

## Supporting Information for

### **Salen-Cobalt catalyzed degradation of polypropylene carbonate and its application in one-pot tandem synthesis of propylene carbonate**

Qingyun Ge,<sup>a</sup> Baihu Dong,<sup>a</sup> Yunqi Chen,<sup>a</sup> Xinqiang Wang,<sup>a</sup> Xiang Wang,<sup>a</sup> Chaogang Fan,<sup>a,b</sup>

Chuhua Chen,<sup>a,b</sup> Shaohui Lin,<sup>\*a</sup> Qinmin Pan,<sup>\*a</sup> and Flora T. T. Ng<sup>b</sup>

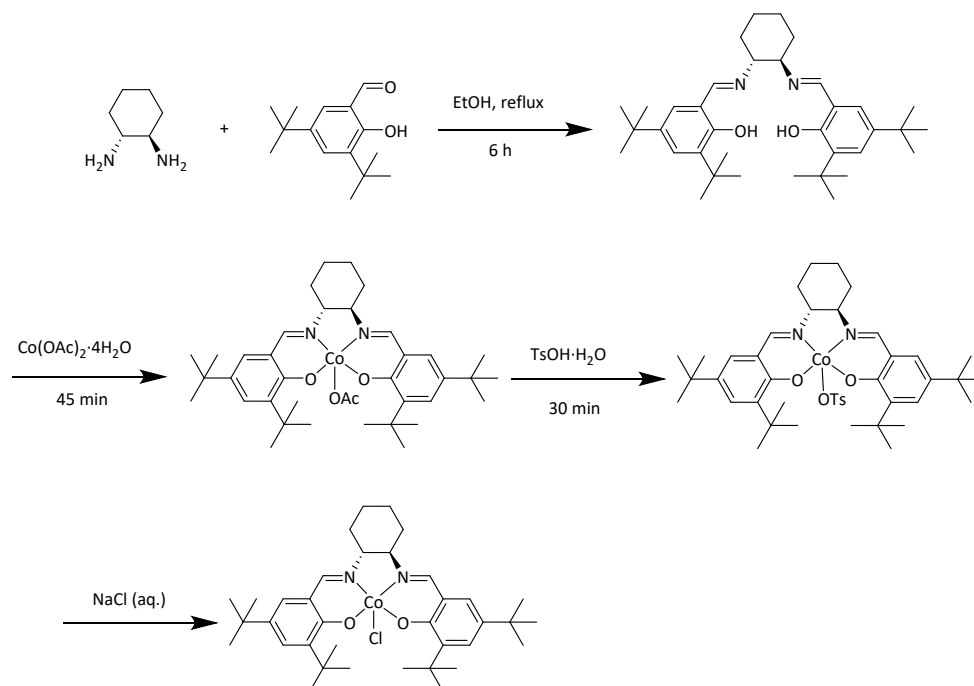
<sup>a</sup>State and Local Joint Engineering Laboratory for Novel Functional Polymeric Materials, Jiangsu Key Laboratory of Advanced Functional Polymer Design and Application, Key Laboratory of Organic Synthesis of Jiangsu Province, Green Polymer and Catalysis Technology Laboratory (GAPCT), College of Chemistry, Chemical Engineering and Materials Science, Soochow University, 199 Ren'ai Road, Suzhou 215123, P. R. China.

<sup>b</sup>Department of Chemical Engineering, University of Waterloo, 200 University Ave. West, Waterloo, Ontario, N2L 3G1, Canada.

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## 1. Synthesis of Salen-Co(III)-Cl



Scheme S1 Synthesis of Salen-Co(III)-Cl

**The preparation of (R,R)-N,N-bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediamine (Salen):** To a solution of (R,R)-1,2-cyclohexanediamine (1.14 g, 10 mmol) in MeOH (60 mL) in a 250 mL three-necked flask, 3,5-di-tertbutyl-2-hydroxybenzaldehyde (4.68 g, 20 mmol) in ethanol (80 mL) was slowly added. The mixture was stirred and refluxed at 80 °C for 6 h. When cooled to room temperature, the solid was filtered out and washed with ethanol. After filtration and dried in vacuum, a yellow solid (5.06 g, 93 %) was obtained.  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  13.66 (s, 2H), 8.31 (s, 2H), 7.31 (d,  $J = 2.6$  Hz, 2H), 7.00 (s, 2H), 1.99 – 1.83 (m, 5H), 1.74 (d,  $J = 11.3$  Hz, 3H), 1.40 (s, 18H), 1.23 (s, 18H). (Figure S1)

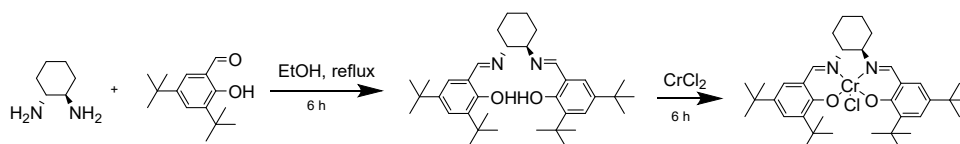
**The preparation of Salen-Co(II)-OAc:** Under an atmosphere of  $\text{N}_2$ , a solution of cobalt(II) acetate tetrahydrate (2.74 g, 11 mmol) in MeOH (40 mL) was added to a solution of Salen ligand (4.91 g, 9 mmol) in  $\text{CH}_2\text{Cl}_2$  (40 mL) via syringe. The bright-red solid precipitates were gradually formed after dropping. The reaction mixture

was stirred at room temperature for 30 minutes, followed by 15 minutes in an ice water bath (0 °C). The solid was filtered out, rinsed with 0 °C methanol solution. The red solid was collected and dried in vacuum (4.79 g, 82%).

**The preparation of Salen-Co(III)-OTs:** To a 250 mL three-neck flask, Salen-Co(II)-OAc (4.52 g, 7.5 mmol), p-toluenesulfonic acid monohydrate (1.52 g, 8 mmol) and dichloromethane (75 mL) were added. After the reaction mixture was vigorously stirred in an air atmosphere for 30 min, the solvent was removed by vacuum. The resulting solid was suspended in pentane and filtered to afford the green Salen-Co(III)-OTs (5.27 g, 91%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 7.81 (s, 2H), 7.46 (d, *J* = 10.0 Hz, 6H), 7.10 (d, *J* = 7.7 Hz, 3H), 3.61 (s, 2H), 3.06 (d, *J* = 11.7 Hz, 2H), 2.28 (s, 4H), 2.00 (s, 2H), 1.91 (s, 2H), 1.74 (s, 16H), 1.59 (s, 2H), 1.30 (s, 17H). (Figure S2)

**The preparation of Salen-Co(III)-Cl:** The green solid Salen-Co(III)-OTs (5 g, 6.5 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (150 mL) and transferred to a 500 mL separating funnel. After washing the organic layer with saturated NaCl solution (3×100 mL), the organic layer was collected and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> powder followed by removal of the volatiles under reduced pressure. The remaining solid was suspended in hexane under vigorous stirring and a precipitate was formed and isolated. The collected solid was dried under vacuum to a constant weight, affording the product as a dark green solid (2.62 g, 63 %). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 7.82 (s, 2H), 7.47 (s, 2H), 7.44 (s, 2H), 3.63 – 3.58 (m, 2H), 3.10 – 3.03 (m, 2H), 2.03 – 1.96 (m, 3H), 1.90 (s, 2H), 1.74 (s, 17H), 1.59 (d, *J* = 11.2 Hz, 2H), 1.30 (s, 23H). (Figure S3)

## 2. Synthesis of Salen-Cr(III)-Cl



Scheme S2 Synthesis of Salen-Cr(III)-Cl

The synthesis method of Salen ligand is the same as above.

**The preparation of Salen-Cr(III)-Cl:** The Salen ligand (1.39g, 2.57 mmol), CrCl<sub>2</sub> (0.365g, 2.83 mmol) and THF (50 mL) were added to a 100 mL three-neck flask. The reaction mixture was stirred for 3 h under an atmosphere of N<sub>2</sub>. Then the reaction mixture was exposed to air and stirred for another 3 h. After the reaction mixture was poured into the diethyl ether, the organic layer was washed with saturated NH<sub>4</sub>Cl aqueous solution (3×100 mL) and saturated NaCl solution (3×100 mL) followed by drying with anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration to remove solid impurities and drying agent, solvent was removed in vacuum, yielding a dark brown powder.

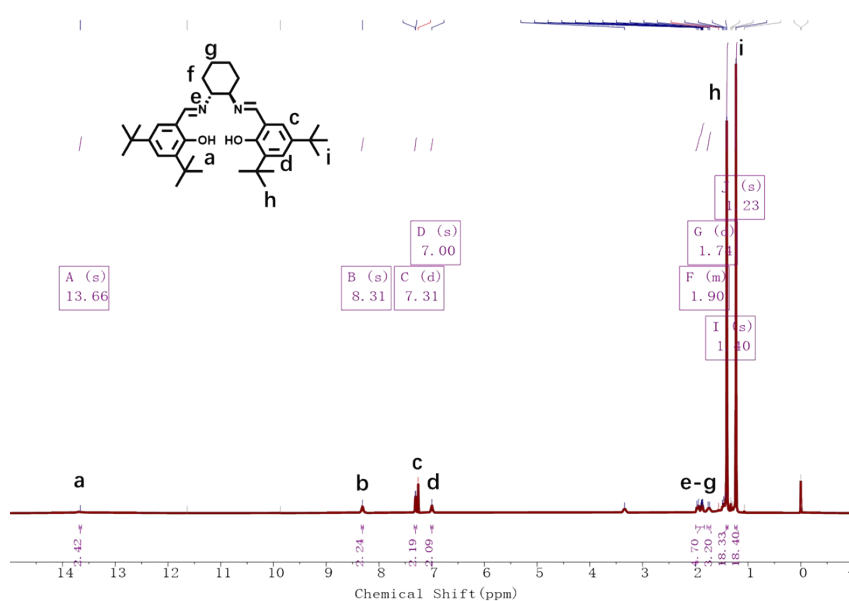


Figure S1 <sup>1</sup>H NMR spectra of Salen ligand in CDCl<sub>3</sub>

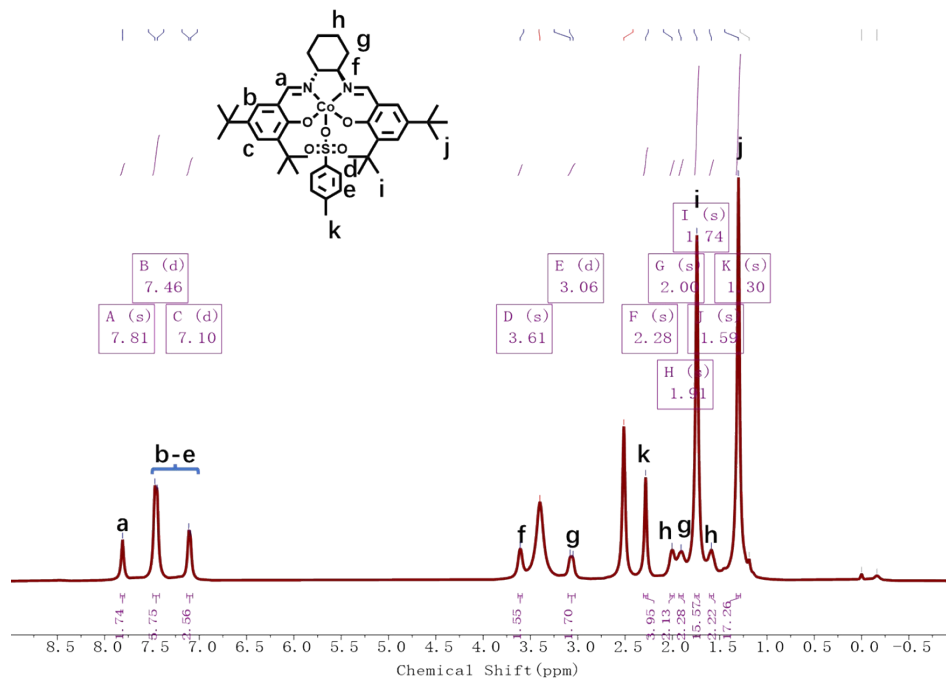


Figure S2  $^1\text{H}$  NMR spectra of Salen-Co(III)-OTs in  $\text{DMSO-}d_6$

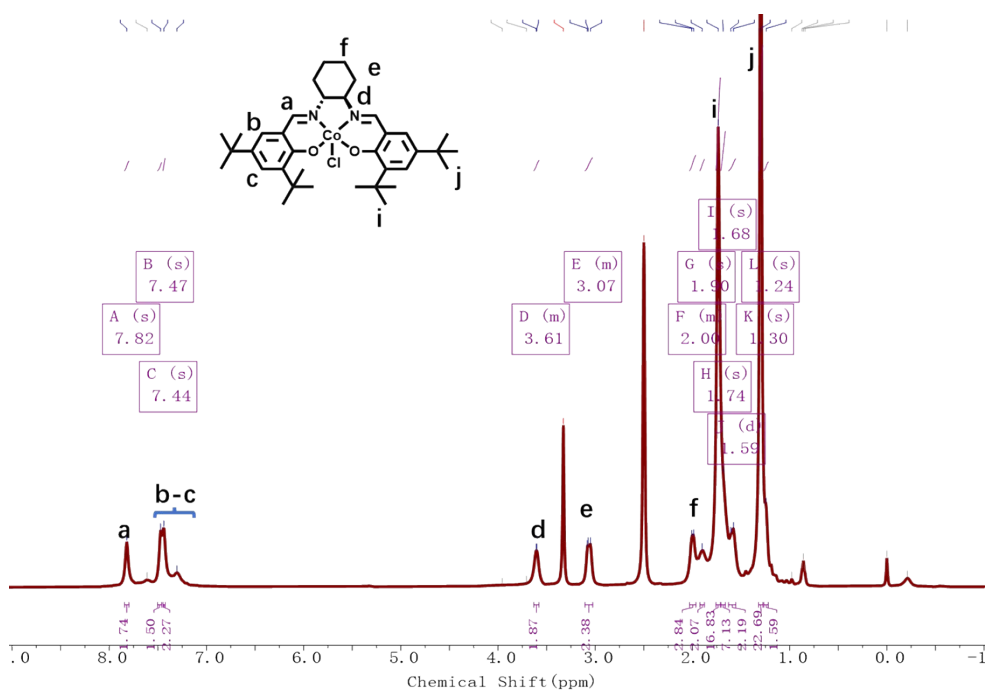


Figure S3  $^1\text{H}$  NMR spectra of Salen-Co(III)-Cl in  $\text{DMSO-}d_6$ .

### 3. $^1\text{H}$ NMR spectra of polypropylene carbonate degradation in $\text{CH}_2\text{Cl}_2$

Based on the integral values of the  $^1\text{H}$  NMR characteristic peaks, the percentage concentration of the polypropylene carbonate (PPC) and the degradation product cyclic propylene carbonate (CPC) was calculated by the following formula:

$$A_{\text{PPC}} = A_{1.3} + A_{4.1-4.3} + A_{5.0} \quad (1)$$

$$A_{\text{CPC}} = A_{1.5} + A_{4.0} + A_{4.6} + A_{4.9} \quad (2)$$

$$A_{\text{TOTAL}} = A_{\text{PPC}} + A_{\text{CPC}} \quad (3)$$

$$\text{CPC \%} = A_{\text{CPC}} / A_{\text{TOTAL}} \quad (4)$$

$$\text{PPC \%} = A_{\text{PPC}} / A_{\text{TOTAL}} \quad (5)$$

A is the integral value corresponding to the characteristic peak of the  $^1\text{H}$  NMR spectra. e.g.,  $A_{\text{CPC}}$  is the total integral value of the  $^1\text{H}$  NMR characteristic peak of CPC, and  $A_{1.3}$  is the integral value of the  $^1\text{H}$  NMR characteristic peak with a chemical shift of 1.3 ppm. PPC % and CPC % are percentage concentration of polymer PPC and degradation product CPC in the total product.

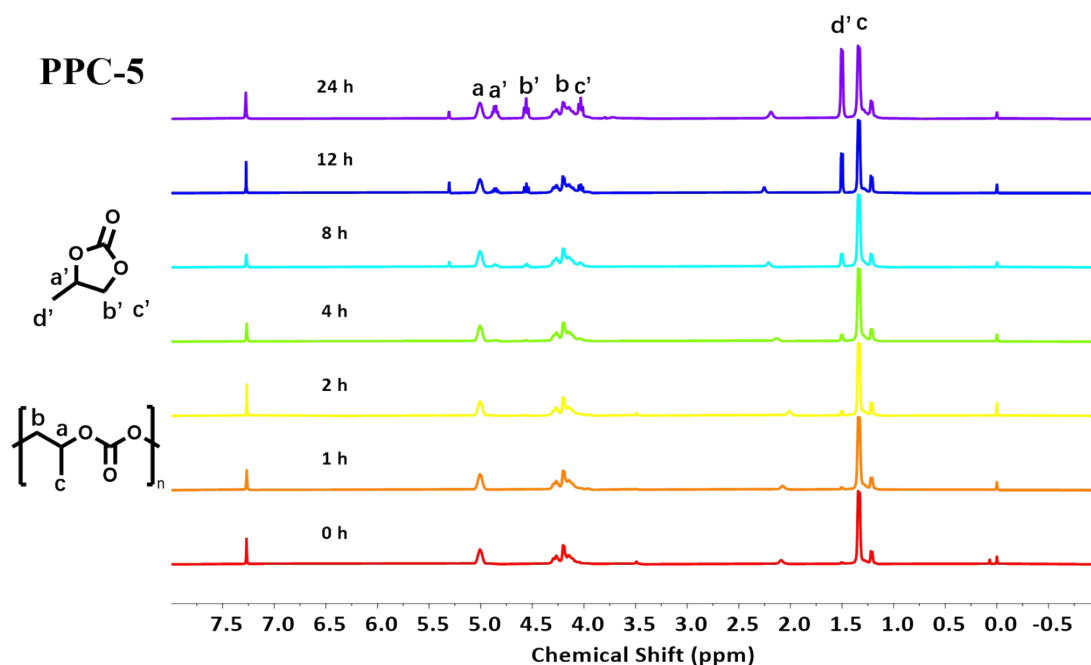


Figure S4  $^1\text{H}$  NMR spectra of polypropylene carbonate degradation in  $\text{CH}_2\text{Cl}_2$  (5 mL)

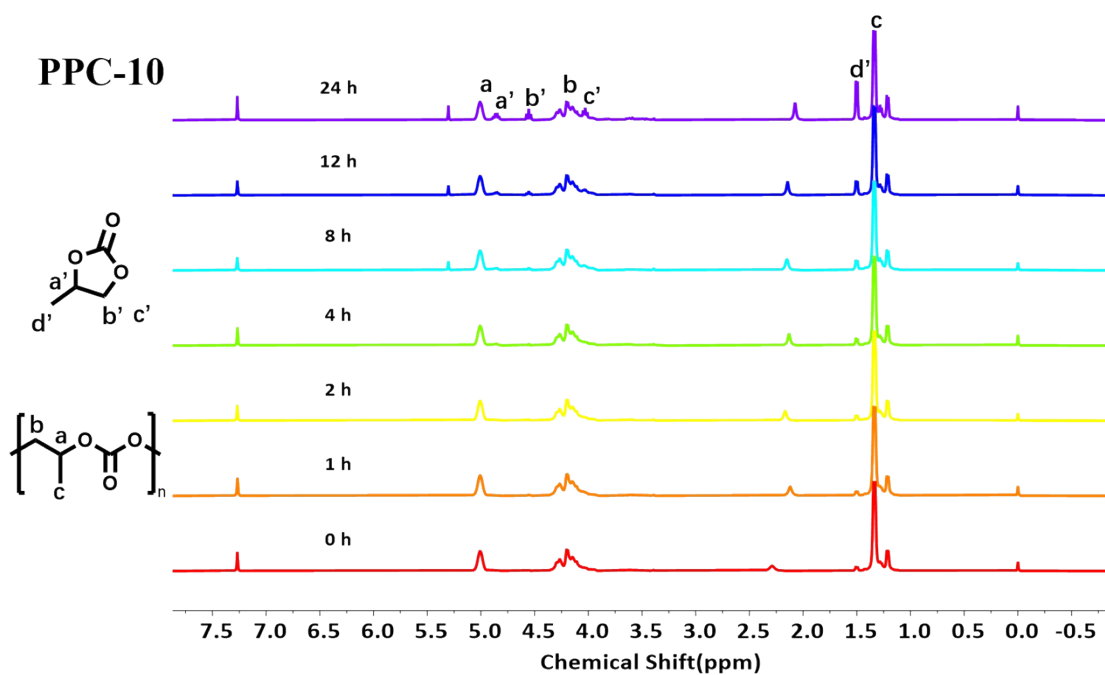


Figure S5  $^1\text{H}$  NMR spectra of polypropylene carbonate degradation in  $\text{CH}_2\text{Cl}_2$  (10 mL)

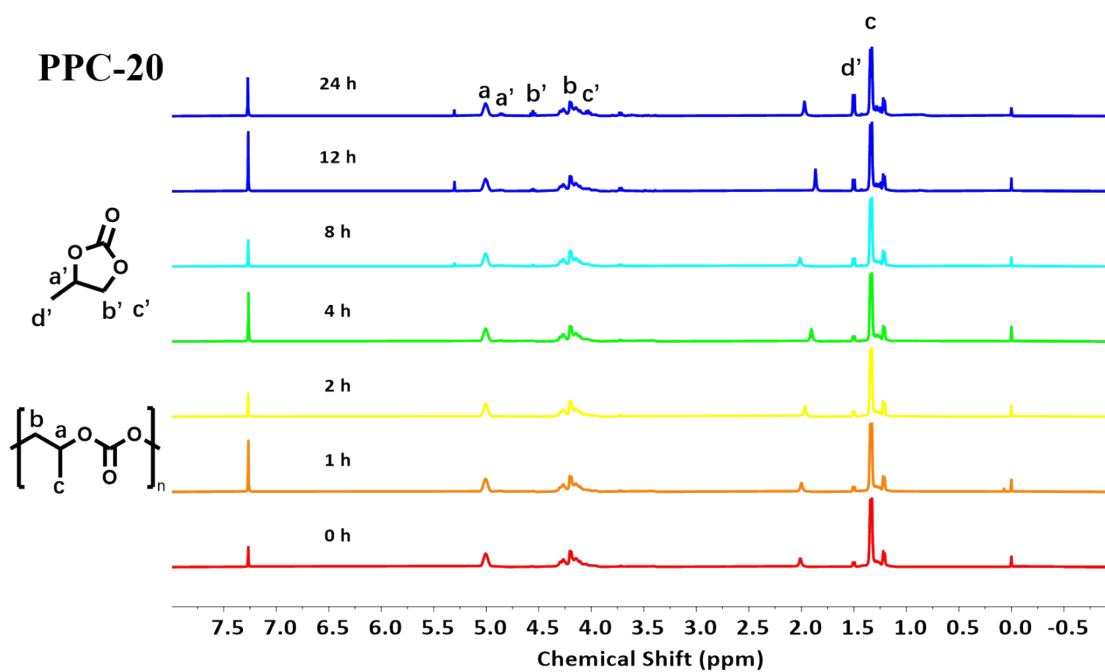


Figure S6  $^1\text{H}$  NMR spectra of polypropylene carbonate degradation in  $\text{CH}_2\text{Cl}_2$  (20 mL)



Table S1 The percentage concentration of PPC's repeating units and degradation product CPC in the total product.

Time/h	20 mL		10 mL		5 mL	
	PPC/%	CPC/%	PPC/%	CPC/%	PPC/%	CPC/%
0	95.95	4.05	96.71	3.29	98.44	1.56
1	95.63	4.37	96.79	3.21	97.56	2.44
2	94.93	5.07	95.85	4.15	96.48	3.52
4	94.70	5.30	95.68	4.32	94.88	5.12
8	93.15	6.85	92.60	7.40	88.42	11.58
12	92.22	7.78	90.07	9.93	81.54	18.46
24	85.93	14.07	78.68	21.32	61.41	38.59

**4. The percentage/molar concentration of PPC's repeating units versus the time of degradation in  $\text{CH}_2\text{Cl}_2$**

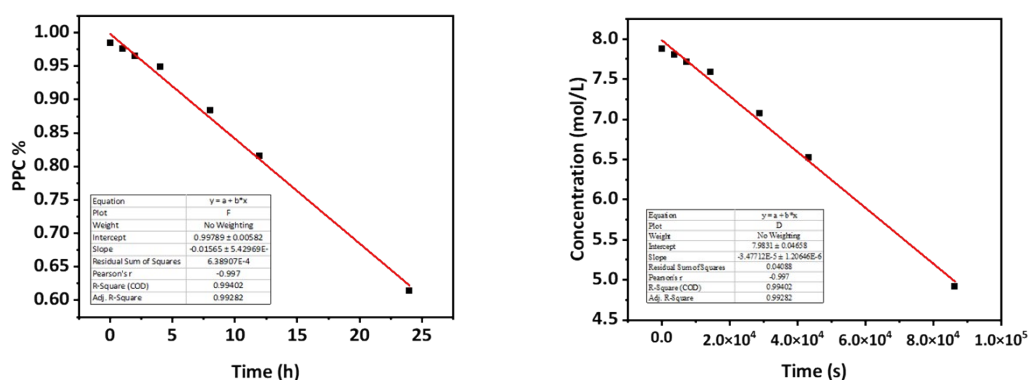


Figure S7 Plot of the percentage/molar concentration of PPC's repeating units versus the time of degradation in 5 mL  $\text{CH}_2\text{Cl}_2$

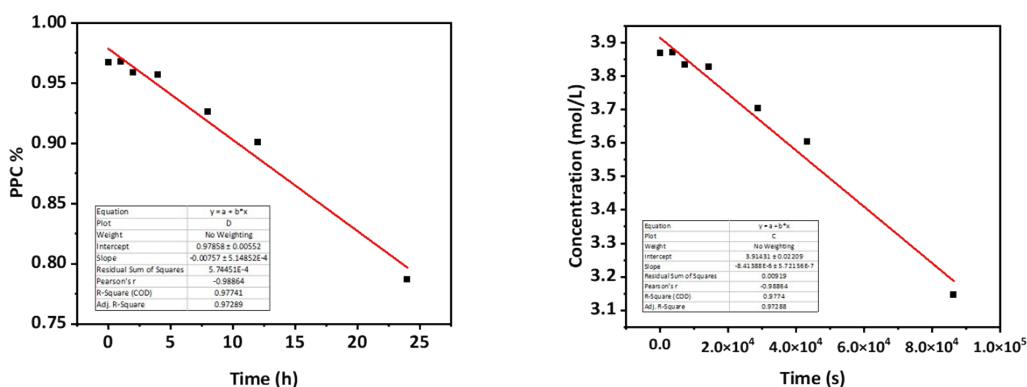


Figure S8 Plot of the percentage/molar concentration of PPC's repeating units versus the time of degradation in 10 mL CH<sub>2</sub>Cl<sub>2</sub>

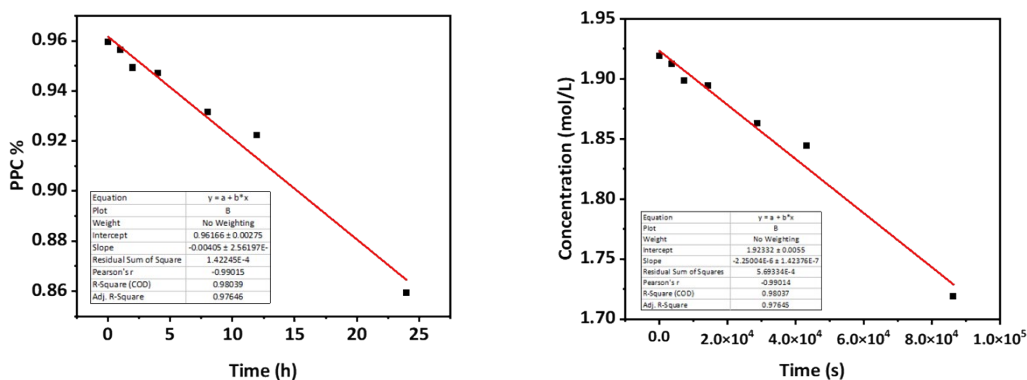


Figure S9 Plot of the percentage/molar concentration of PPC's repeating units versus the time of degradation in 20 mL CH<sub>2</sub>Cl<sub>2</sub>

### 5. Algorithmic processes of the actual molar concentration of PPC and CPC

Take the degradation of PPC dispersed in 5 mL CH<sub>2</sub>Cl<sub>2</sub> as an example. The number-average molecular weight of polymer PPC is known. There are about  $M_{nPPC}/M_{units} (\approx 25)$  repeating units in each polymer chain. The amount of PO monomer input is  $m_{PO}/M_{PO} (= 0.04 \text{ mol})$ , and the amount of polymer PPC is about 1.6 mmol. In a 5 mL CH<sub>2</sub>Cl<sub>2</sub>, the concentration of polymer PPC<sub>0</sub> was 3.2 mol/L. Based on the percentage of PPC and CPC, the actual molar concentration of PPC and CPC can be obtained. Calculations are as follows:

$$[PPC_0] = \frac{\frac{m_{PO}/M_{PO}}{Mn_{PPC}/M_{unit}}}{5 \text{ mL}} = \frac{2.32 \text{ g}/58 \text{ g}\cdot\text{mol}^{-1}}{2,500 \text{ g}\cdot\text{mol}^{-1}/102 \text{ g}\cdot\text{mol}^{-1}} \approx 3.2 \text{ mol}\cdot\text{L}^{-1}$$

$$[PPC] = [PPC_0] * PPC \%$$

$$[CPC] = [PPC_0] * \frac{Mn_{PPC}}{M_{units}} * CPC \%$$

[PPC<sub>0</sub>] is the initial concentration of the polymer PPC. [PPC] and [CPC] is the actual molar concentration of PPC and CPC. m<sub>PO</sub> and M<sub>PO</sub> is the mass and relative molecular weight of the monomer PO. M<sub>units</sub> is the relative molecular weight of the repeating units of the polymer. PPC % and CPC % is the percentage of polymer PPC and degradation products CPC in the product, which is calculated from the integral value of the <sup>1</sup>H NMR spectra.

#### 6. The percentage concentration of PPC's repeating units and CPC without solvent

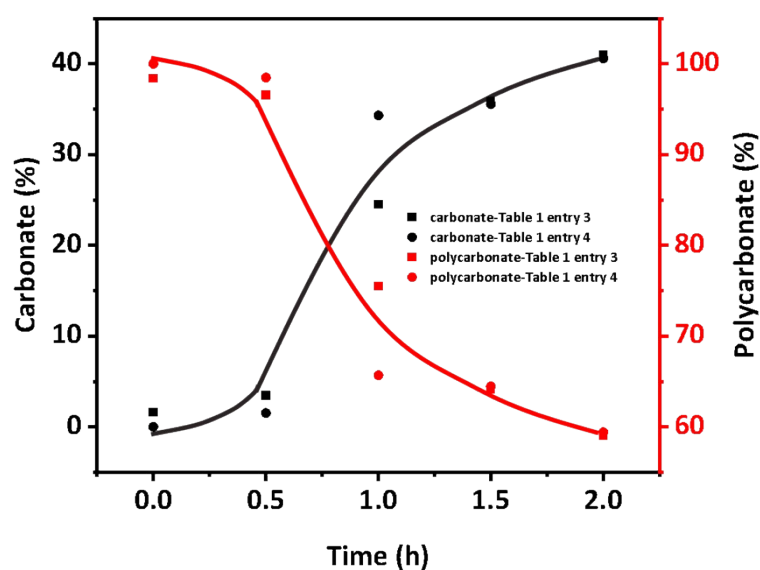


Figure S10 The ratio of CPC and PPC's repeating units without solvent (Table 1 Entry 3 and Table 1 Entry 4.).