Table 2, Entry 5). Resonances  $> 7.26$  ppm assignable to PPN phenyl groups.



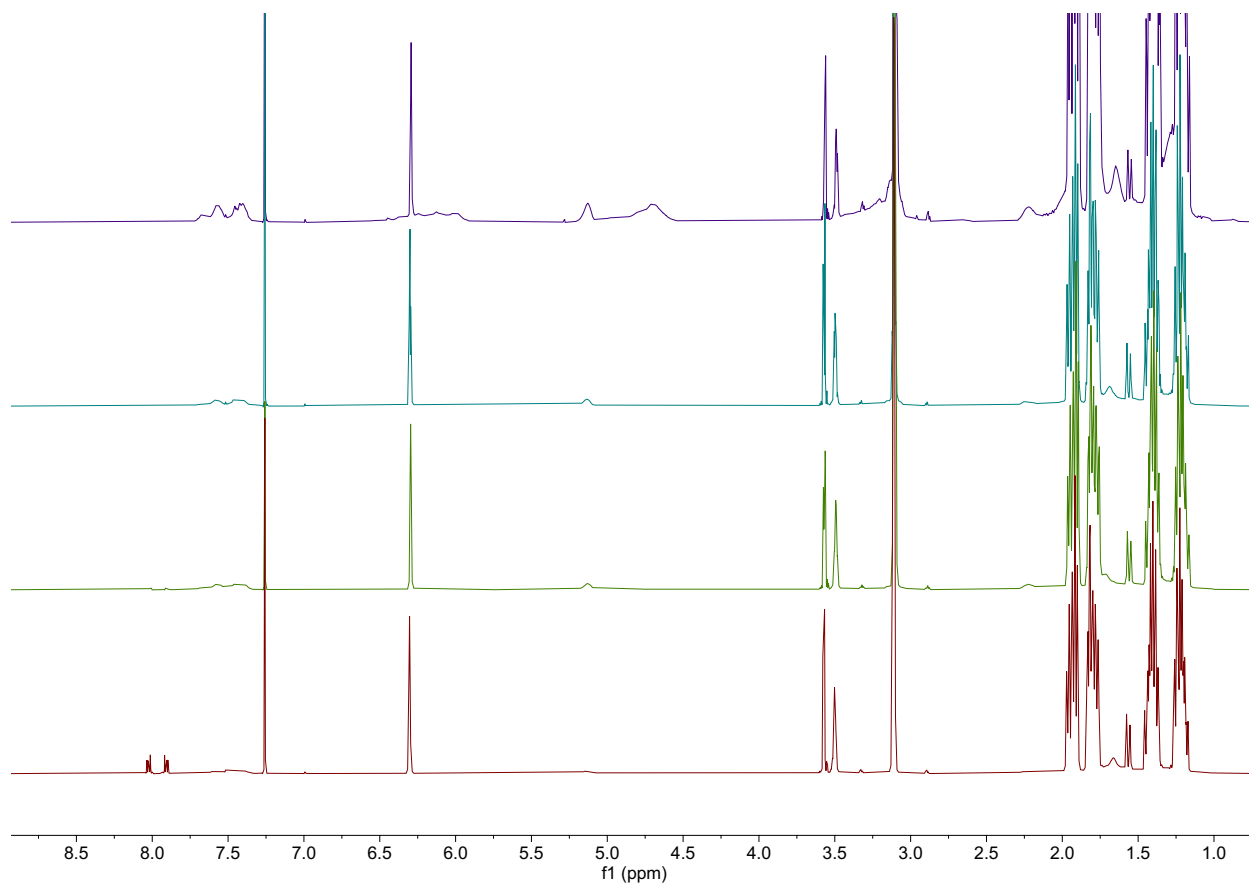
**Fig. S13**  $^1\text{H}$  NMR spectra of CHO/PA-*b*-CHO/CPMA monitored at 110 °C (Fig. 3b).



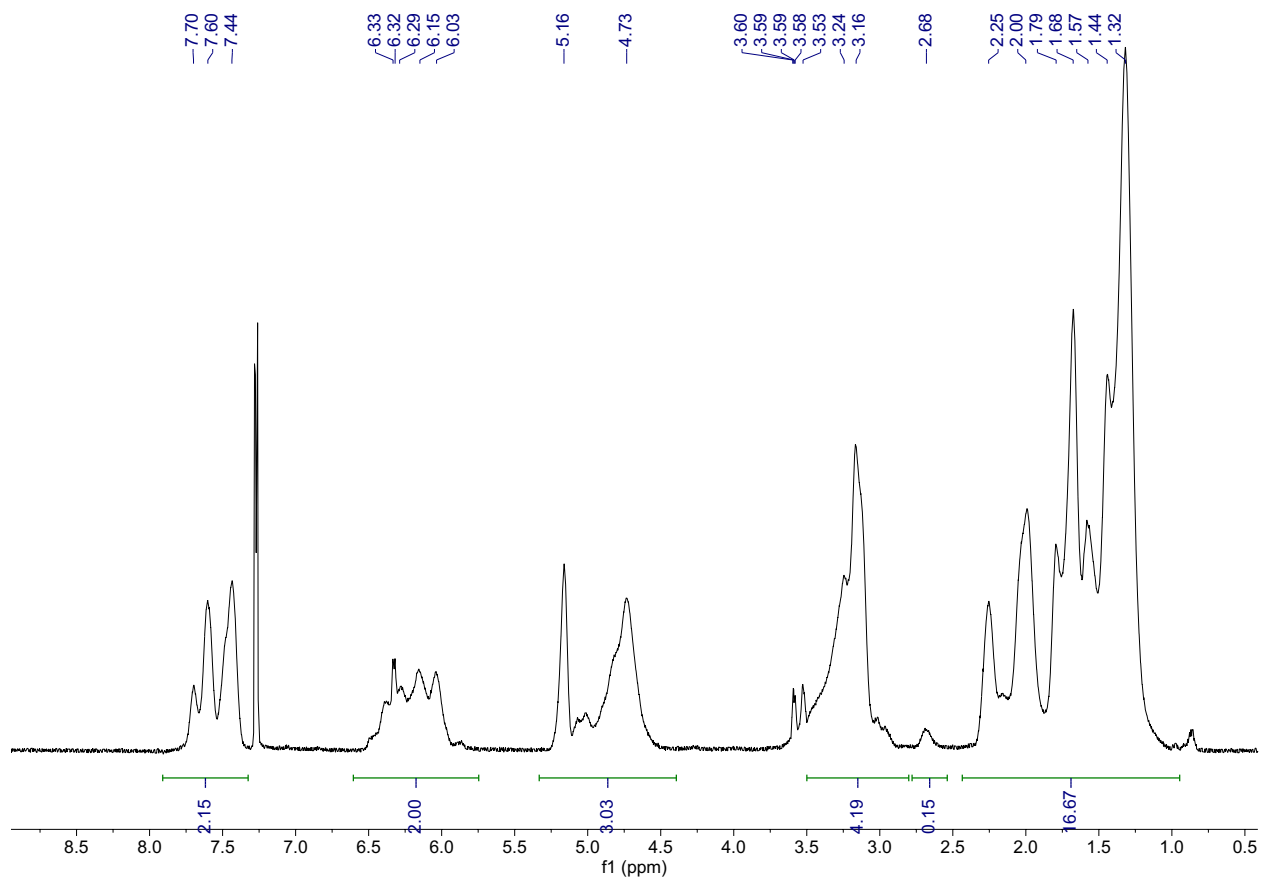
**Fig. S14**  $^1\text{H}$  NMR spectra of CHO/PA-*b*-CHO/CPMA in  $\text{CDCl}_3$  monitored by aliquots.



**Fig. S15**  $^1\text{H}$  NMR spectra of BO/PA-*b*-BO/CPMA in  $\text{CDCl}_3$  monitored by aliquots.

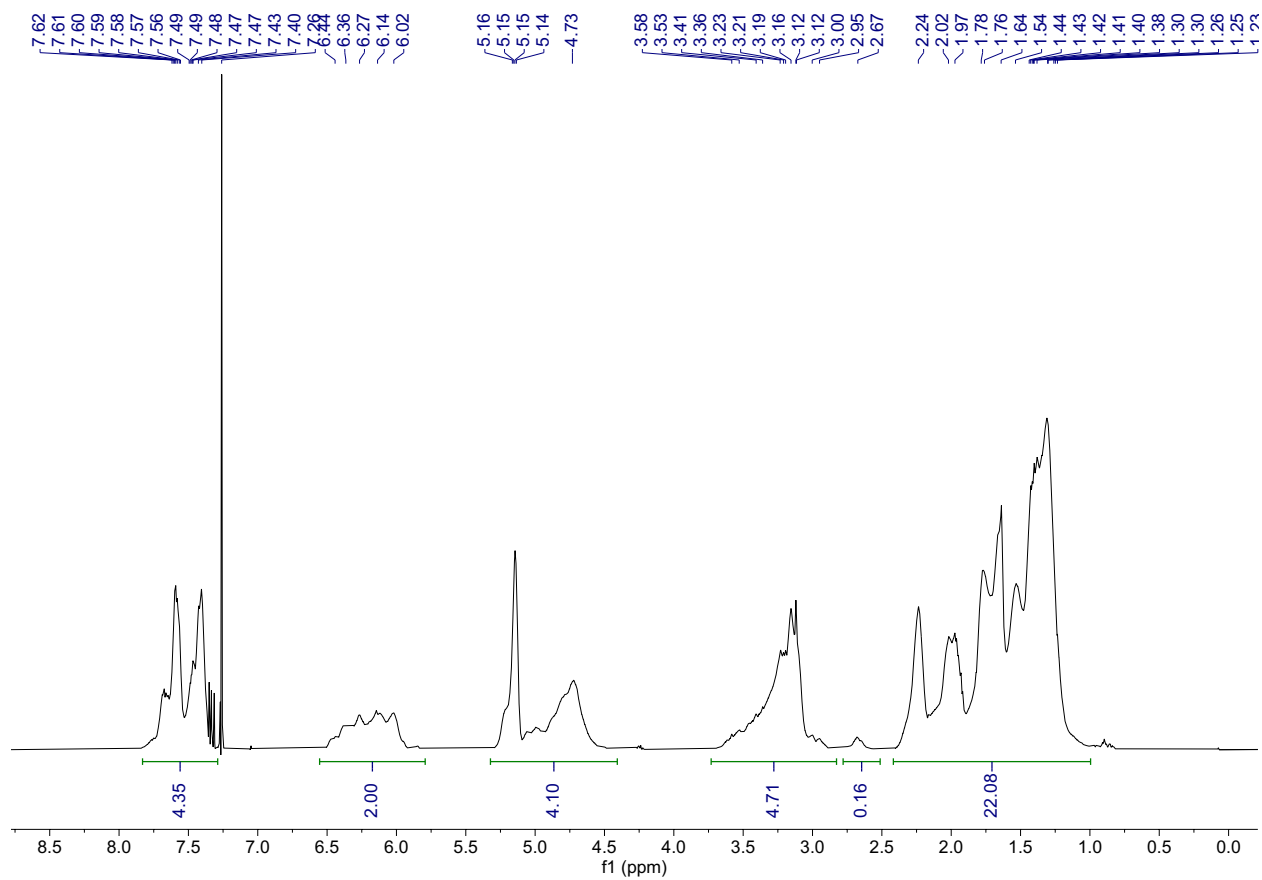


**Fig. S16** <sup>1</sup>H NMR spectra of aliquots for CHO/PA-*b*-CHO/CPMA in CDCl<sub>3</sub> (Table S4, Entry 1). Aliquots taken at 30 min, 1 hr, 1.5 hr, and 4 hr.

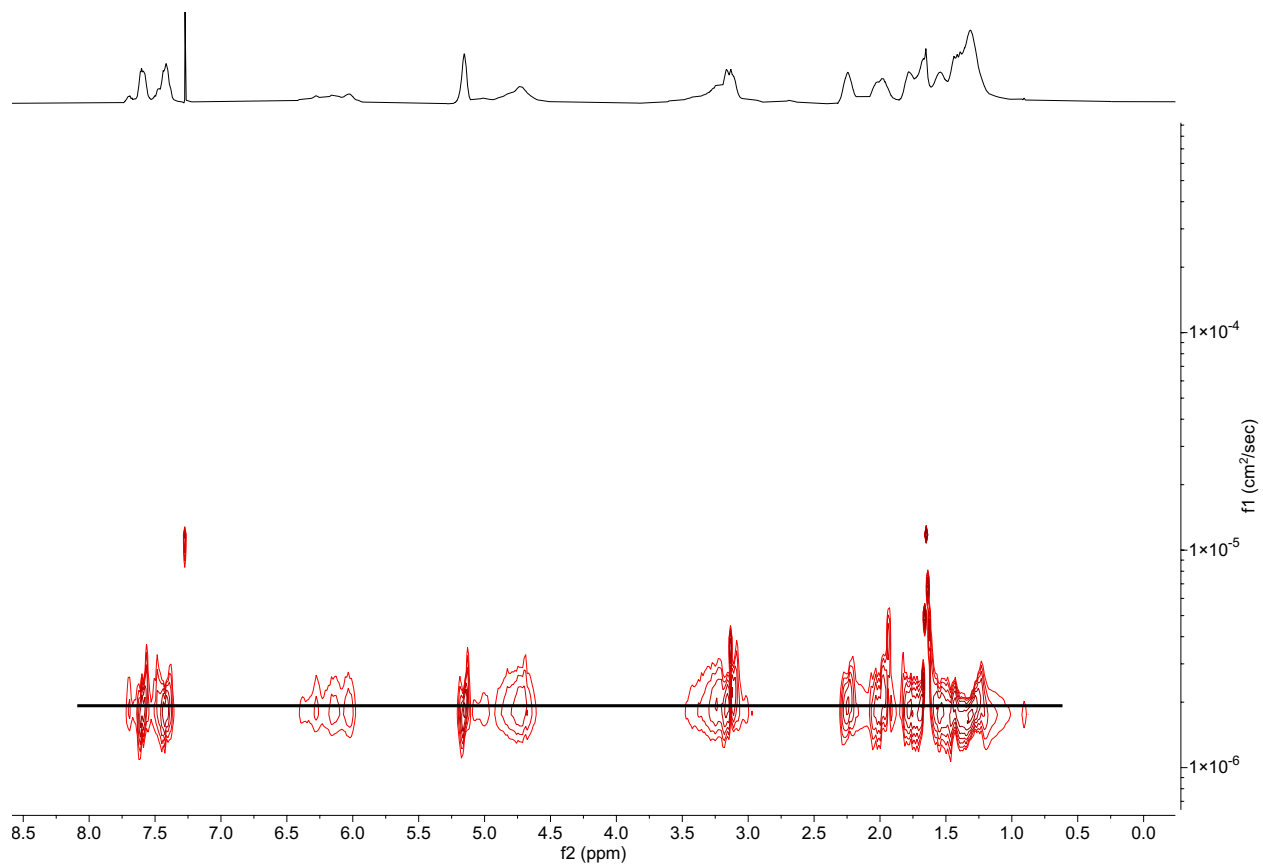


**Fig. S17**  $^1\text{H}$  NMR of CHO/PA-*b*-CHO/CPMA in  $\text{CDCl}_3$  (Table S4, Entry 1)

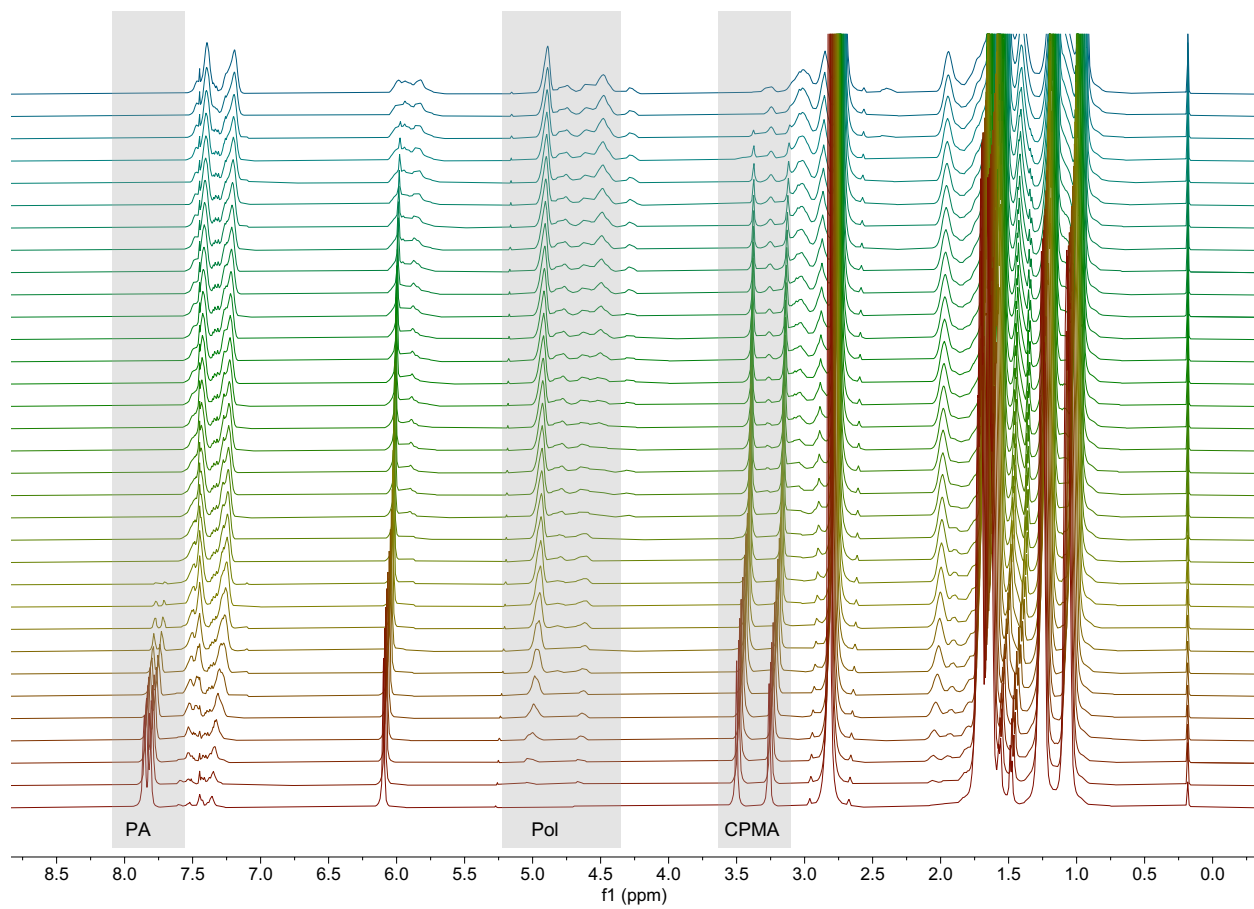




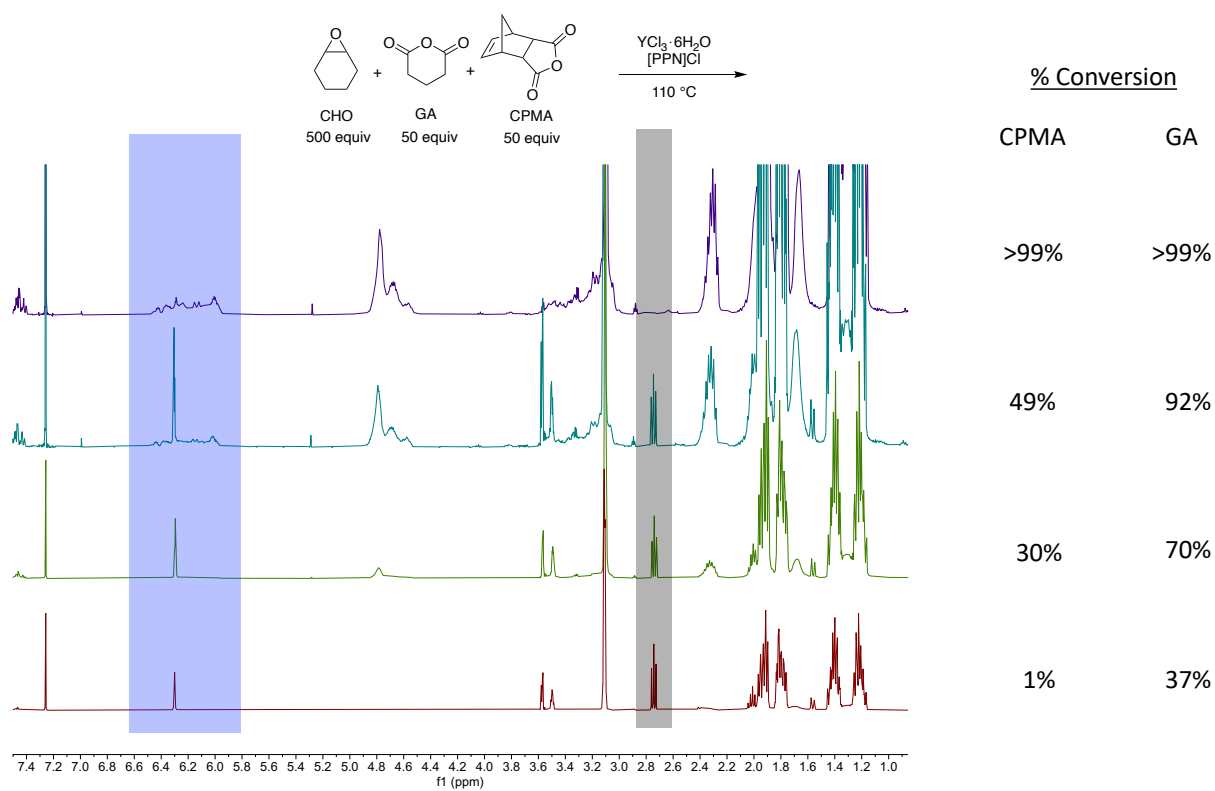
**Fig. S18**  $^1\text{H}$  NMR of CHO/PA-*b*-CHO/CPMA in  $\text{CDCl}_3$  (Table S4, Entry 2).



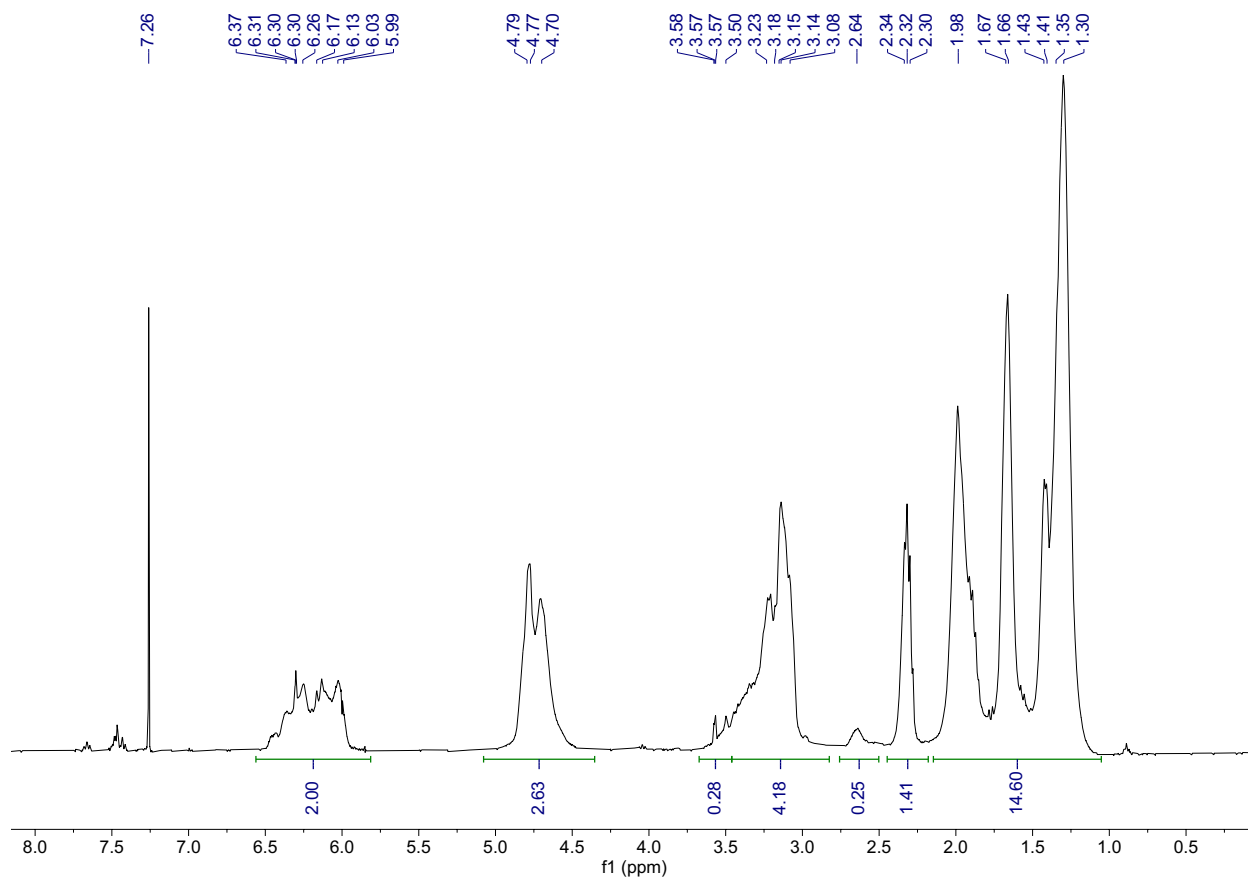
**Fig. S19**  $^1\text{H}$  DOSY of CHO/PA-*b*-CHO/CPMA in  $\text{CDCl}_3$  (Table S4, Entry 2).



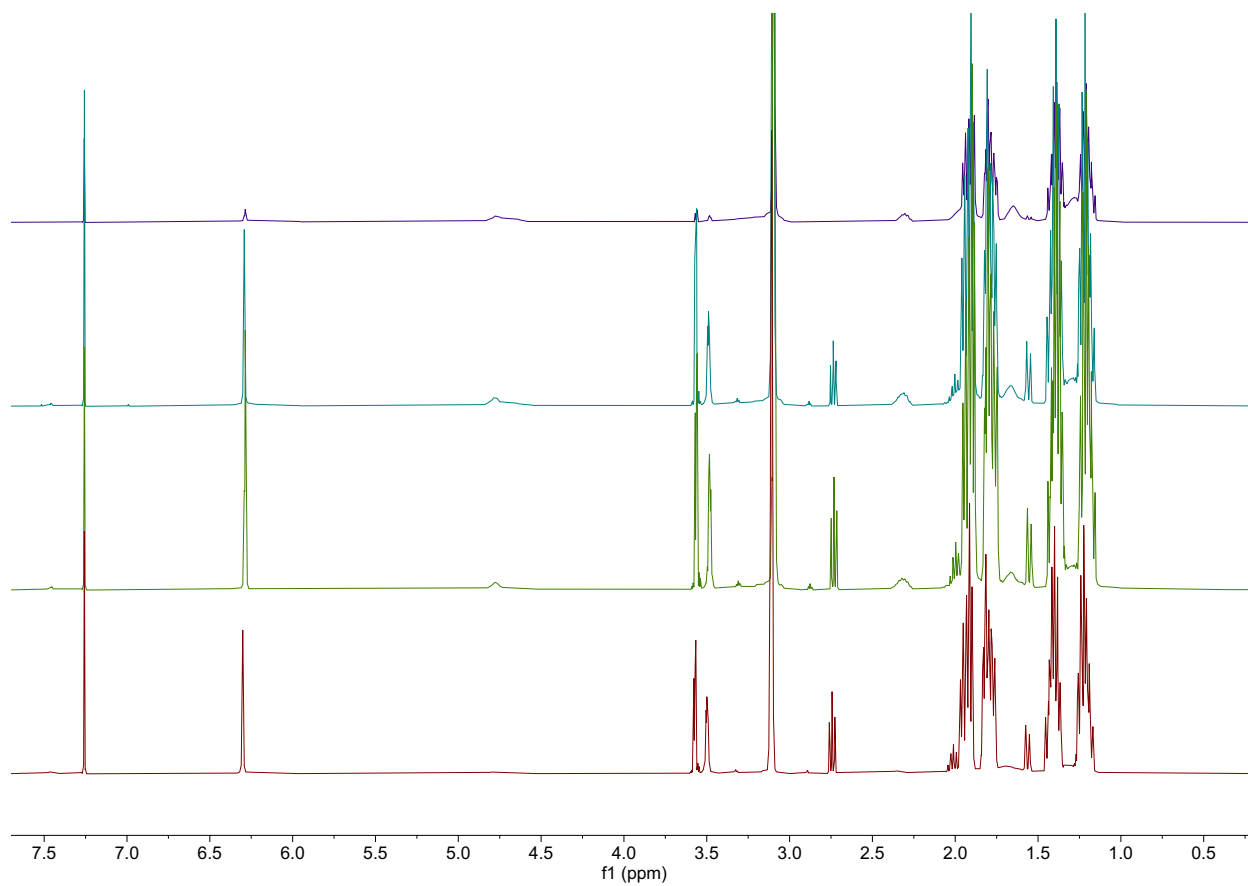
**Fig. S20** <sup>1</sup>H NMR spectra of CHO/GA-*r*-CHO/CPMA monitored at 110 °C (Fig. 3c).



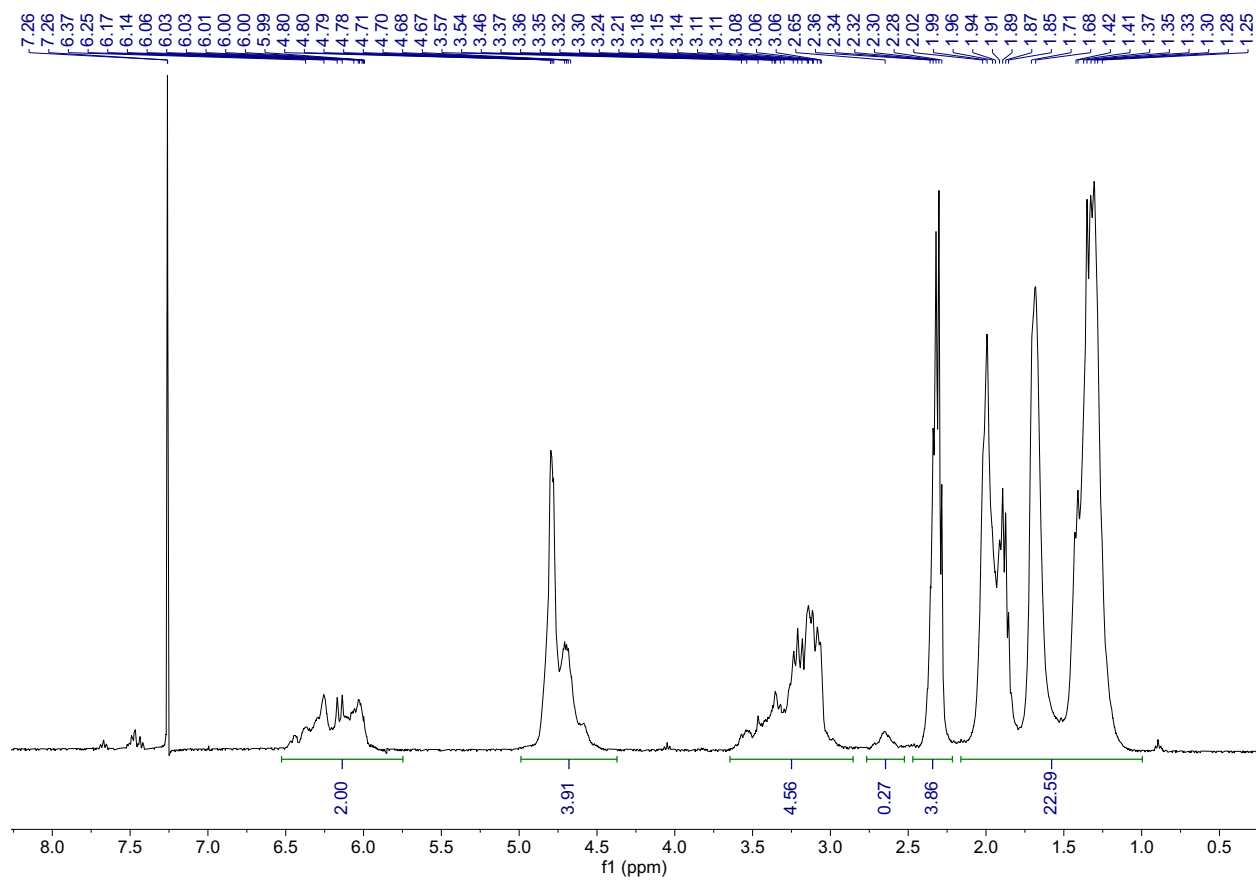
**Fig. S21**  $^1\text{H}$  NMR spectra of CHO/GA-*r*-CHO/CPMA in  $\text{CDCl}_3$  monitored by aliquots.



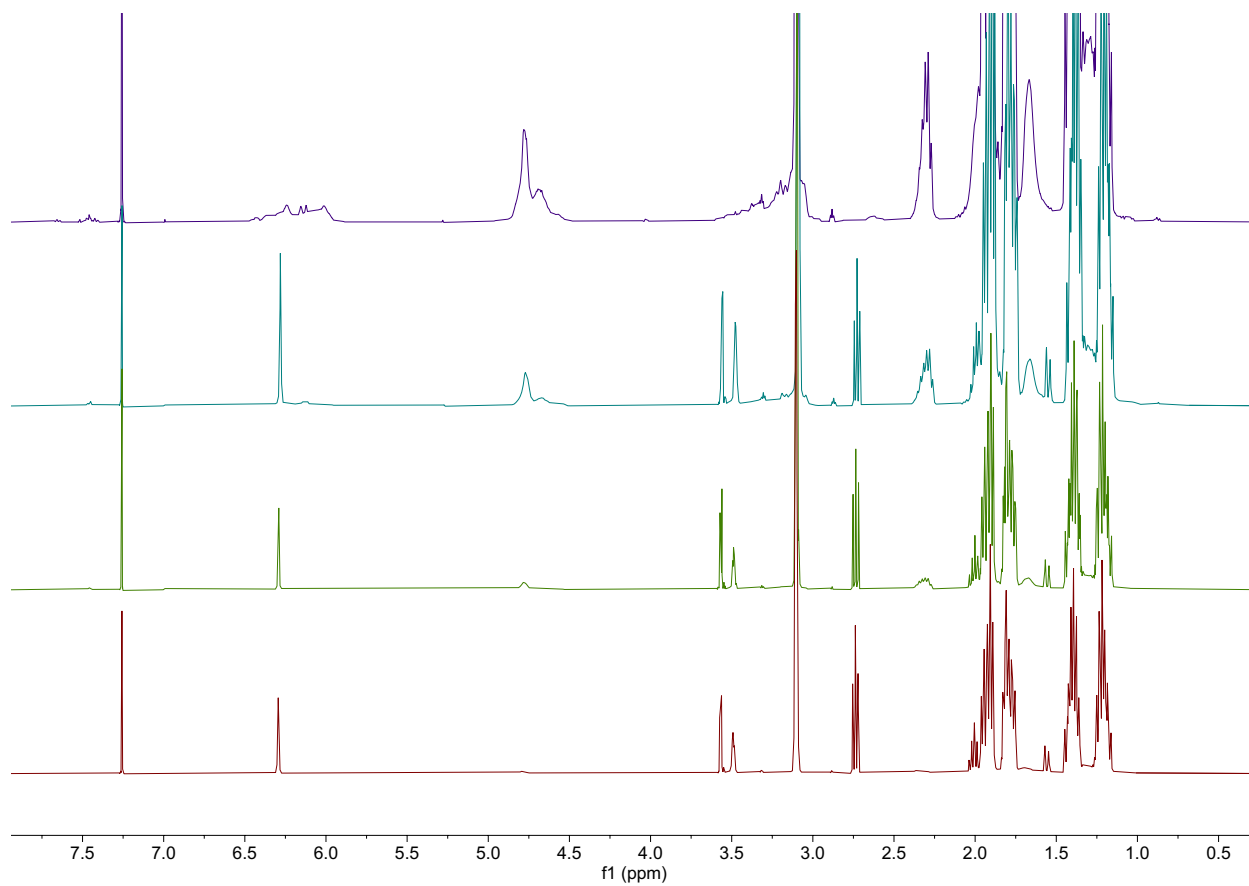
**Fig. S22**  $^1\text{H}$  NMR spectrum of CHO/GA-*r*-CHO/CPMA in  $\text{CDCl}_3$  (Table S4, Entry 3).



**Fig. S23** <sup>1</sup>H NMR spectra stack of CHO/GA-*r*-CHO/CPMA in CDCl<sub>3</sub> (Table S4, Entry 3). Aliquots taken at 30 min, 1 hr, 1.5 hr, and 4 hr (from bottom to top).

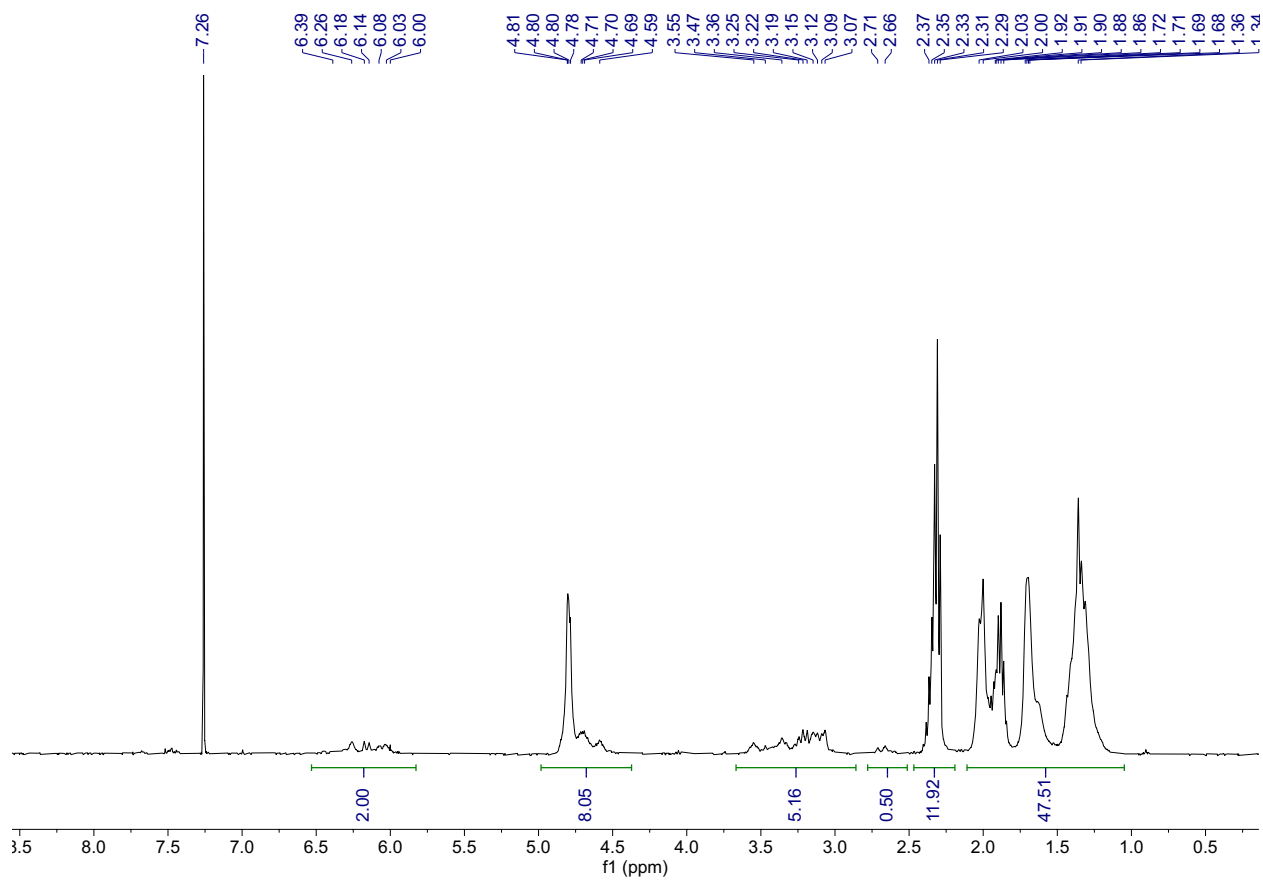


**Fig. S24**  $^1\text{H}$  NMR of CHO/GA-*r*-CHO/CPMA in  $\text{CDCl}_3$  (Table S4, Entry 4).

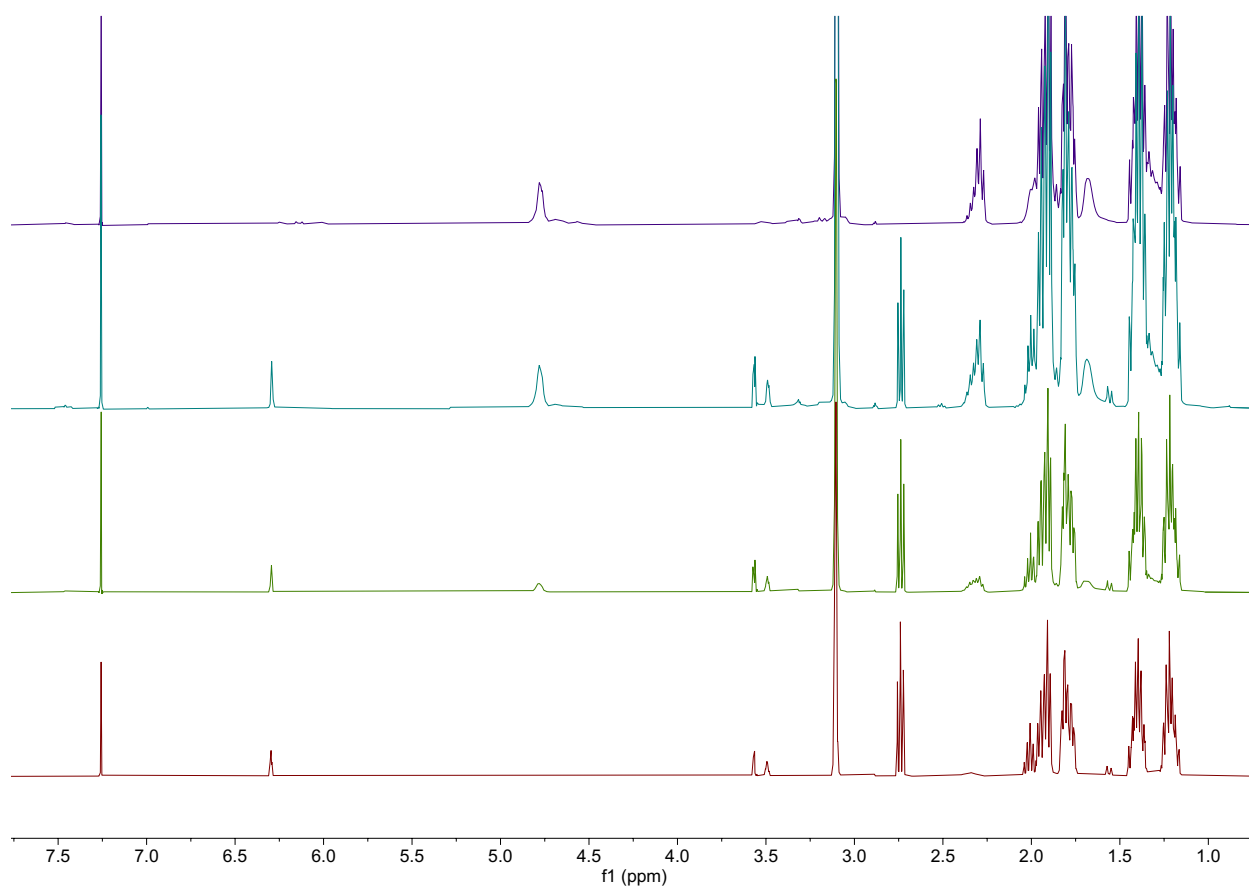


**Fig. S25** <sup>1</sup>H NMR spectra stack of CHO/GA-*r*-CHO/CPMA in CDCl<sub>3</sub> (Table S4, Entry 4). Aliquots taken at 30 min, 1 hr, 1.5 hr, and 4 hr (from bottom to top).

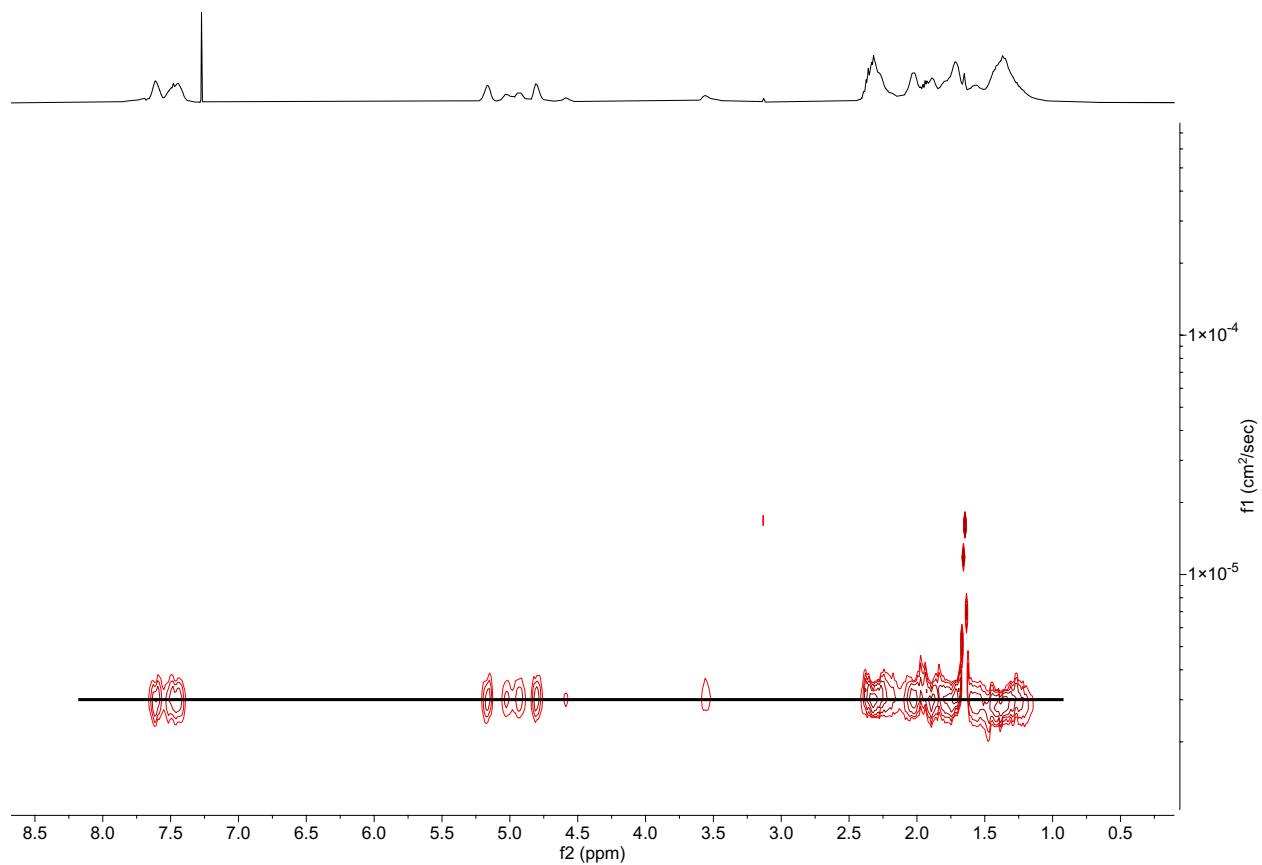




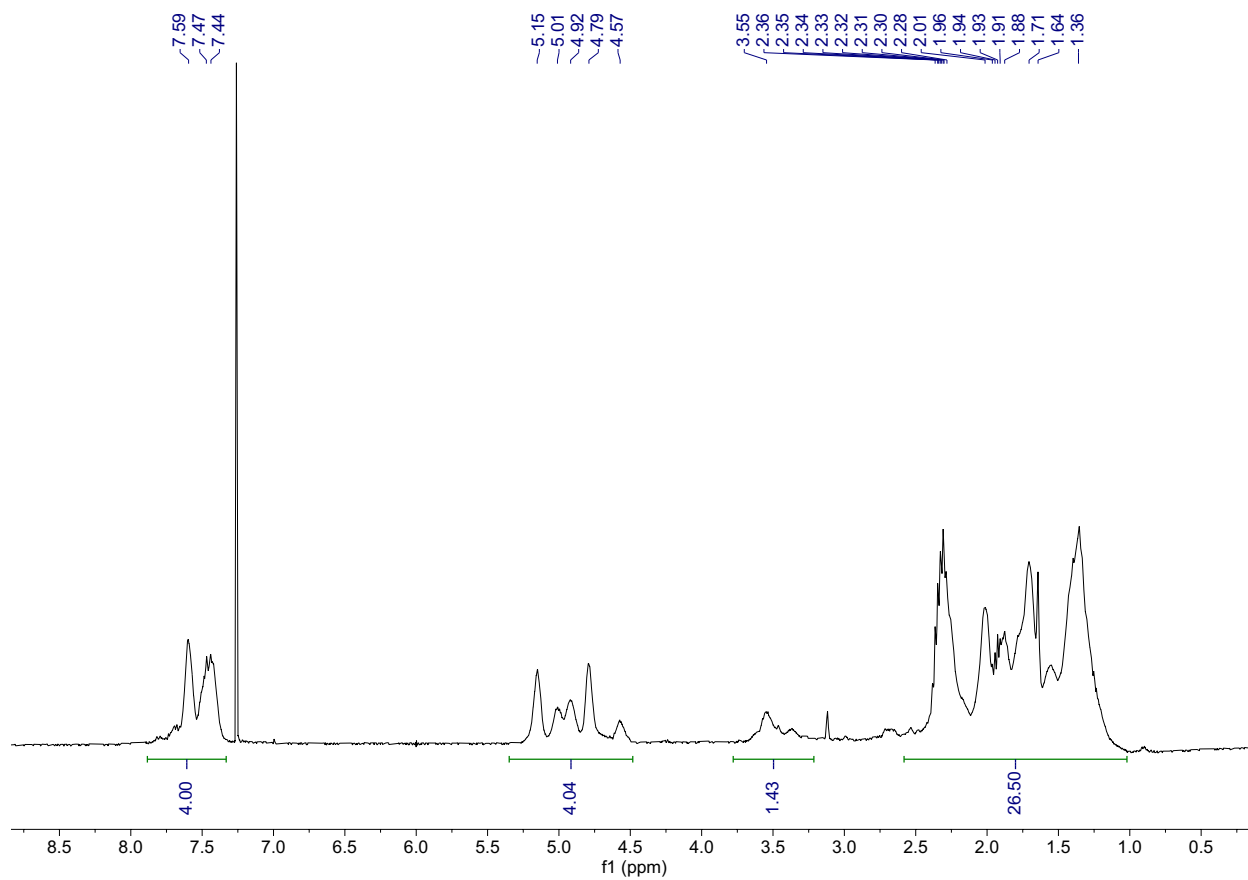
**Fig. S26**  $^1\text{H}$  NMR of CHO/GA-*r*-CHO/CPMA in  $\text{CDCl}_3$  (Table S4, Entry 5).



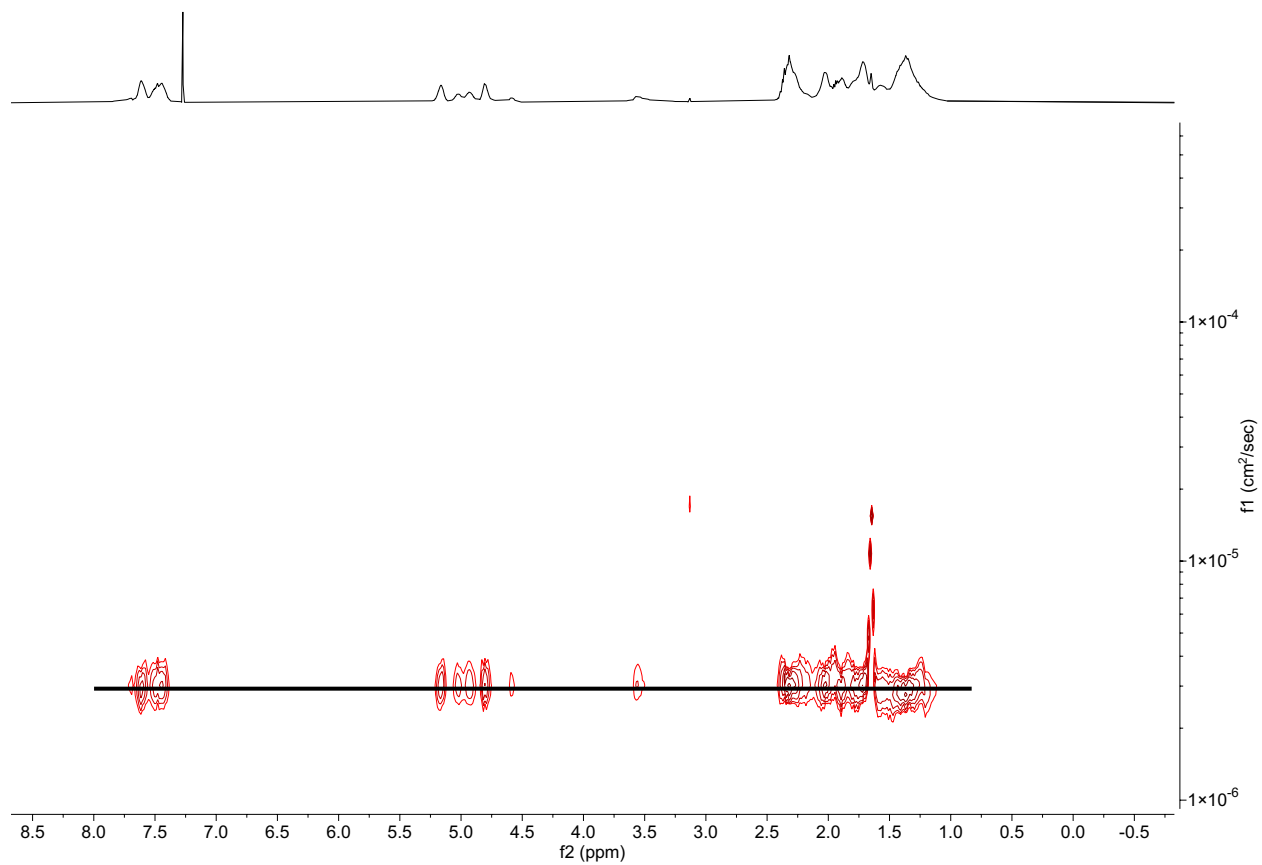
**Fig. S27** <sup>1</sup>H NMR spectra stack of CHO/GA-*r*-CHO/CPMA in CDCl<sub>3</sub> (Table S4, Entry 5). Aliquots taken at 30 min, 1 hr, 1.5 hr, and 4 hr (from bottom to top).



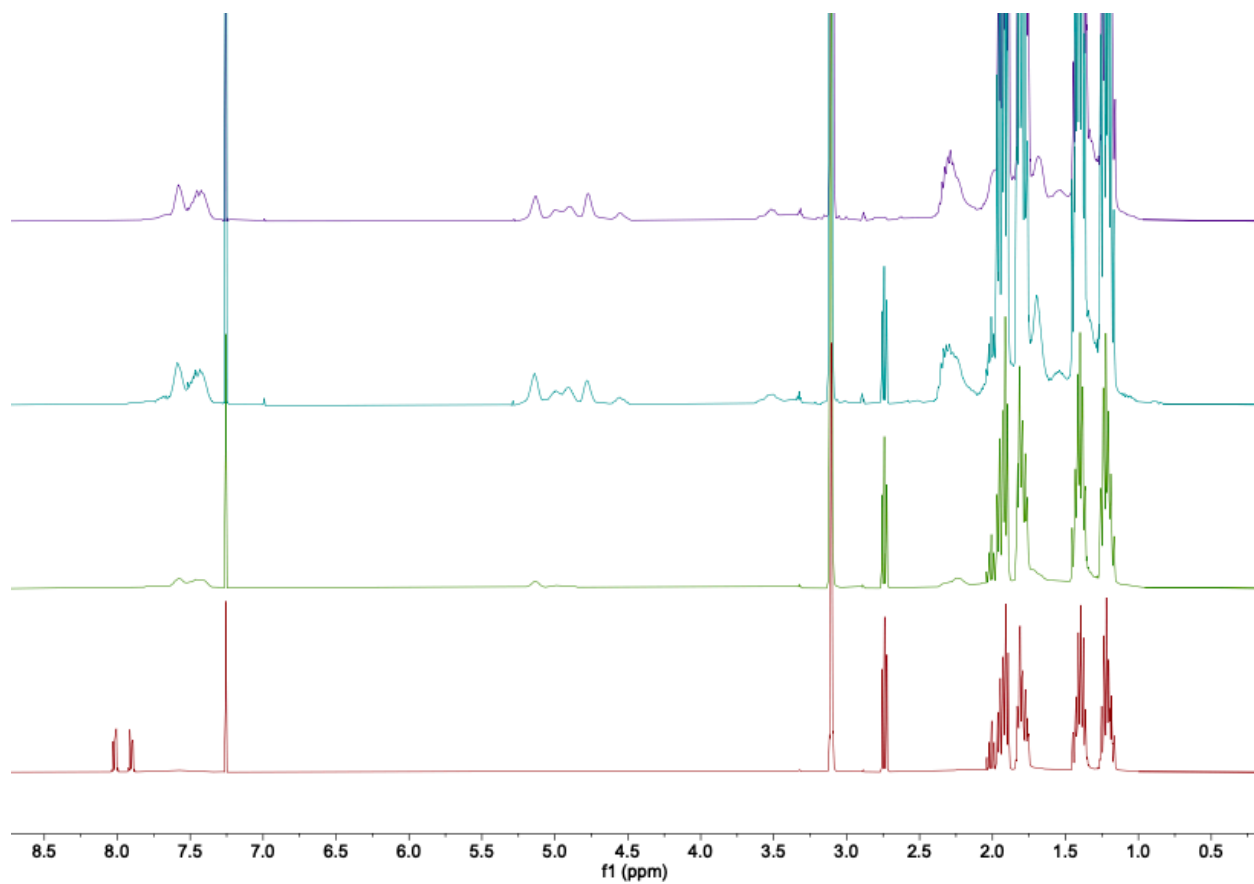
**Fig. S28**  $^1\text{H}$  DOSY of CHO/GA-*r*-CHO/CPMA in  $\text{CDCl}_3$  (Table S4, Entry 5).



**Fig. S29** <sup>1</sup>H NMR of CHO/PA-*r*-CHO/GA in CDCl<sub>3</sub> (Table S4, Entry 6).

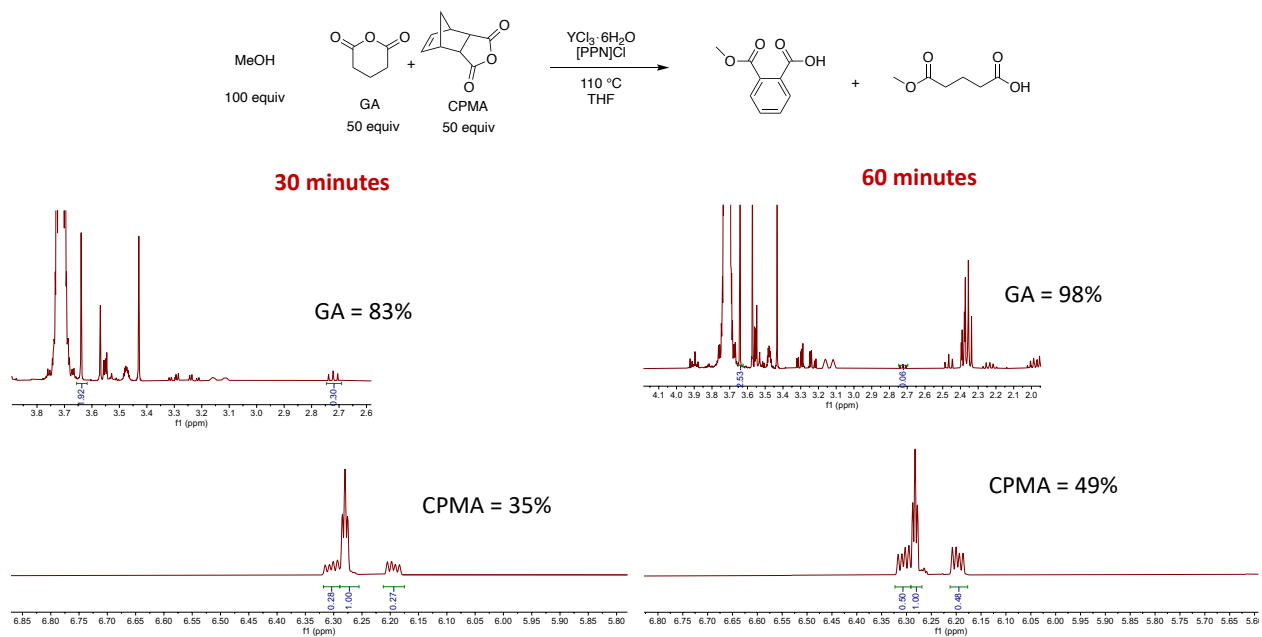


**Fig. S30**  $^1\text{H}$  DOSY of CHO/PA-*r*-CHO/GA in  $\text{CDCl}_3$  (Table S4, Entry 6).

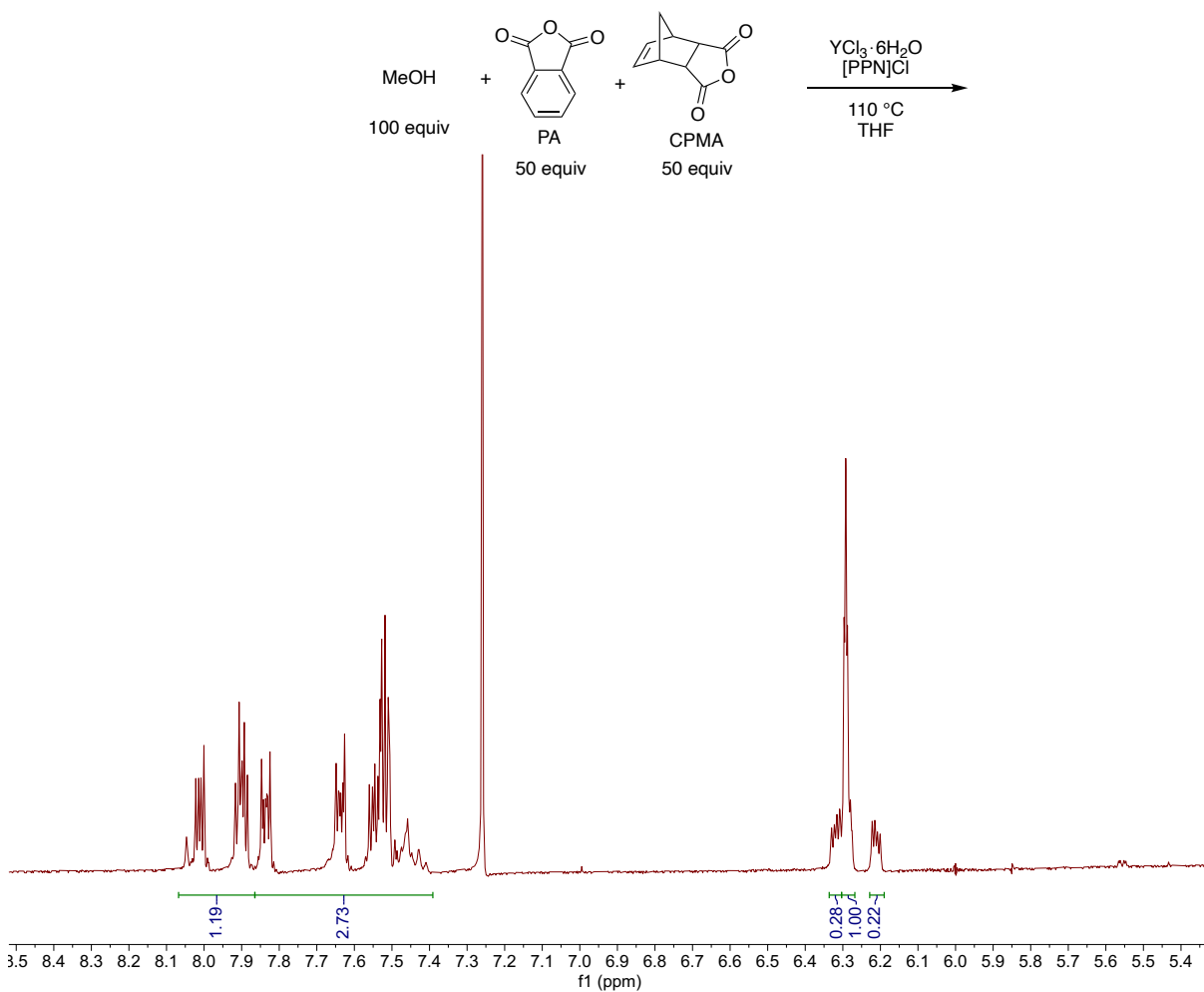


**Fig. S31** <sup>1</sup>H NMR spectra stack of CHO/GA-*r*-CHO/CPMA in CDCl<sub>3</sub> (Table S4, Entry 6). Aliquots taken at 30 min, 1 hr, 1.5 hr, and 4 hr (from bottom to top).

**5.2 Anhydride ring-opening studies.** To get reactivity ratios between anhydride mixtures, we adopted a procedure from Satoh and coworkers that involves the use of an alcohol and observing the ring opened anhydride products by  $^1\text{H}$  NMR.<sup>4</sup>



**Fig. S32**  $^1\text{H}$  NMR analysis of aliquots from the reaction of GA and CPMA with 100 equivalents of MeOH, catalyzed by  $\text{YCl}_3 \cdot 6\text{H}_2\text{O}/[\text{PPN}]\text{Cl}$ . Reaction was performed in THF and heated at  $110^\circ\text{C}$ . Aliquots taken at 30 minutes and 60 minutes.



**Fig. S33**  $^1\text{H}$  NMR analysis of aliquots from the reaction of PA and CPMA with 100 equivalents of MeOH, catalyzed by  $\text{YCl}_3 \cdot 6\text{H}_2\text{O}/[\text{PPN}]\text{Cl}$ . Reaction was performed in THF and heated at  $110^\circ\text{C}$ . Aliquot taken at 1 hr. Ring-opening of CPMA occurs before ring-opening of PA is complete, conflicting with data from Fig. S60.



## 6. GPC Data

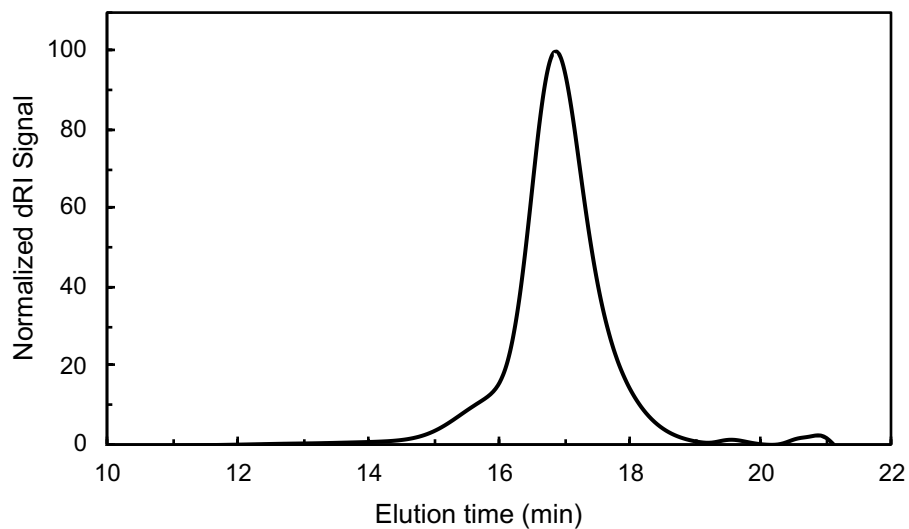


Fig. S34 GPC trace corresponding to Table 2, Entry 1.

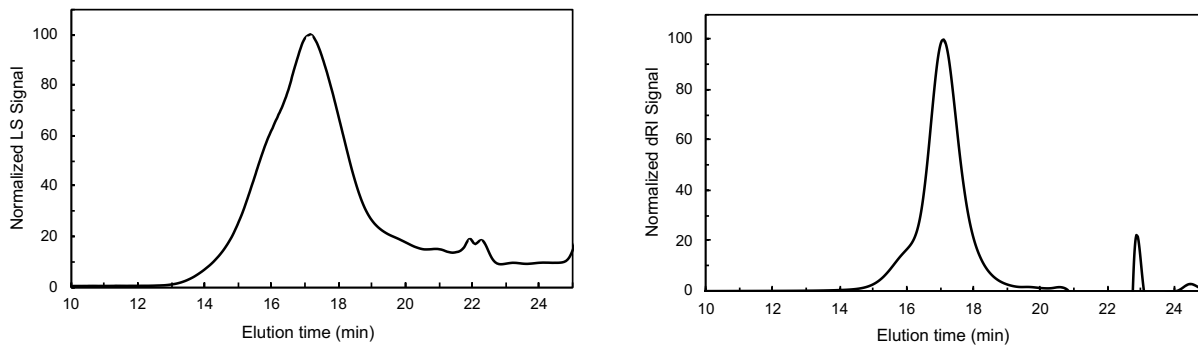
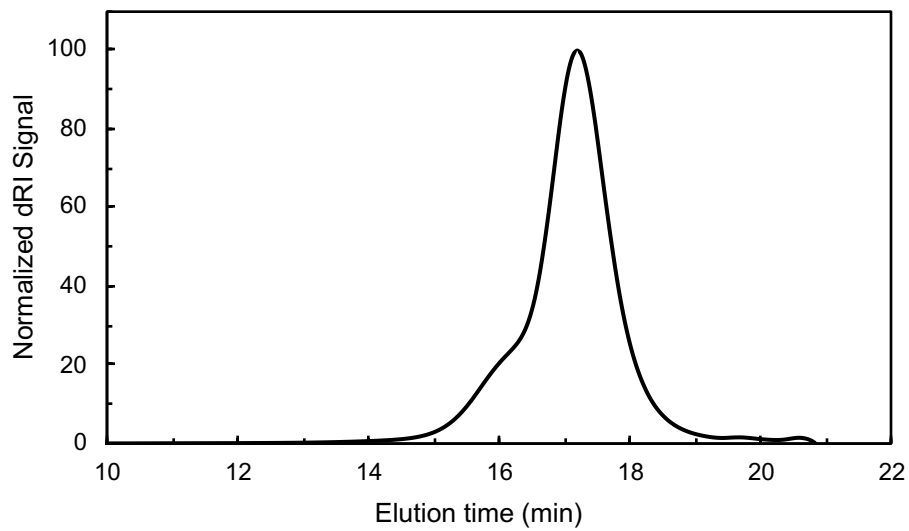
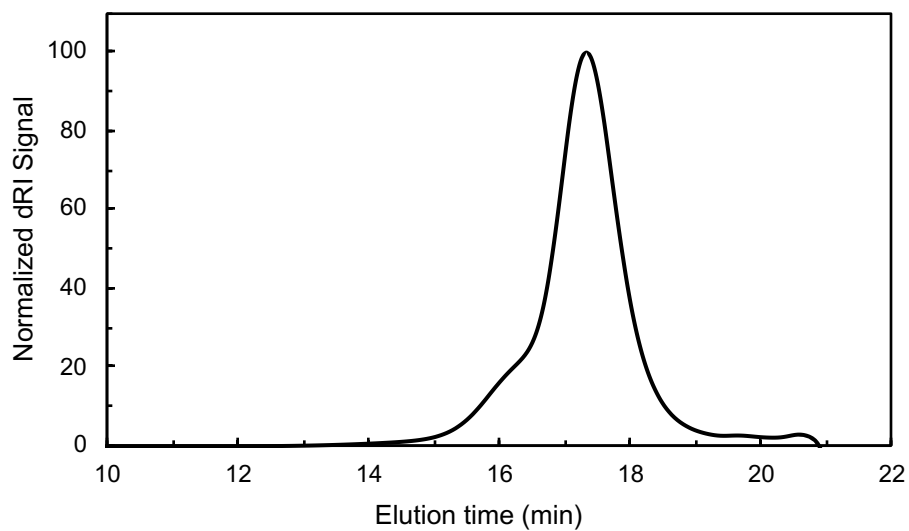


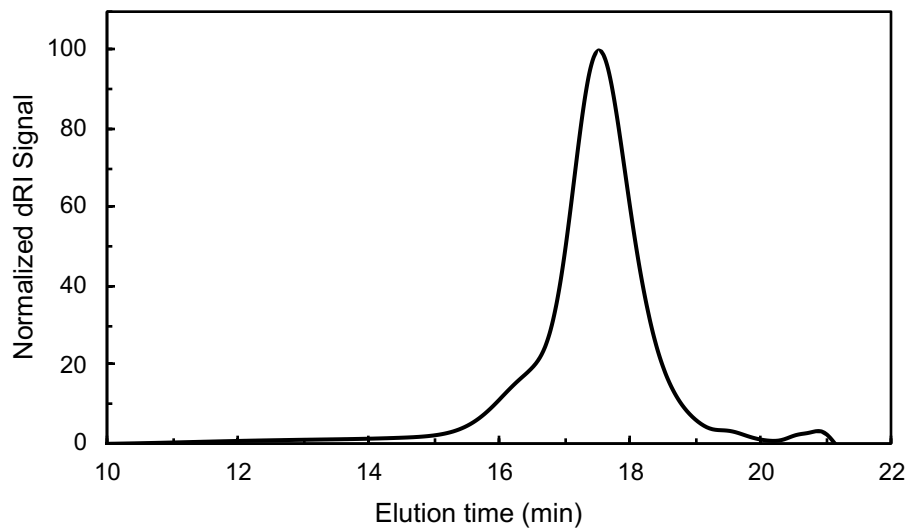
Fig. S35 GPC traces (MALS detector left, RI detector right) corresponding to Table 2, Entry 2.



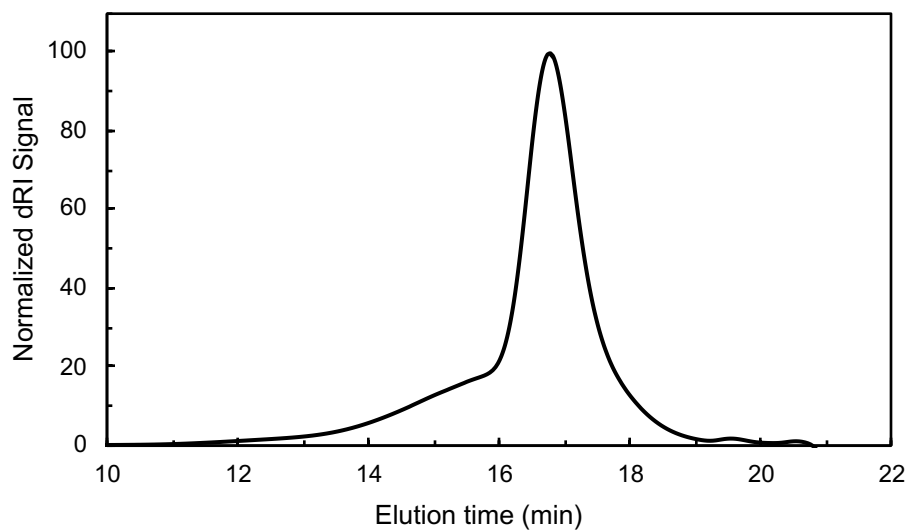
**Fig. S36** GPC trace corresponding to Table 2, Entry 3.



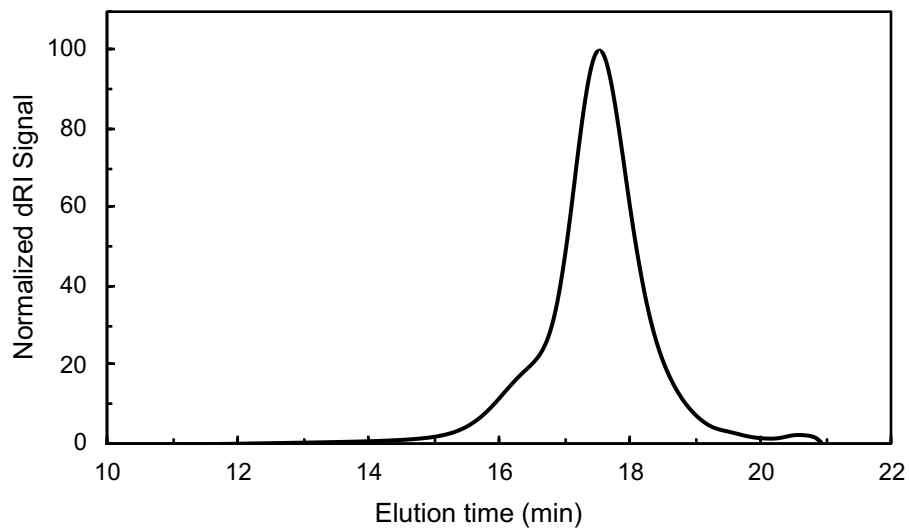
**Fig. S37** GPC trace corresponding to Table 2, Entry 4.



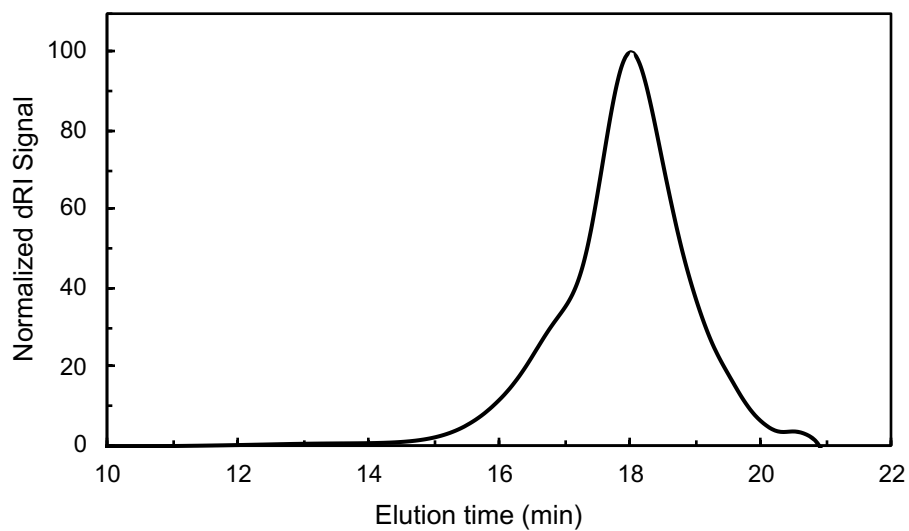
**Fig. S38** GPC trace corresponding to Table 2, Entry 5.



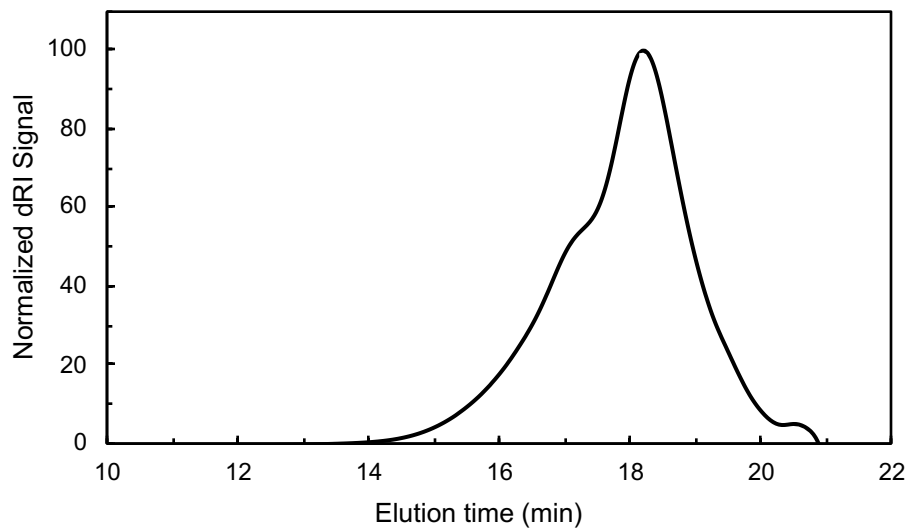
**Fig. S39** GPC trace corresponding to Table S3, Entry 1.



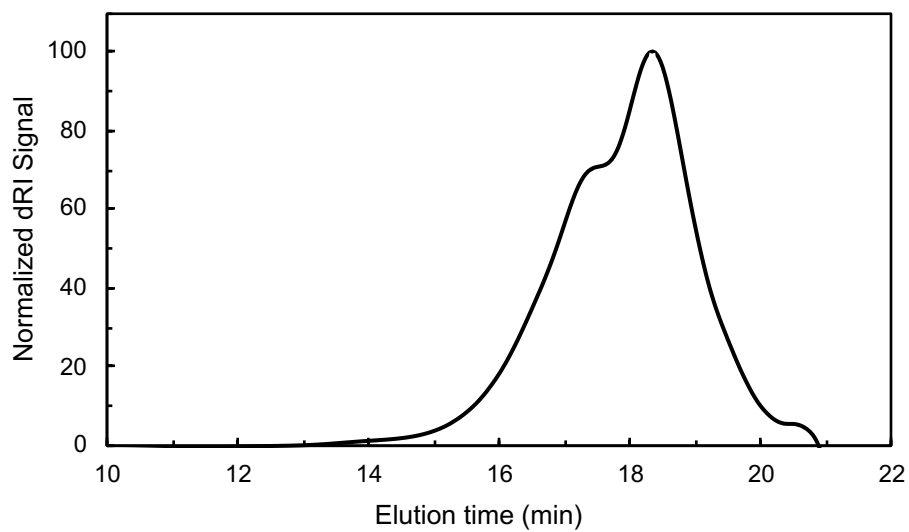
**Fig. S40** GPC trace corresponding to Table S3, Entry 7.



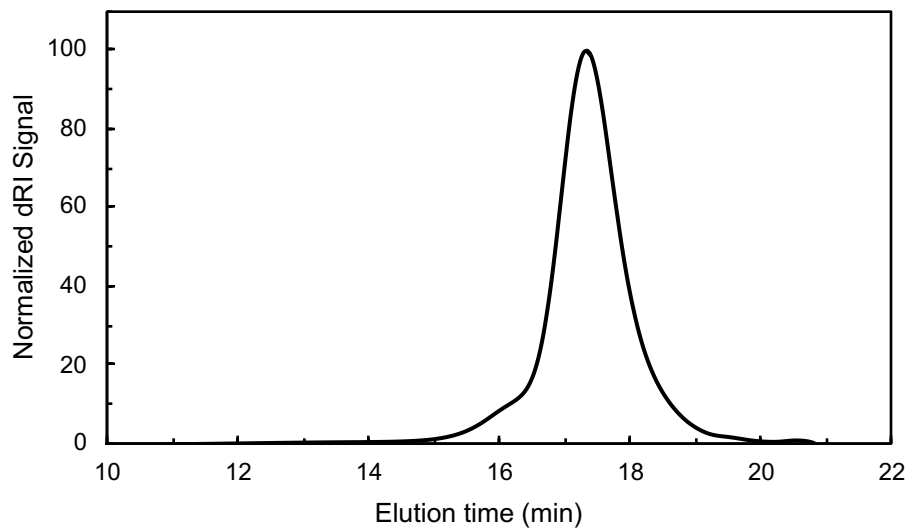
**Fig. S41** GPC trace corresponding to Table S4, Entry 3.



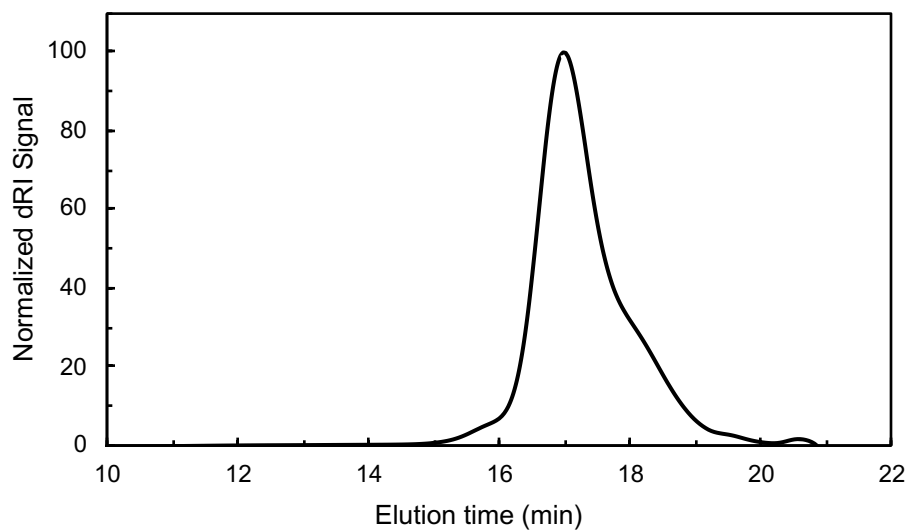
**Fig. S42** GPC trace corresponding to Table S4, Entry 4.



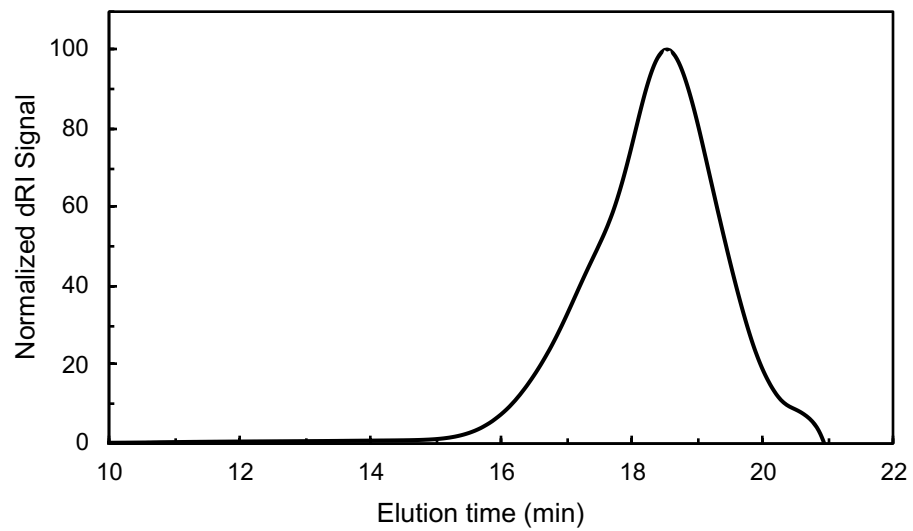
**Fig. S43** GPC trace corresponding to Table S4, Entry 5.



**Fig. S44** GPC trace corresponding to Table S4, Entry 1.

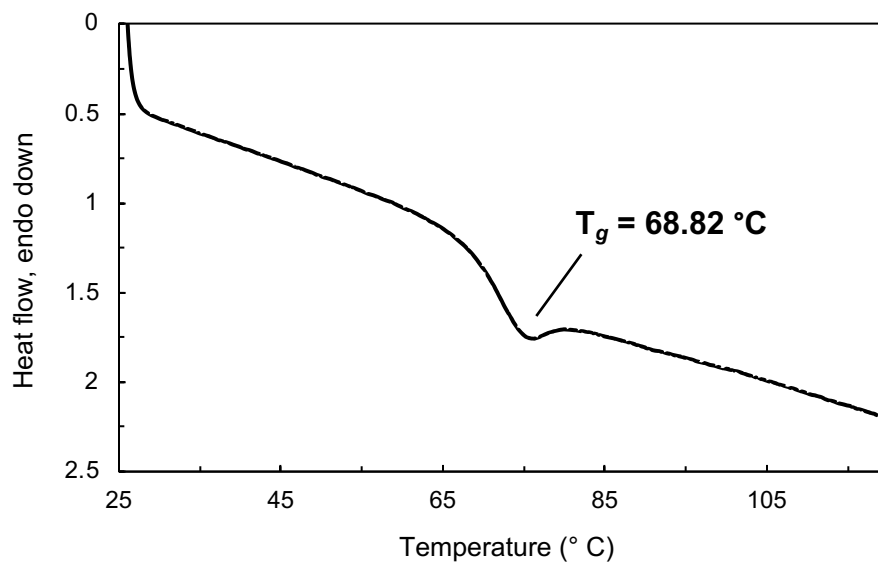


**Fig. S45** GPC trace corresponding to Table S4, Entry 2.

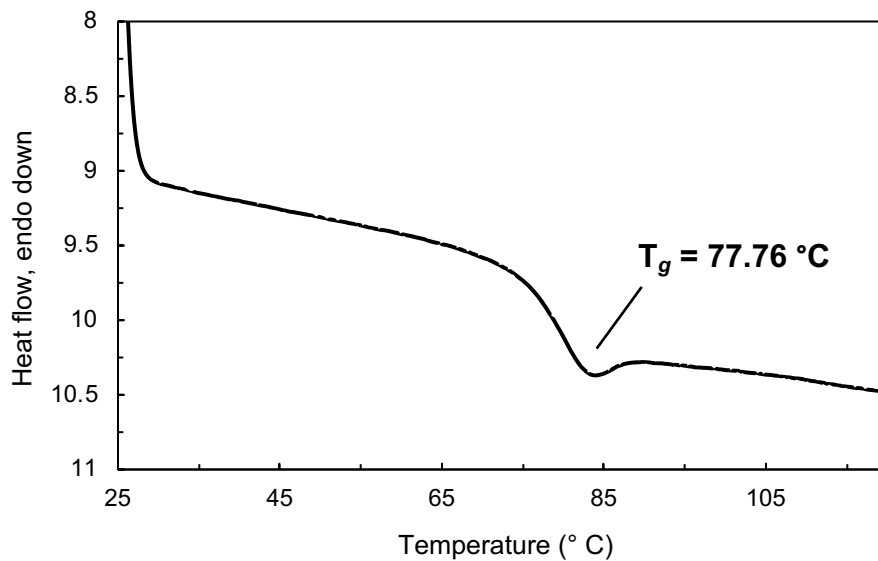


**Fig. S46** GPC trace corresponding to Table S4, Entry 6.

## 7. Differential Scanning Calorimetry Data

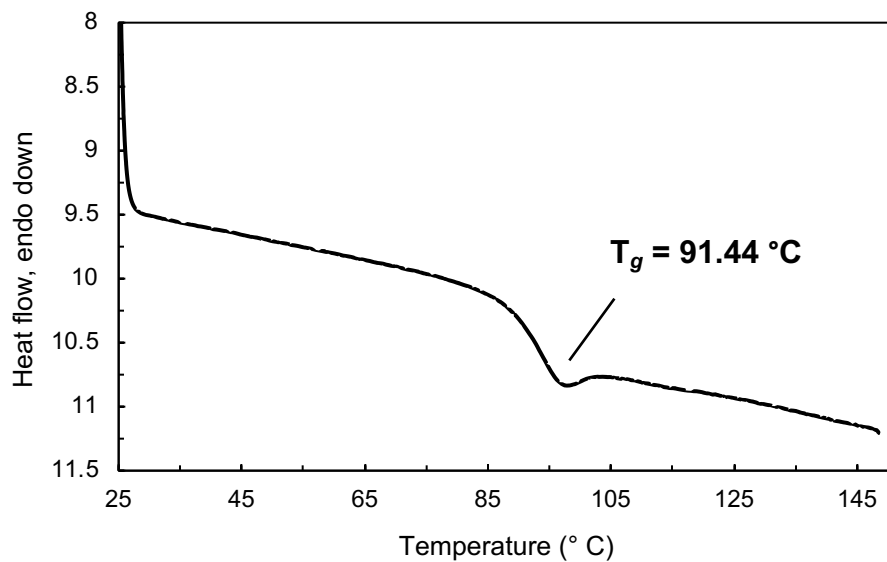


**Fig. S47** DSC trace of CHO/CPMA-*r*-BO/CPMA from Table 2, Entry 1.

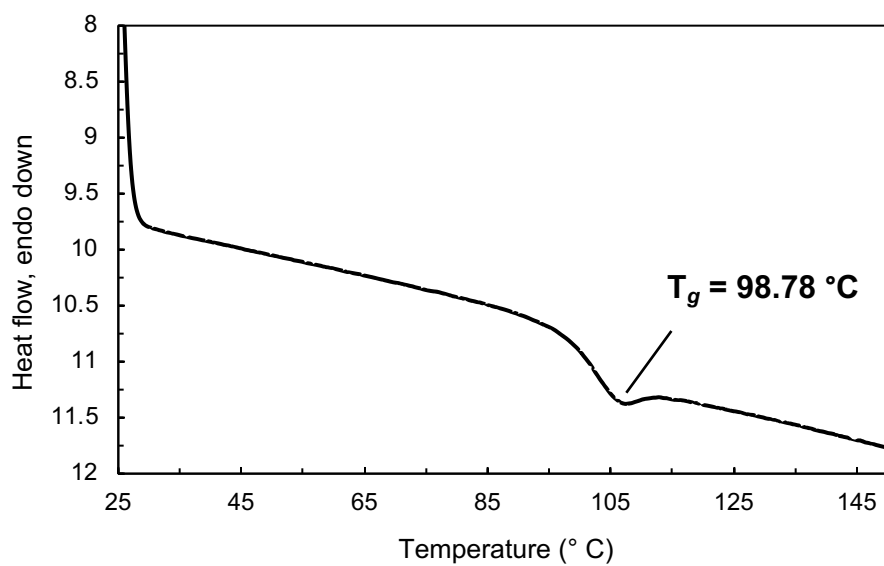


**Fig. S48** DSC trace of CHO/CPMA-*r*-BO/CPMA from Table 2, Entry 2.

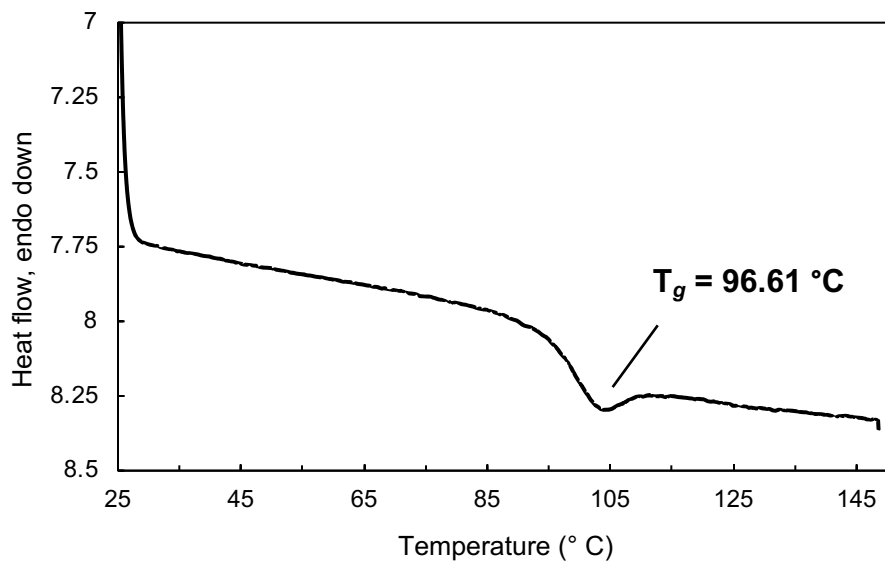




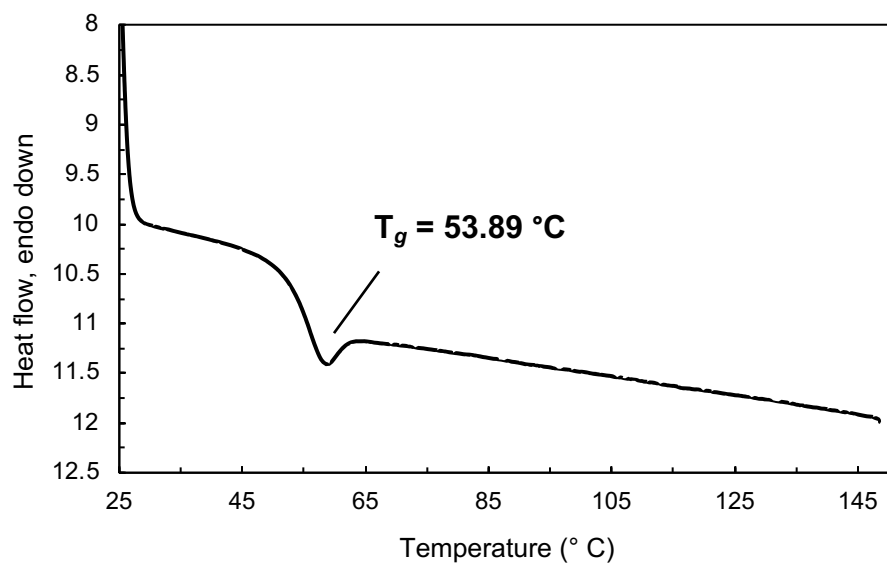
**Fig. S49** DSC trace of CHO/CPMA-*r*-BO/CPMA from Table 2, Entry 3.



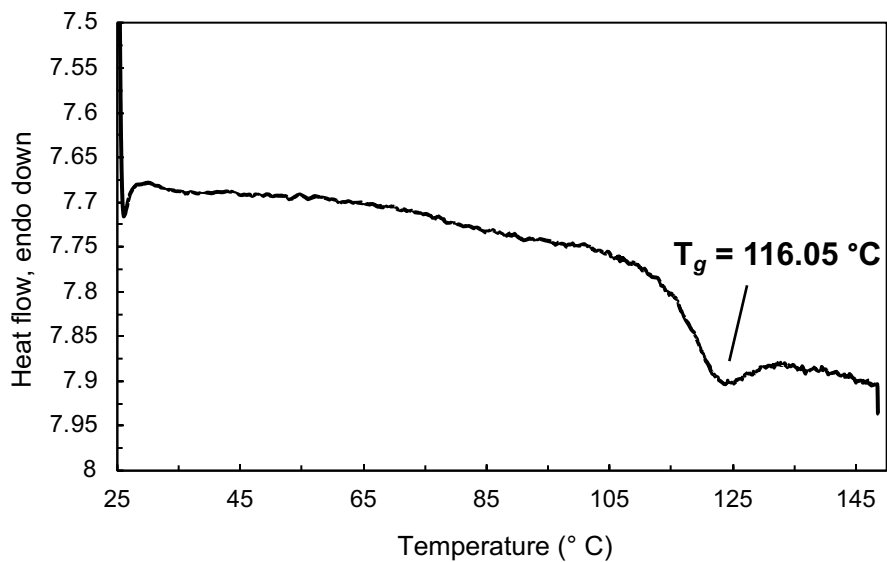
**Fig. S50** DSC trace of CHO/CPMA-*r*-BO/CPMA from Table 2, Entry 4.



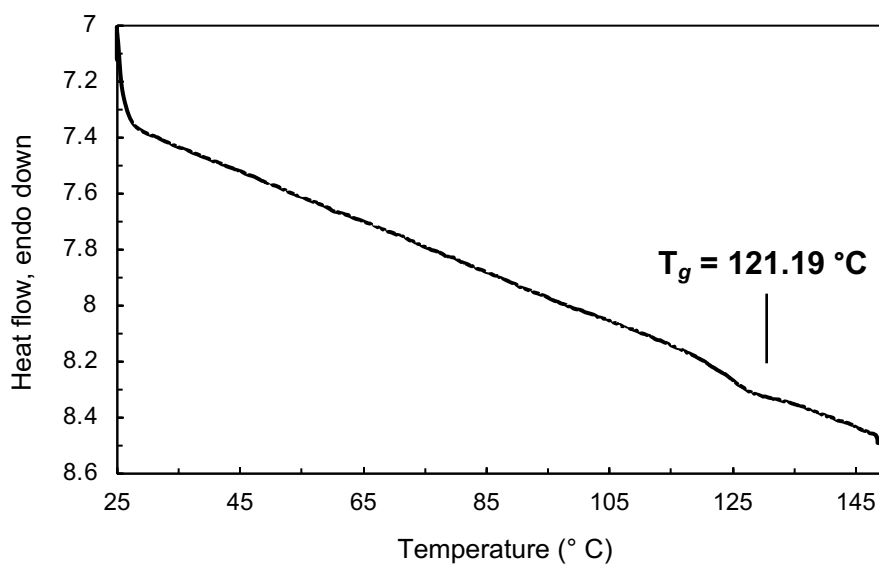
**Fig. S51** DSC trace of CHO/CPMA-*r*-BO/CPMA from Table 2, Entry 5.



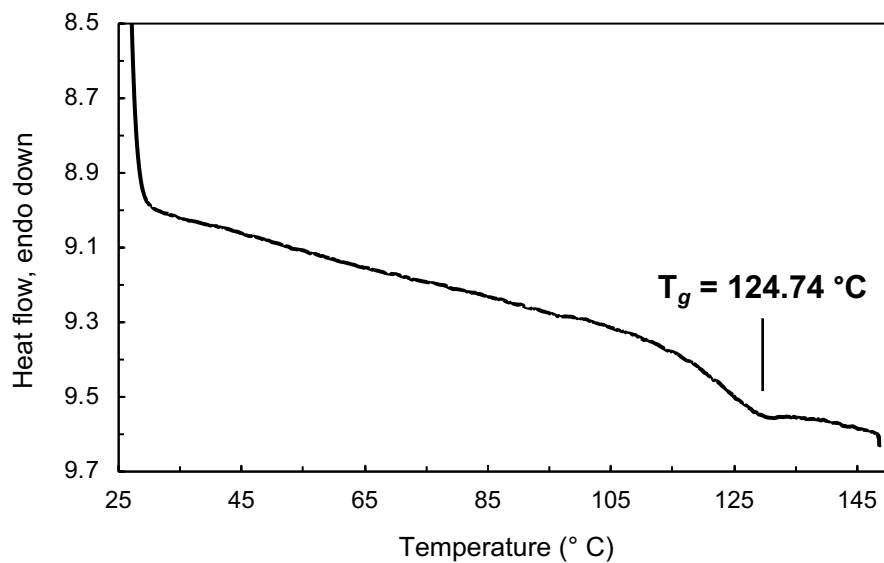
**Fig. S52** DSC trace of BO/CPMA from Table S4, Entry 1.



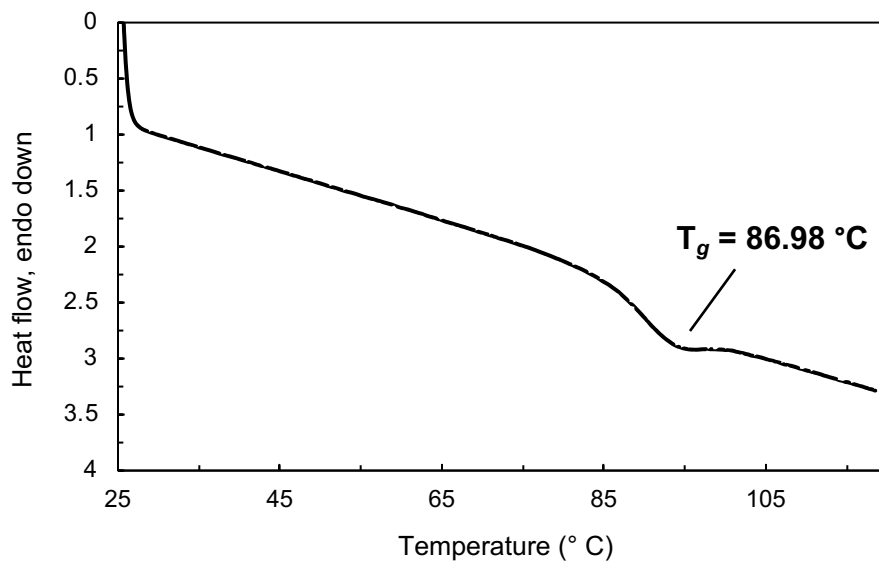
**Fig. S53** DSC trace of CHO/CPMA from Table S4, Entry 7.



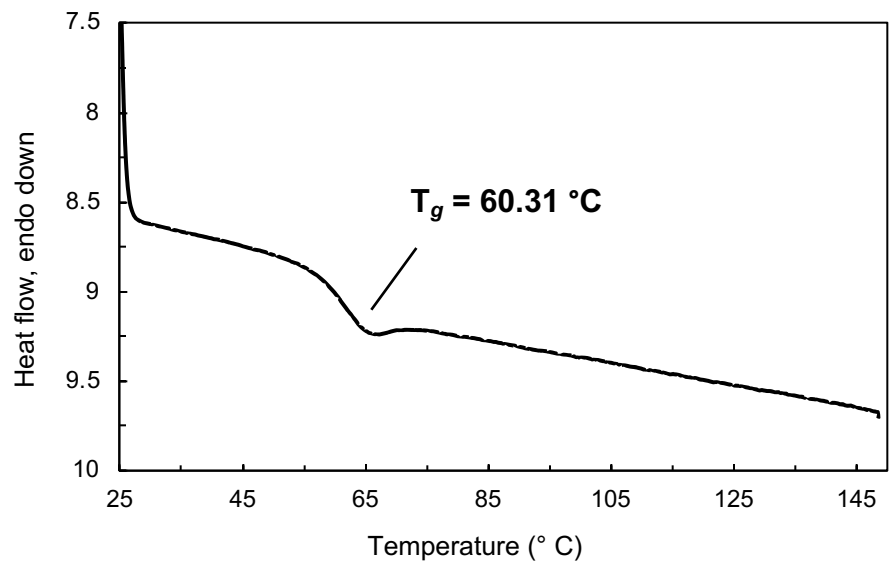
**Fig. S54** DSC trace of CHO/PA-*b*-CHO/CPMA from Table S5, Entry 1.



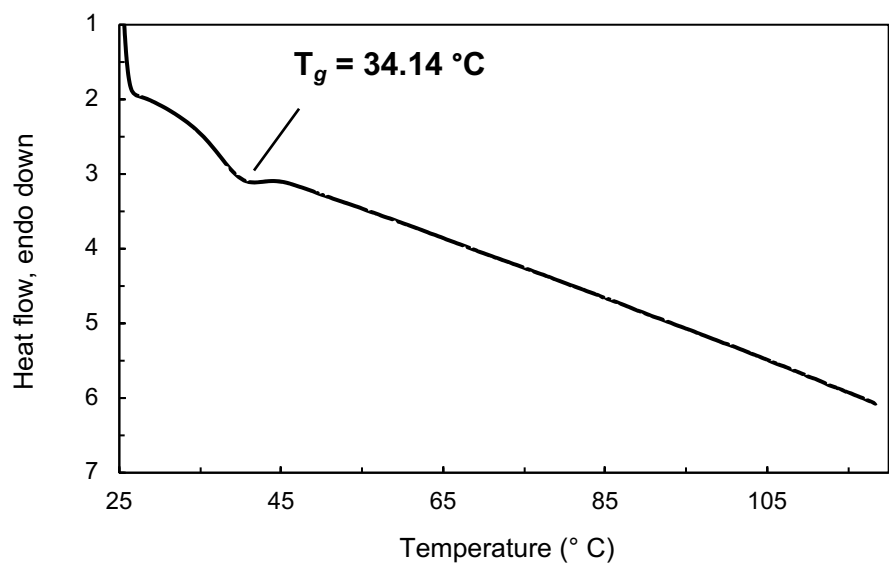
**Fig. S55** DSC trace of CHO/PA-*b*-CHO/CPMA from Table S5, Entry 2.



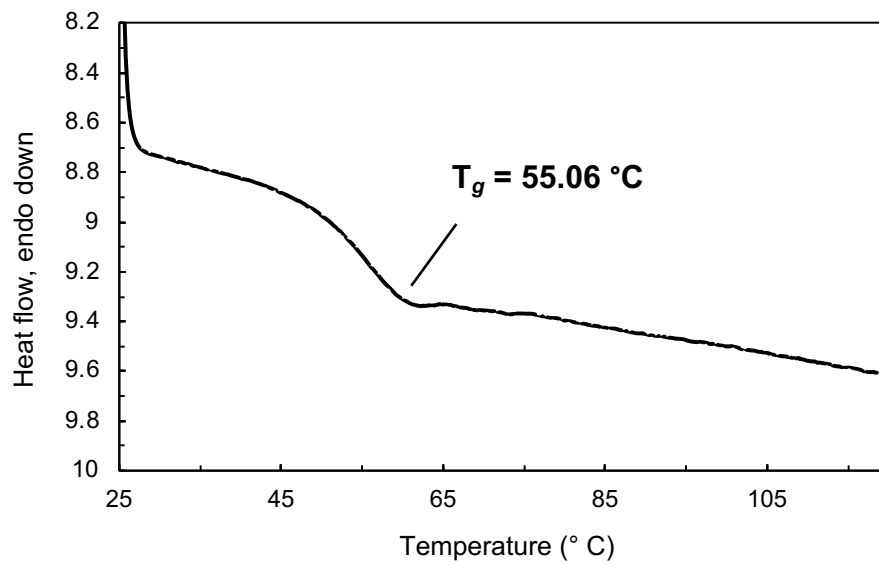
**Fig. S56** DSC trace of CHO/GA-*r*-CHO/CPMA from Table S5, Entry 3.



**Fig. S57** DSC trace of CHO/GA-*r*-CHO/CPMA from Table S5, Entry 4.



**Fig. S58** DSC trace of CHO/GA-*r*-CHO/CPMA from Table S5, Entry 5.



**Fig. S59** DSC trace of CHO/GA-*r*-CHO/PA from Table S5, Entry 6.

## 8. Reactivity Ratios

### 8.1 Calculation of reactivity ratios

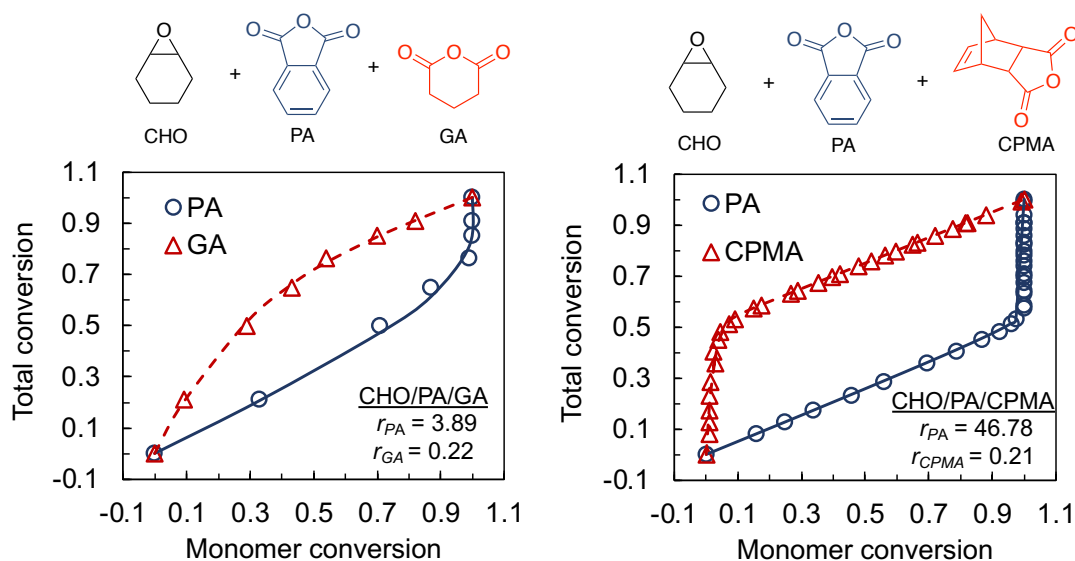
Due to the rate-determining step of the ROCOP of epoxides and cyclic anhydrides involving only epoxide ring opening, turn-over frequency data from individual ROCOP reactions does not allow accurate predictions of polymer sequence in the presence of multiple anhydrides. Therefore, a nonterminal compositional drift copolymerization kinetics model was employed to determine the reactivity ratios of multiple anhydride pairs.<sup>4-6</sup> Following the experimental procedure described in section 2.1, Equations 3 and 4 were used to calculate reactivity ratios of a mixture of two anhydrides. For these equations,  $p_A$  and  $p_B$  are the respective conversions of A and B monomer with  $p_A = 1 - (A(t)/A_0)$ . The calculated reactivity ratios are then fit to the experimental data as shown in Fig. 4 of the manuscript and Fig S60.

$$p_{AB}(p_A) = 1 - n_A(1 - p_A) - (1 - n_A)(1 - p_A)^{r_B} \quad (3)$$

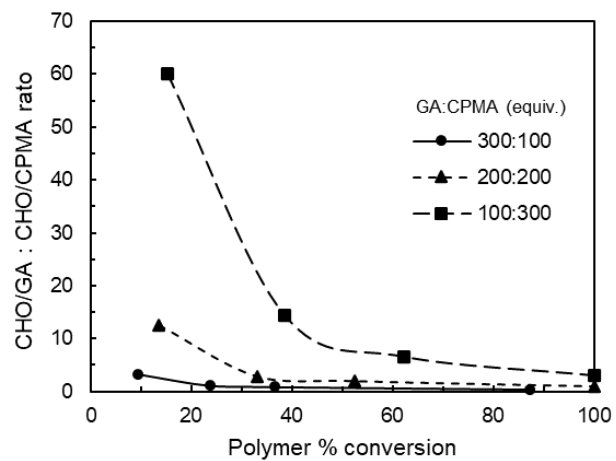
$$p_{AB}(p_B) = 1 - (1 - n_A)(1 - p_B) - n_A(1 - p_B)^{r_A} \quad (4)$$

### 8.2 Additional reactivity ratio plots

The reactivity ratios of most monomer pairs are reported in the main text, and the order of reactivity is highlighted at the end of Fig. 6. Below in Fig. S60 is two additional anhydride mixtures polymerized in the presence of CHO.



**Fig. S60** Plot of CHO/PA/GA and CHO/PA/CPMA consumption in the presence of CHO.

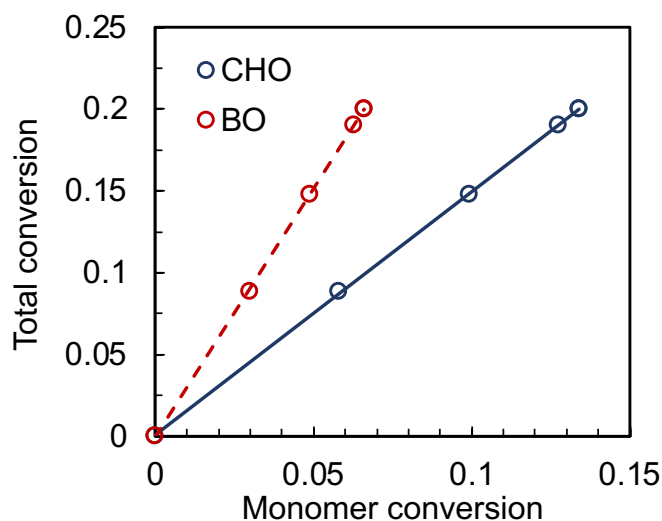
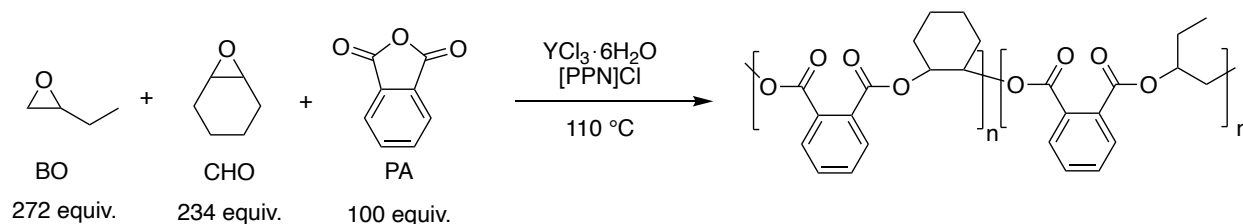


**Fig. S61** Plot of % incorporation of CHO/GA vs. CHO/CPMA in varying GA:CPMA feed ratio equivalence.



### 8.3 Data for Epoxide Mixtures

As described in the manuscript, the Mayo-Lewis equation can be used to predict copolymer sequence for mixtures of epoxide in the presence of one anhydride. For this to be true, two assumptions must be met: the polymerization must follow nonterminal polymerization kinetics, and that the initial monomer feed ratio remains relatively unchanged. When two competing epoxides are present, the epoxide ring opening (ERO) is also the rate determining step (RDS), which suggests that the observed rate of each separate polymerization of monomer pairs should inform the polymer sequence that is achieved. Additionally, support that the epoxide feed ratio isn't changing drastically enough to influence the reactivity ratios, Fig. S62 is a plot of BO and CHO conversion in the presence of PA (from the  $^1\text{H}$  NMRs of Fig. S7). This linear plot is also highlighted in Fig. 6 of the main text.



**Fig. S62** Plot of CHO and BO conversion (x-axis) against total epoxide conversion (y-axis) for the ROCOP of BO/PA and CHO/PA.

## 9. References

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