Supporting Information

Zwitterionic copolymerization of γ-butyrolactone with 3,3-bis(chloromethyl) oxacyclobutane catalyzed by scandium triflates

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CONTENTS

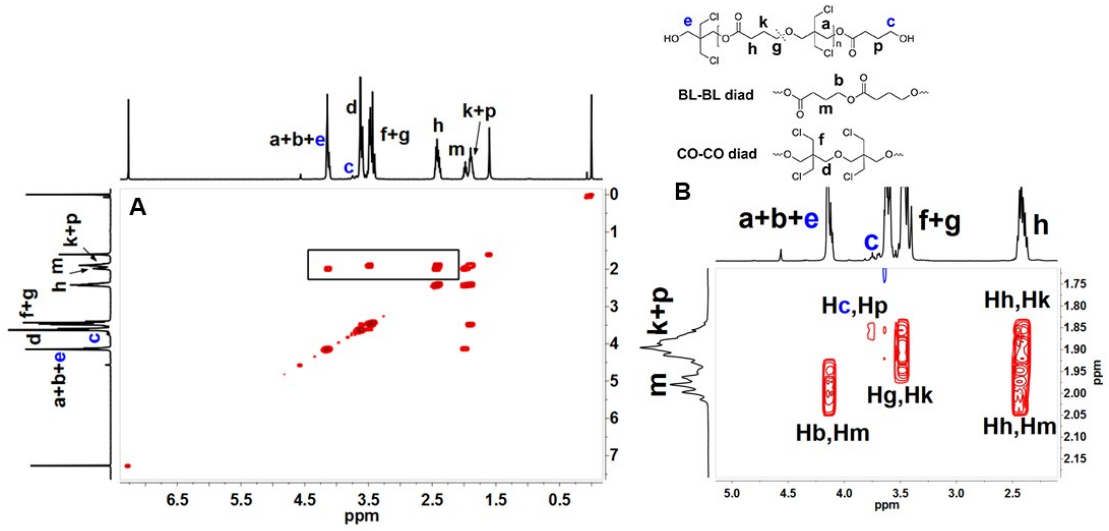


Figure S1. ^{1}H-^{1}H COSY NMR spectra of Sample 1 in Table 1 in $CDCl_3$ (A) and enlarged spectra (B).

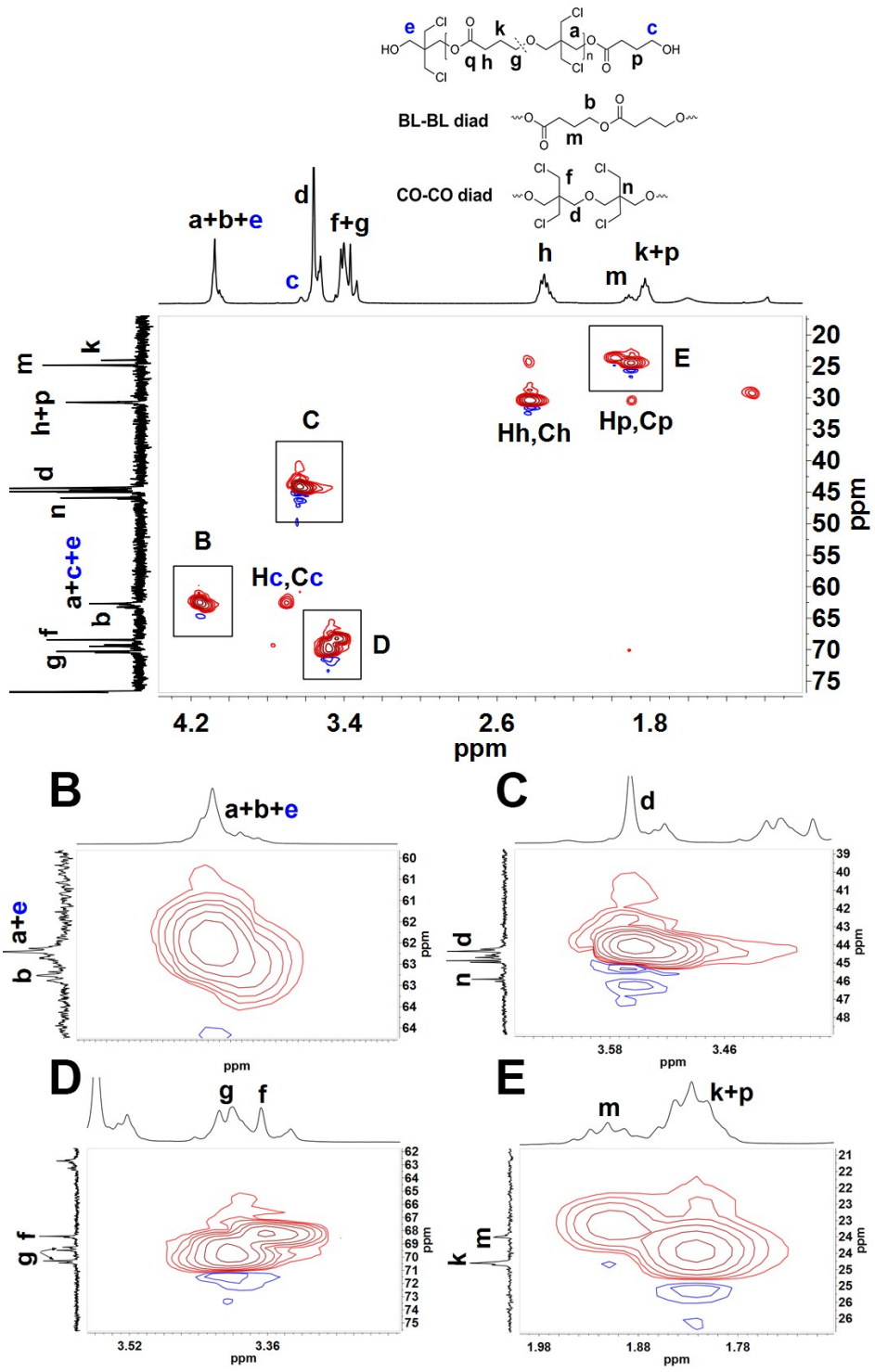


Figure S2. ^{1}H-^{13}C HSQC NMR spectra of Sample 4 in Table 1 in $CDCl_3$ (A) and enlarged spectra (B-E).

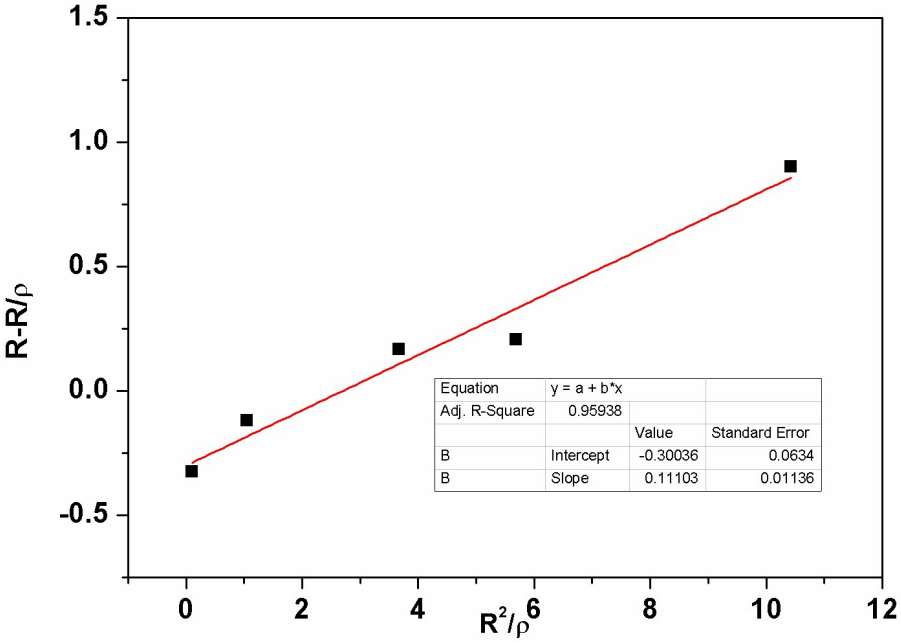


Figure S3. Plot of (R-R/ρ) versus (R^2/ρ) for the copolymerization of BL with CO and the linearly fitting whose intercept is r_1 [0.11, CO] and slope is $-r_2$ [0.30, BL] by the Fineman-Ross method.

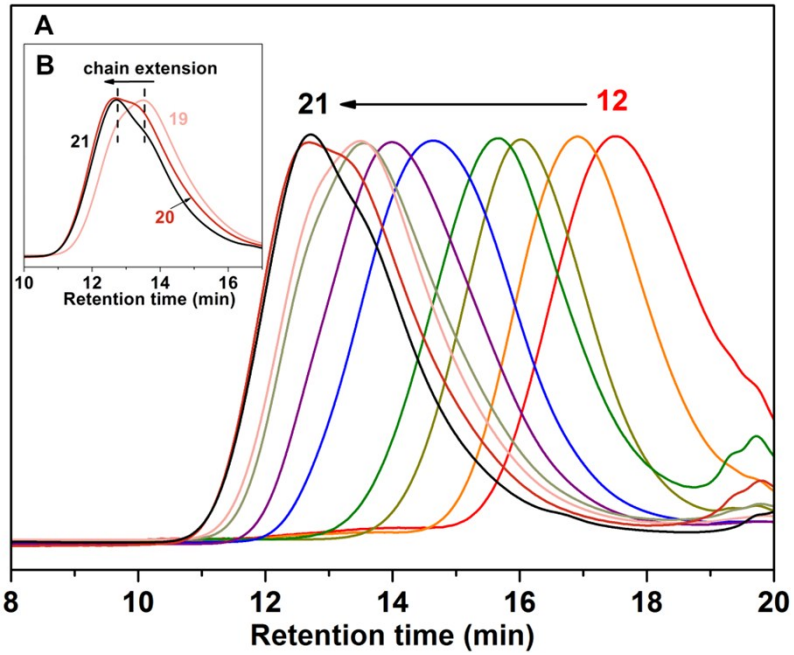


Figure S4. SEC traces of PBC copolymers in Table S1 (A) and enlarged graph (B).

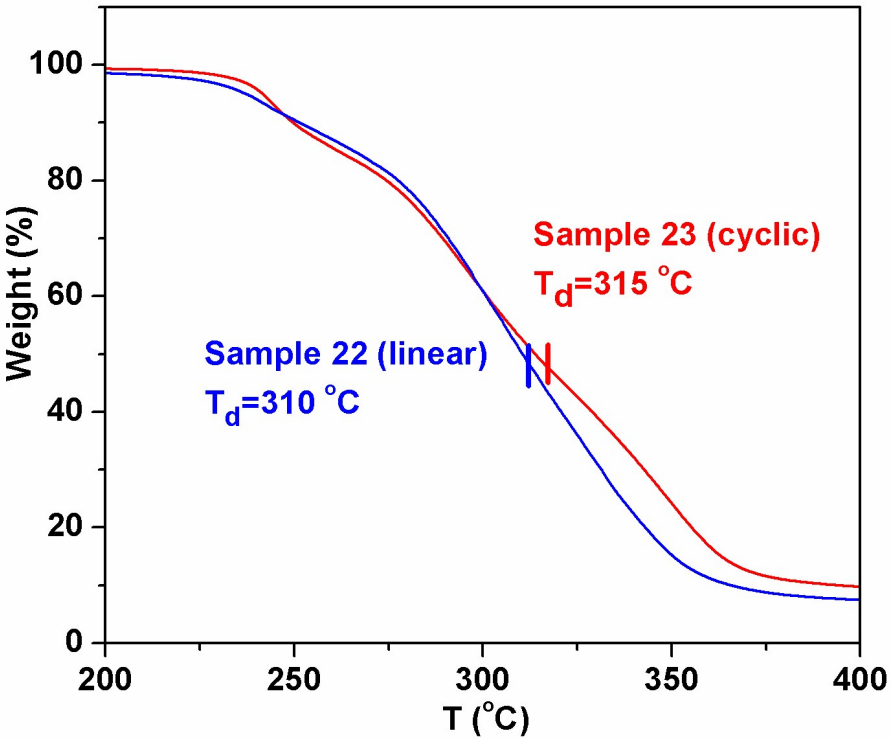


Figure S5. TGA traces of Samples 22 and 23.

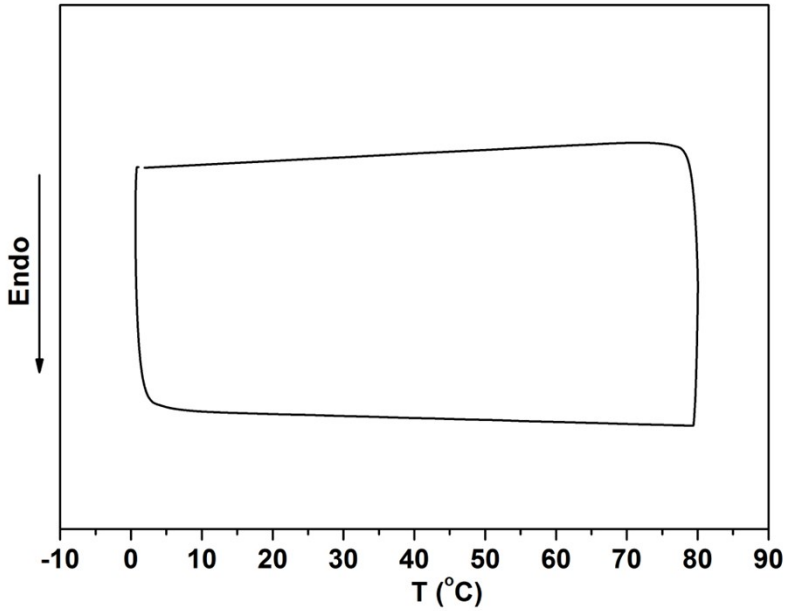
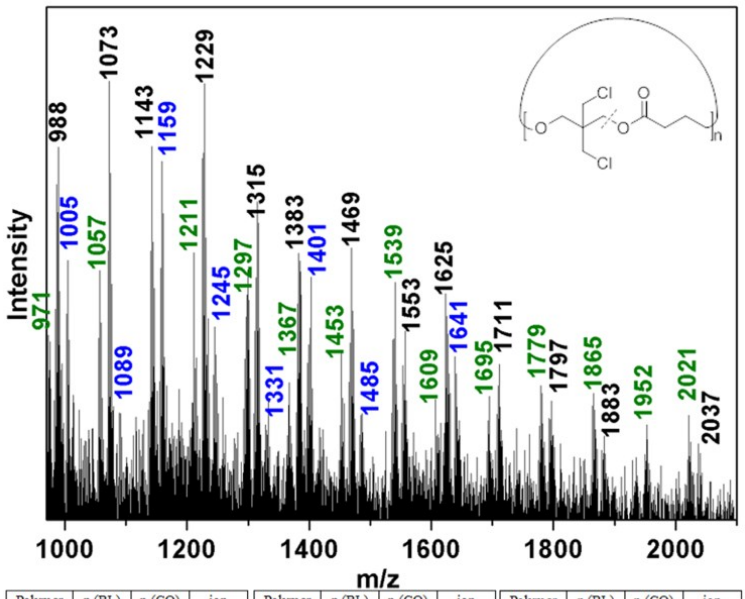


Figure S6. DSC curves of Sample 22 in Table S2.

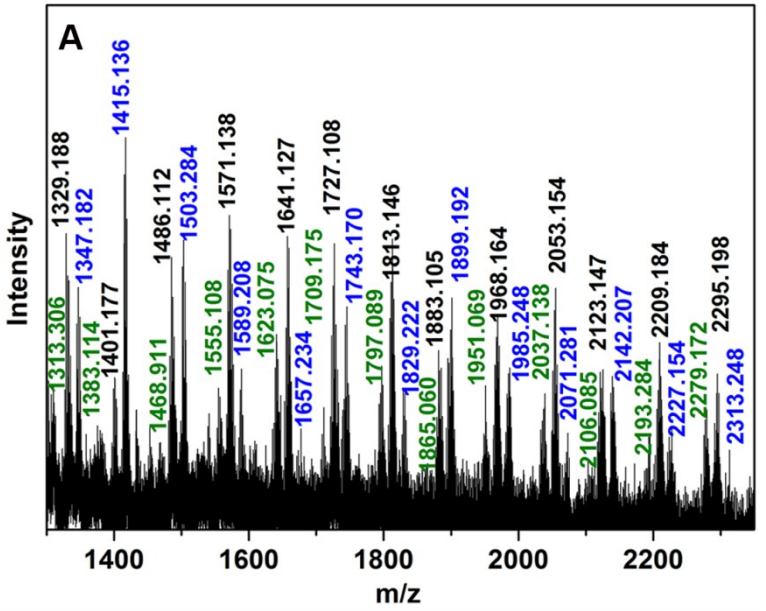


Polymer	n (BL)	n (CO)	ion
988	4	4	
1073	5	4	
1143	4	5	
1229	5	5	
1315	6	5	
1383	5	6	
1469	6	6	Na^+
1553	7	6	
1625	6	7	
1711	7	7	
1797	8	7	
1883	9	7	
2037	9	8	

Polymer	n (BL)	n (CO)	ion
971	2	5	
1057	3	5	
1211	3	6	
1297	4	6	
1367	3	7	
1453	4	7	
1539	5	7	Na^+
1609	4	8	
1695	5	8	
1779	6	8	
1865	7	8	
1952	8	8	
2021	7	9	

Polymer	n (BL)	n (CO)	ion
1005	4	4	
1089	5	4	
1159	4	5	
1245	5	5	
1331	6	5	K^+
1401	5	6	
1485	6	6	
1641	6	7	

Figure S7. MALDI-ToF mass spectra of cyclic copolymer (Sample 26 in Table S2, A) the corresponding mass values.



B

Polymer	n (BL)	n (CO)	ion	Chemical structure
1329	6	5		
1401	5	6		
1486	6	6		
1571	7	6		
1641	6	7		
1727	7	7		
1813	8	7	Na^+	
1883	7	8		
1968	8	8		
2053	9	8		
2123	8	9		
2209	9	9		
2295	10	9		

Polymer	n (BL)	n (CO)	ion	Chemical structure
1347	6	5		
1415	5	6		
1503	6	6		
1589	7	6		
1657	6	7		
1743	7	7		
1829	8	7	K^+	
1899	7	8		
1985	8	8		
2071	9	8		
2142	8	9		
2227	9	9		
2313	10	9		

Polymer	n (BL)	n (CO)	ion	Chemical structure
1313	6	5		
1383	5	6		
1469	6	6		
1555	7	6		
1623	6	7		
1709	7	7		
1797	8	7	Na^+	
1865	7	8		
1951	8	8		
2037	9	8		
2106	8	9		
2193	9	9		
2279	10	9		

Figure S8. MALDI-ToF mass spectra of linear copolymer (Sample 2 in Table 1, A) with the corresponding mass values and structures (B).

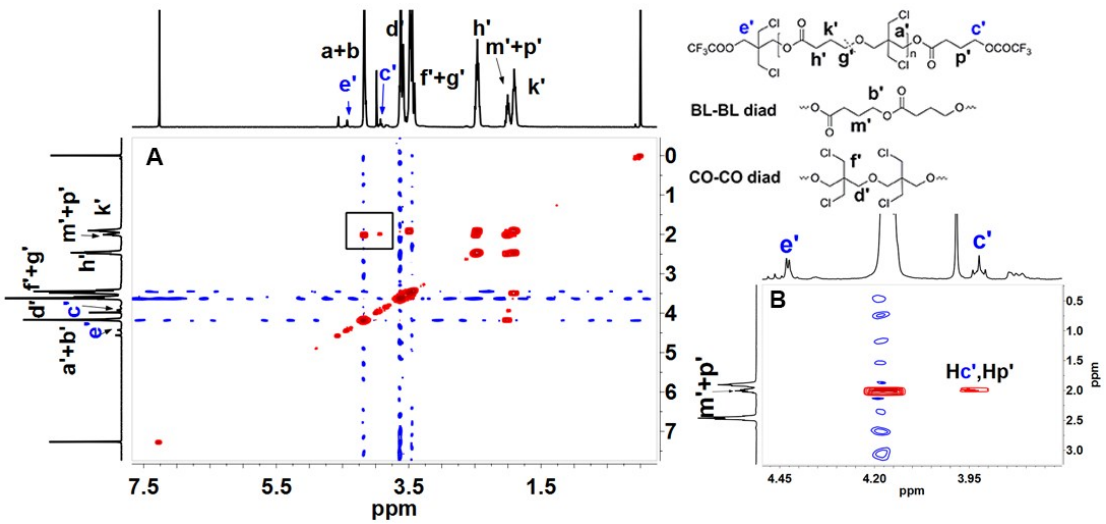


Figure S9. ^{1}H-^{1}H COSY NMR spectra of Sample 1 in Table 1 in $CDCl_3$ after TFA treatment.

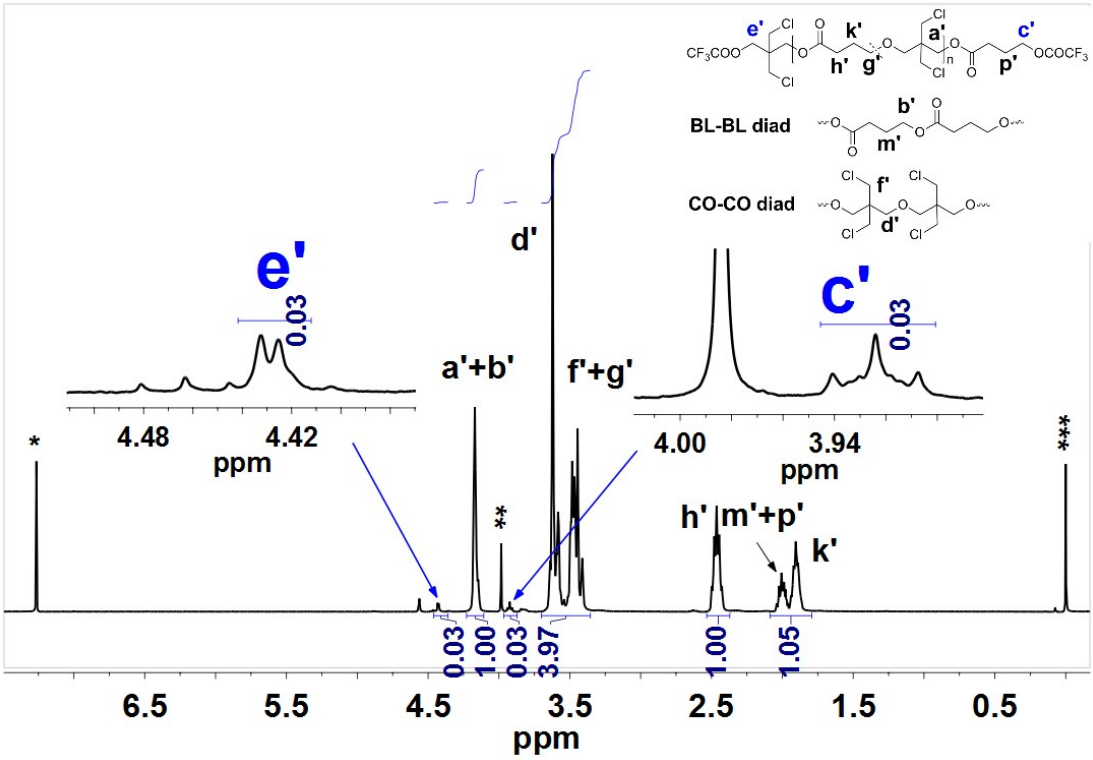


Figure S10. ^{1}H NMR spectra of PBC (Sample 1 in Table 1) after TFA treatment. Molar ratio of BL:CO repeating units in the copolymer is calculated by

$$\frac{4Ih'}{I(f'+d'+a)'} = \frac{4Ih'}{I(f'+d'+g)'=1}$$

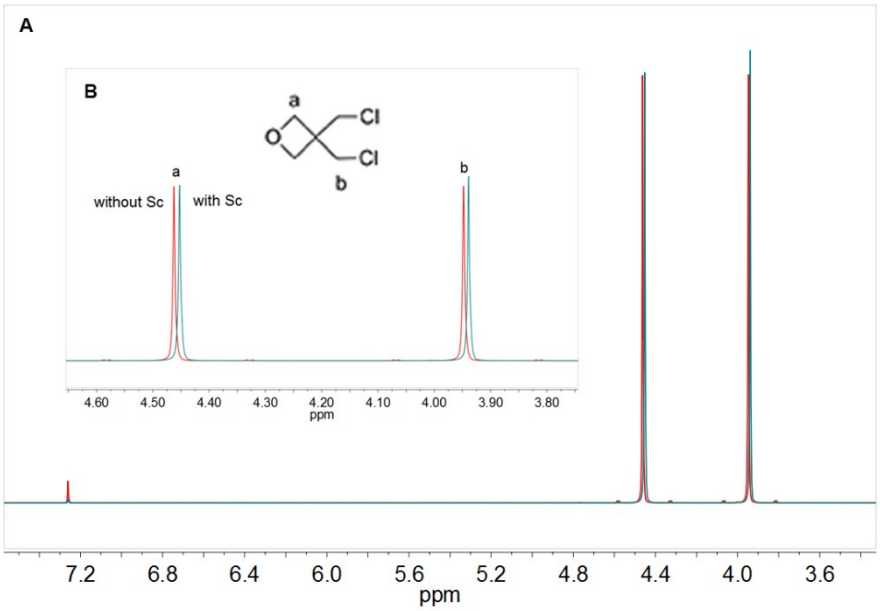


Figure S11. ^{1}H NMR spectra of CO with (green) and without (red) $Sc(OTf)_3$ (A) and the enlarged spectra (B).

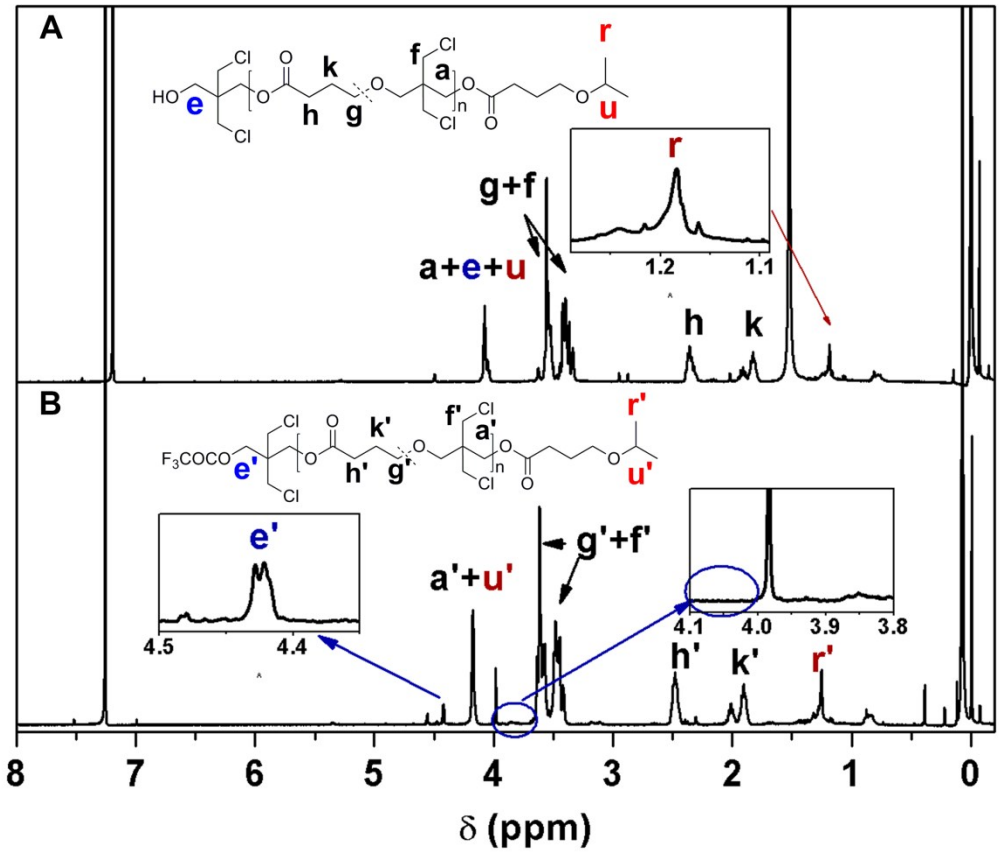


Figure S12. ^{1}H NMR spectra of PBC terminated by isopropanol (A), with TFA treatment then (B).

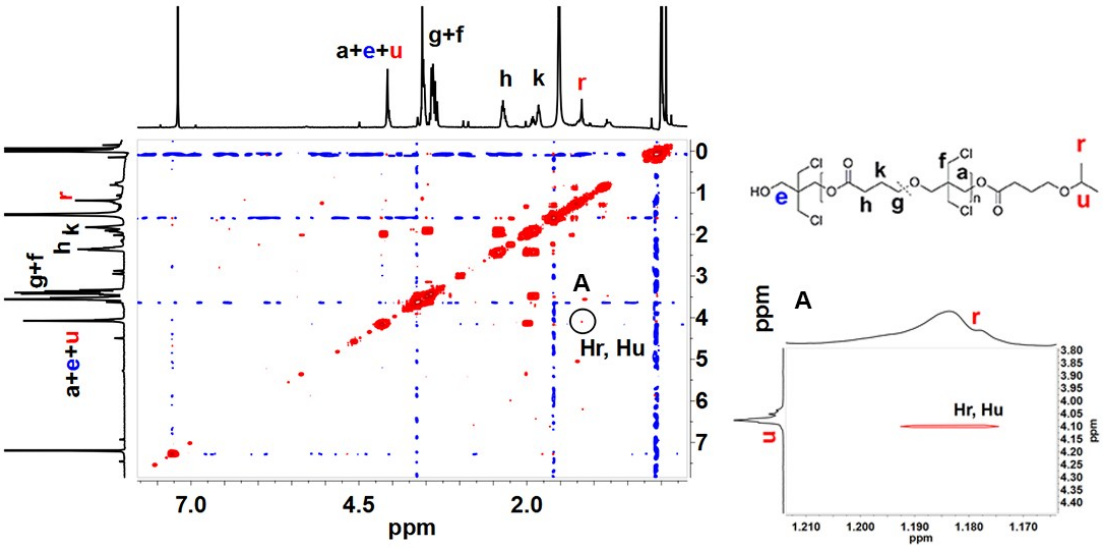


Figure S13. ^{1}H-^{1}H COSY NMR spectra of PBC terminated by isopropanol.

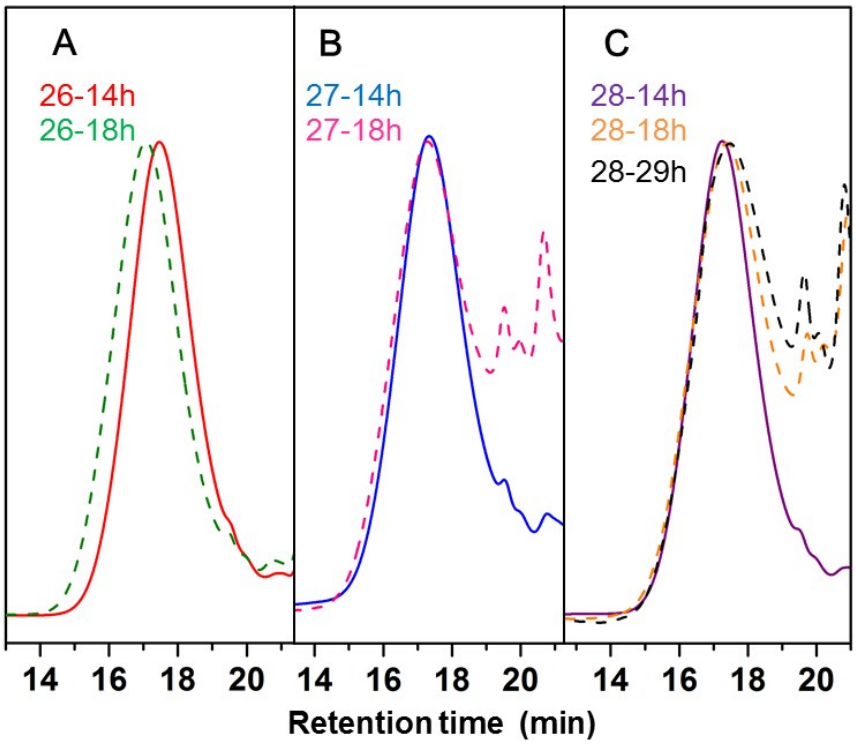


Figure S14. SEC traces of copolymers in Table S3.

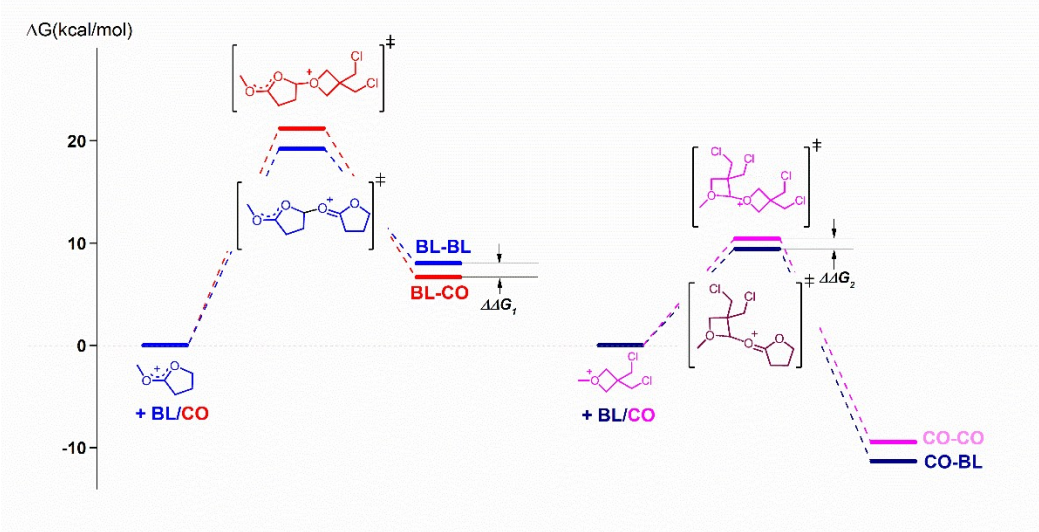


Figure S15. DFT calculated energy profiles of the copolymerization of CO and BL with TSs under tight criteria of wB97XD/6-311++G(d,p). $\Delta\Delta G_1$ = 1.36 kcal/mol, $\Delta\Delta G_2$ = 1.00 kcal/mol.

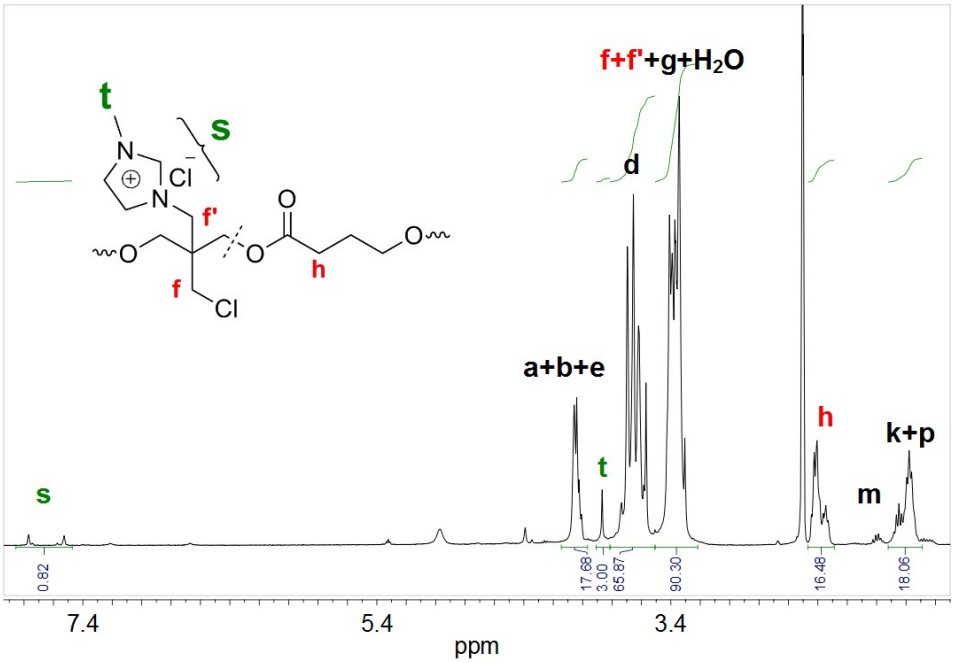


Figure S16. ^{1}H NMR spectra of PBC-MI and integrals in DMSO-*d6*. The other signals (black) are assigned in Figure 1A. Modification ratio of MI is calculated as $\frac{It}{3Ih} \times \frac{1}{1.4}$.

Table S1. Kinetic study of CO with BL. [a]

Sample	Time (h)	Conv (%) [b]		BL mol% in polymer [b]	$M_{n.theo}$ [c] (kDa)	$M_{n.SEC}$ [d] (kDa)	$Đ_{SEC}$ [d]
		BL	CO				
12	1	5	16	50	3.8	4.0	1.3
13	3	9	28	50	6.7	6.2	1.3
14	8.2	16	47	53	11.4	10.2	1.3
15	11.7	22	60	53	15.0	13.4	1.3
16	18.7	33	88	53	22.2	20.0	1.5
17	21.7	36	98	53	25.2	26.7	1.6
18	32.7	38	98	53	25.2	36.8	1.7
19	34.7	36	98	53	25.2	37.9	1.7
20	47.7	38	98	53	25.2	48.9	1.7
21	72	38	98	53	25.2	54.0	1.8

[a] All the polymerizations were conducted in bulk at 80 °C with the feed ratio of [Sc]/[BL]/[CO]=1/300/100. [b] Determined by ^{1}H NMR spectroscopy. [c] Calculated according to $M_{n.\,theo} = \frac{[CO]}{[Sc]} \times Conv.(CO) \times 155 + \frac{[BL]}{[Sc]} \times Conv.(BL) \times 86$. [d] $M_{n,SEC}$ and $Đ_{SEC}$ were determined by SEC.

Table S2. Cyclization of CO with BL. [a]

Sample	Time (h)	Conv (%)[b]		$M_{n.theo}$ [c] kDa	$M_{n.SEC}$ [d] kDa	$Đ_{SEC}$ [d]
		BL	CO			
22	19 [e]	35	88	13.6	18.7	1.4
23	19+24 [f]	35	90	13.7	14.9	1.5
24	19+24 [g]	39	95	14.7	20.6	1.5
25	6×24 [h]	39	98	15.1	36.1	1.8
26	41+24 [i]	25	80	3.7	3.3	1.4

[a] Samples 22~25 were synthesized in bulk at 80 °C with the feed ratio Sc/BL/CO = 1/150/66. [b] Determined by ^{1}H NMR spectroscopy. [c] Calculated according to: $M_{n.\,theo} = \frac{[CO]}{[Sc]} \times Conv.(CO) \times 155 + \frac{[BL]}{[Sc]} \times Conv.(BL) \times 86$. [d] $M_{n,SEC}$ and $Đ_{SEC}$ were determined by SEC. [e] Terminated after 19 h. [f] Dissolved in 100 mL dry dichloromethane after 19 h and stirred for another 24 h at room temperature. [g] Terminated after 43 h. [h] Terminated after 6 days. [e,g,h] Used as controls. [i] Sample 26 was synthesized with the feed ratio Sc/BL/CO = 1/60/20. The polymerization solution was dissolved in 100 mL dry dichloromethane after 41 h in bulk at 60 °C and stirred for another 24 h at room temperature.

Table S3. Copolymerization of CO with BL with TBP as cationic trapper. [a]

Sample	Time (h)	TBP	Conv (%) [b]		$M_{n.theo}$ [c]	$M_{n.SEC}$ [d]	$Đ_{SEC}$ [d]
			BL	CO	kDa	kDa	
26	14	-	12	43	4.2	4.4	1.3
	+4	-	17	53	5.2	5.6	1.4
27	14		12	44	4.2	4.7	1.4
	+4	40 eq TBP [e]	13	44	4.3	4.9	1.4
28	14		13	45	4.4	4.9	1.3
	+4	40 eq TBP [f]	14	45	4.4	5.1	1.3
	+0.1	CO & BL [g]	7	20	4.2	5.1	1.3
	+11	CO & BL [h]	7	21	4.3	5.1	1.3

[a] All the polymerizations were conducted in bulk at 60 °C with the feed ratio $Sc(OTf)_3$/BL/CO=1:100:25. [b] Determined by ^1H NMR spectroscopy. [c] Calculated according to: $M_{n.\,theo} = \frac{[CO]}{[Sc]} \times Conv.(CO) \times 155 + \frac{[BL]}{[Sc]} \times Conv.(BL) \times 86$. [d] $M_{n,SEC}$ and $Đ_{SEC}$ were determined by SEC. [e] 40 eq. TBP related to the amount of $Sc(OTf)_3$ was added after polymerization for 14 h and reacted for another 4 h. [f] 40 eq. TBP related to the amount of $Sc(OTf)_3$ was added after polymerization for 14 h and reacted for another 4 h, [g] then another 50 eq CO and 100 eq. BL was added, and [h] reacted for 11 h.