SUPPORTING INFORMATION

for

Regioselective and Alternating Copolymerization of Carbonyl Sulfide with Racemic Propylene Oxide

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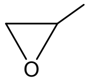
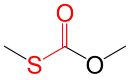
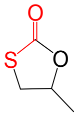
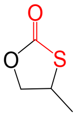
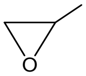
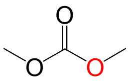
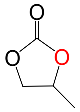
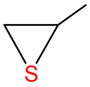
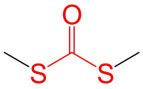
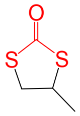
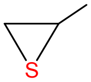
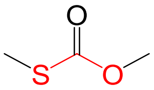
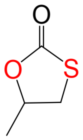
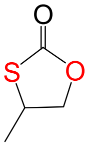
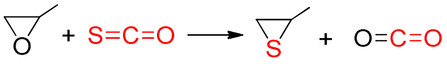
Scheme, Tables and Figures:

Table S1: Possible (thio)carbonate units in the resultant copolymer and cyclic (thio)carbonates from crossed copolymerization of the coexistent species of PO, COS, CO_2, and PS (propylene sulfide).

Possible Reactions	Thiocarbonate units	Cyclic thiocarbonates
 + **COS**	**1** 	**1'**  **4'** 
 + **COO**	**2** 	**2'** 
 + **COS**	**3** 	**3'** 
 + **COO**	**4** 	**1'**  **4'** 

Note that:

(1) O/S exchange reaction: 

, PS had not been captured by GC-MS

spectrum. We thought it was very active and converted to the products promptly after its generation. The capture of CO_2 could prove the production of PS.

(2) O marked with red color in this table represents the oxygen atom from the monomer COS for **2** and **2'.** O from COS might also be at the site of C=O group.

(3) **1'** and **4'** were produced by different backbiting routes, which were described in the text. And both could be differentiated by GC-MS and ^{1}H NMR spectrum.

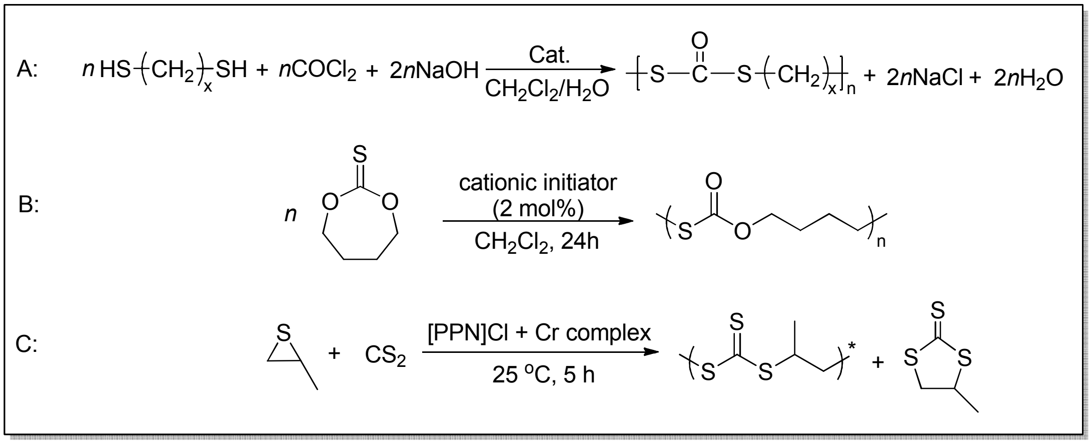
Table S2: *Rac*-PO/COS copolymerization results.

entry[a]	catalyst	cocatalyst[b]	TOF[c] (h^{-1})	copolymer selectivity[d]	PPMTC linkages[d] (%)	Tail-to-Head linkages[e] (%)	O/S ER product[f]	M_n[g] (kg/mol)	PDI[g] (M_w/M_n)
1	**a**	DMAP	8	60/40	77	N.D	N.D	<1.0	1.88
2	**a**	DTMeAB	112	91/9	97	96.2	F	5.9	1.32
3[h]	**a**	[PPN]Cl	184	90/10	98	98.8	N.F	16.9	1.42
4[i]	**a**	[PPN]Cl	321	96/4	>99	97.5	N.F	12.1	1.15
5[j]	**a**	[PPN]Cl	164	96/4	>99	98.5	N.F	10.3	1.08
6[k]	**a**	[PPN]Cl	328	95/5	>99	97.2	F	11.3	1.17
7	**b**	DMAP	172	96/4	>99	97.8	N.F	9.7	1.12
8	**b**	DTMeAB	216	97/3	>99	98.3	F	13.4	1.10
9	**b**	$P(Ph)_3$	N.D	N.D	N.D	N.D	N.D	N.D	N.D
10	**b**	BTPhPB	N.D	N.D	N.D	N.D	N.D	N.D	N.D
11	**b**	$N(Ph)_3$	N.D	N.D	N.D	N.D	N.D	N.D	N.D
12	**b**	*N*-MeIm	N.D	N.D	N.D	N.D	N.D	N.D	N.D
13	**c**	DMAP	86	90/10	>99	97.1	N.F	8.0	1.22
14	**c**	DTMeAB	148	92/8	>99	97.4	F	9.0	1.16

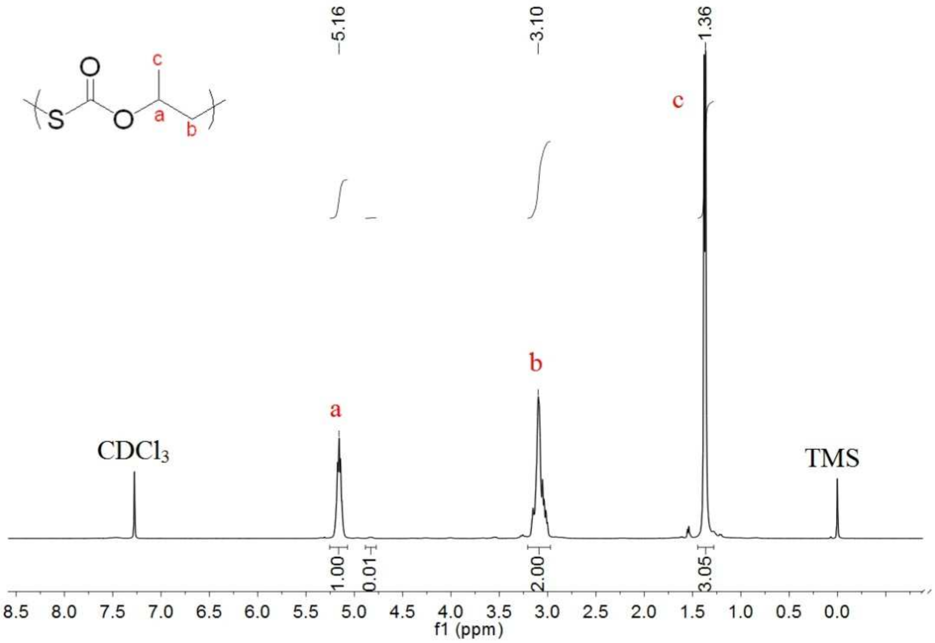
[a] The reaction was performed in neat PO (2.0 ml, 28.6 mmol; catalyst/cocatalyst = 1/1, catalyst/PO = 1/1000, COS/PO = 2/1, all in molar ratio) in a 10 ml autoclave at 25 °C for 3 h. [b] $P(Ph)_3$ = triphenylphosphine, BTPhPB = Benzyltriphenylphosphonium bromide, $N(Ph)_3$ = triphenylamine, *N*-MeIm = Methylimidazole. [c] (Mol epoxide consumed)/(mol Cr h). [d] Determined by using ^{1}H NMR spectroscopy. The product selectivity is represented by the molar ratio of polymer **(1)**/cyclic product. PPMTC linkage is the molar percentage of monothiocarbonate linkage in polymer chain. [e] Determined by using ^{13}C NMR spectroscopy. [f] Determined by using ^{13}C NMR spectroscopy. N.F = not found and F = found. [g] Determined by gel permeation chromatography in THF, calibrated with polystyrene standards. [h] The molar ratio of COS/PO = 1. [i] The molar ratio of COS/PO = 3. [j] CH_2Cl_2 as a solvent. [k] CH_2Cl_2 as a solvent, and the reaction temperature was 60°C.

TOF (turnover frequency), which indicates the molar amounts of epoxide consumed per mole chromium center per hour, was used in the present work to represent the activity of the catalyst system. Besides [PPN]Cl, other quaternary ammonium salts and phosphonium salts were tested in conjunction with **b** for catalyzing the copolymerization (Table S2, entries 7 ~ 12), only DMAP and DTMeAB were effective for the copolymerization. DMAP and DTMeAB were also effective when **a** or **c** was used as the catalyst for the copolymerization. The (Salen)CrCl complex combined with [PPN]Cl was the best binary catalyst system for the copolymerization of PO and COS.

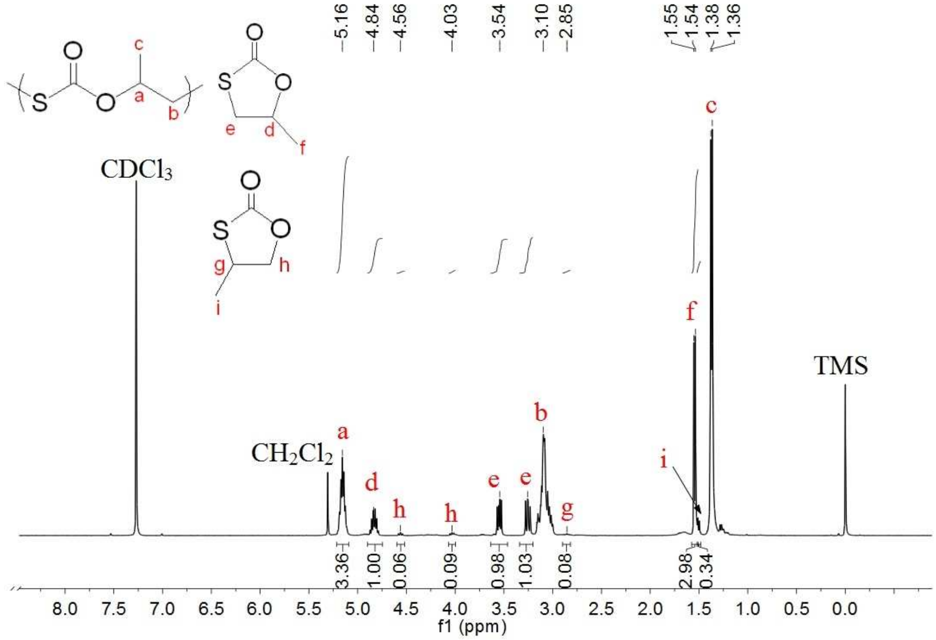
Scheme S1. Three reported methods for synthesizing various poly(thiocarbonate)s. A: Polycondensation. B: Ring-opening polymerization (ROP). C: Alternating copolymerization. [1-3]



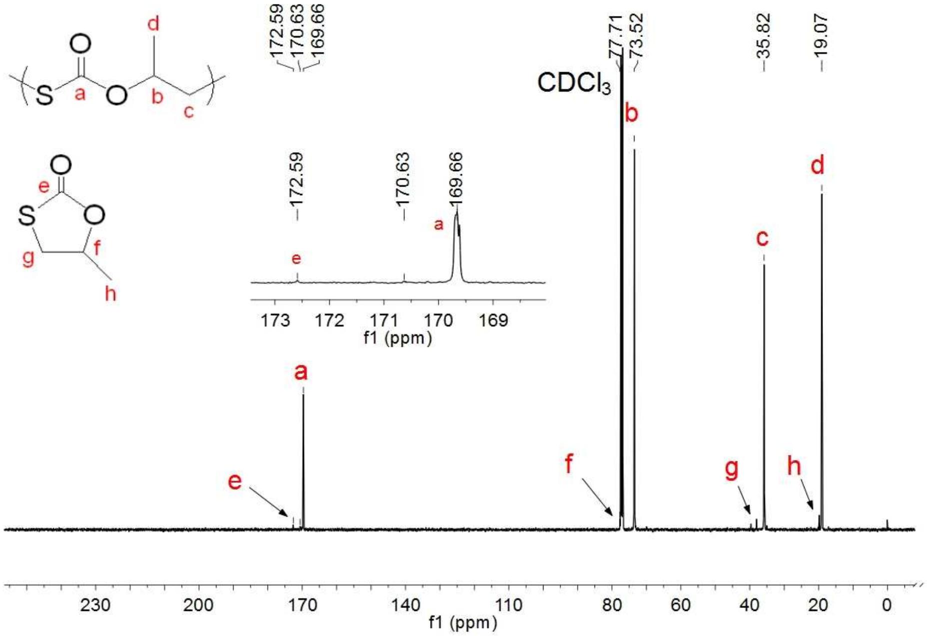
(a)



(b)


5.16
4.84
4.56
4.03
3.54
3.10
2.85
1.55
1.54
1.38
1.36
S
O
O
a
b
c
S
O
O
e
d
f
CDCl$_3$
S
O
O
g
h
i
c
f
TMS
b
a
CH$_2$Cl$_2$
d
h
h
e
e
g
i
3.36
1.00
0.06
0.09
0.98
1.03
0.08
2.98
0.34
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

(c)


172.59
170.63
169.66
77.71
73.52
35.82
19.07
S
O
O
a
b
c
d
CDCl$_3$
b
d
S
O
O
e
f
g
h
172.59
170.63
169.66
e
a
173
172
171
170
169
f1 (ppm)
c
a
e
f
g
h
230
200
170
140
110
80
60
40
20
0
f1 (ppm)

(d)

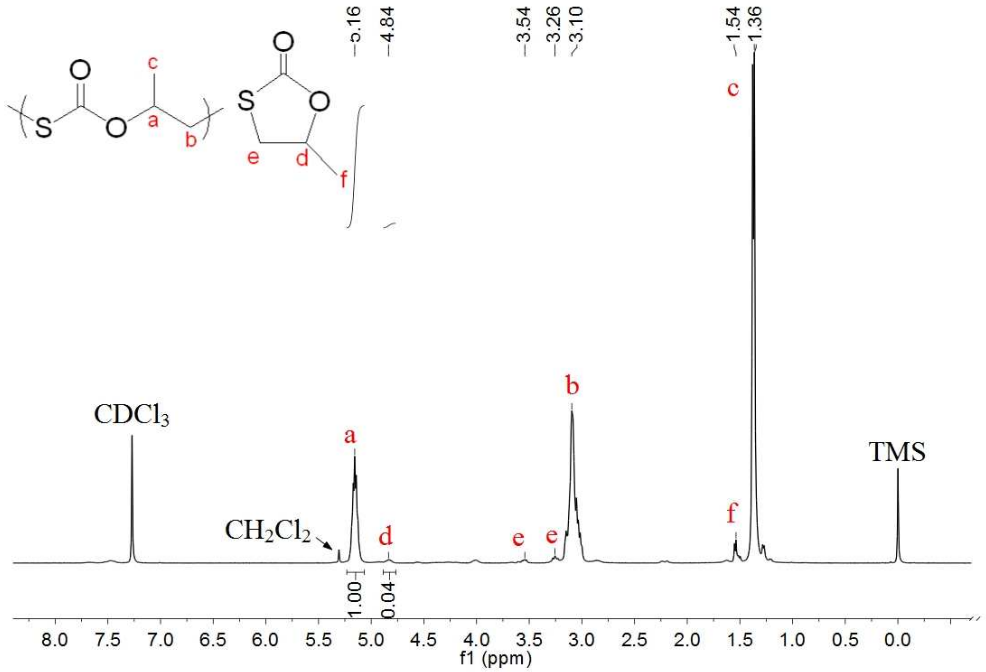


Figure S1. (a) ^{1}H NMR spectrum of the purified copolymer of entry 1 in Table 1. (b) ^{1}H NMR spectrum of the crude product of entry 3 in Table S2. (c) ^{13}C NMR spectrum of the crude product of entry 1 in Table 1. (d) ^{1}H NMR spectrum of the purified copolymer of entry 4 in Table S2.

In most of the NMR spectra of all entries, **1’** was the only cyclic product detected; the amount of **4’** and other cyclic product was negligible. The product selectivity was determined by the weight ratio of copolymer **1**/cyclic propylene thiocarbonate **(1’ + 4’)**, which was determined by the calculation of the integration of peak area in ^{1}H NMR spectrum (i.e. **b** in Figure S1) of the crude product. The selectivity of **1**/**1’** = $118A_a/118(A_d + A_g)$.

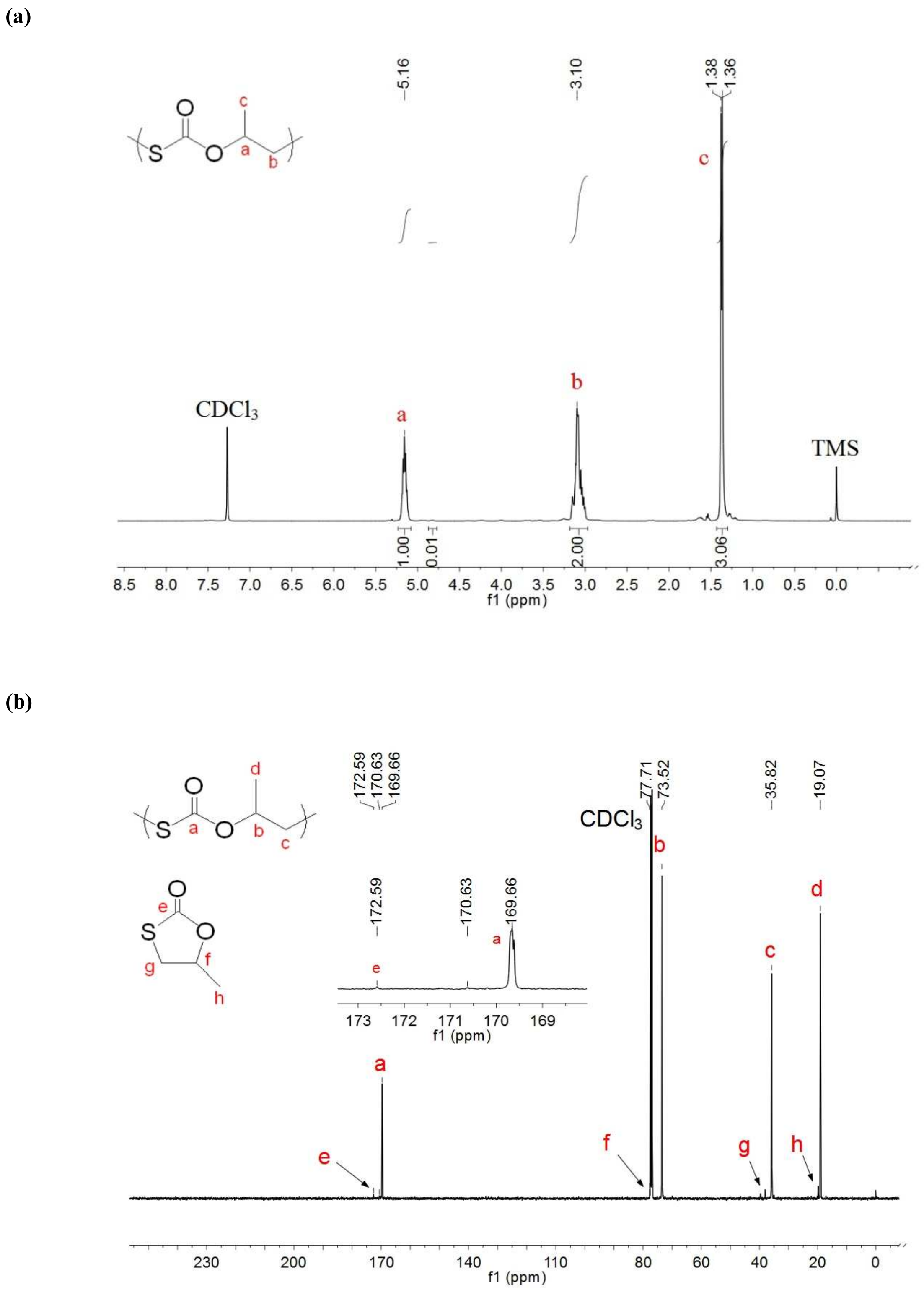
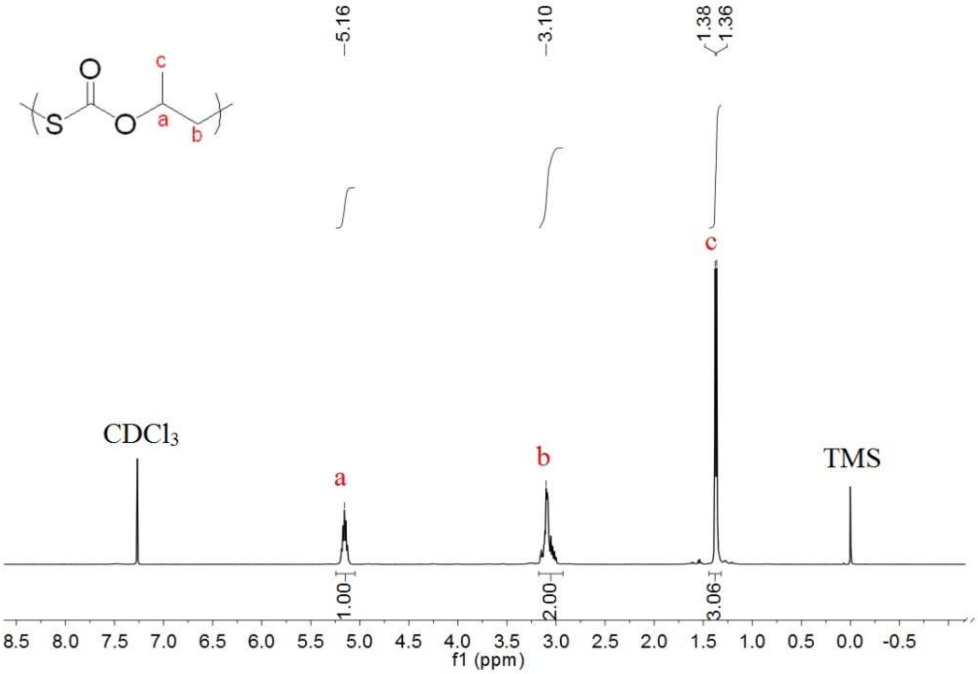


Figure S2. (a) ^{1}H NMR spectrum of the crude product of entry 4 in Table 1. (b) ^{13}C NMR spectrum of the crude product of entry 4 in Table 1.

(a)



(b)

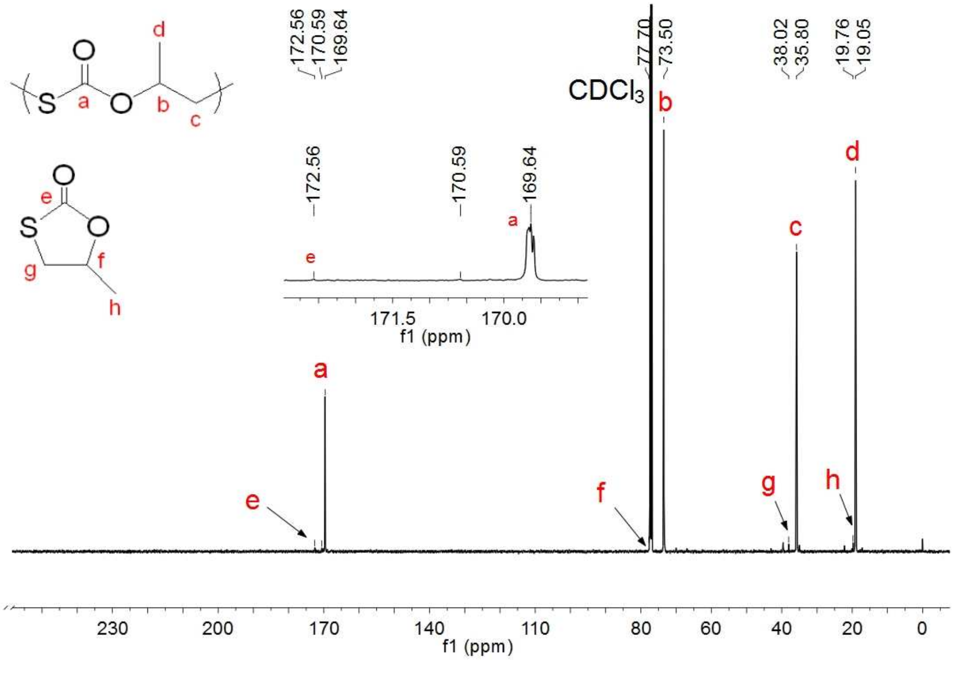
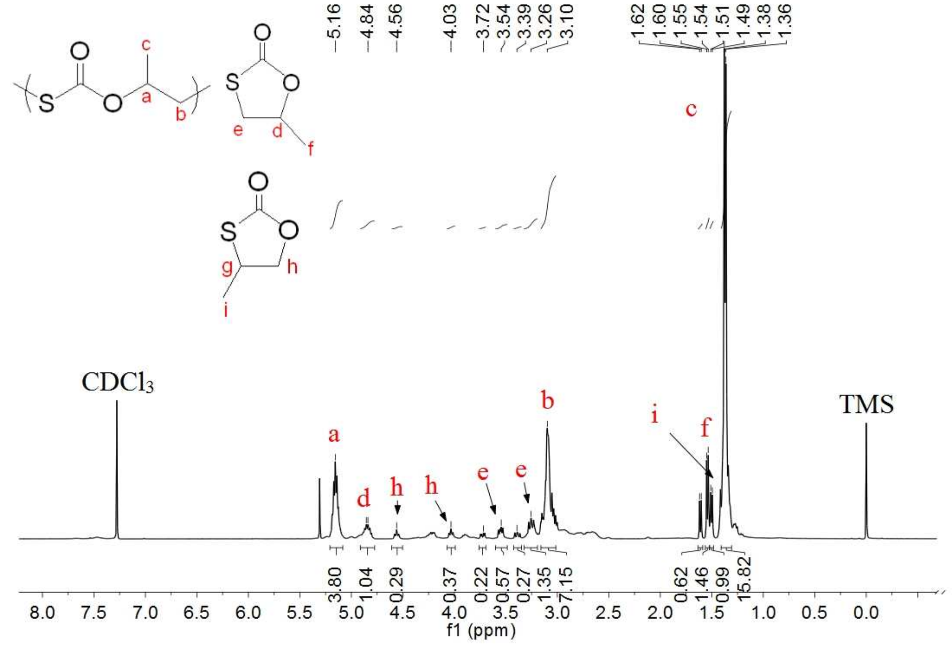


Figure S3. (a) ^{1}H NMR spectrum of the purified copolymer of entry 5 in Table 1. (b) ^{13}C NMR spectrum of the crude product of entry 5 in Table 1.

(a)



(b)

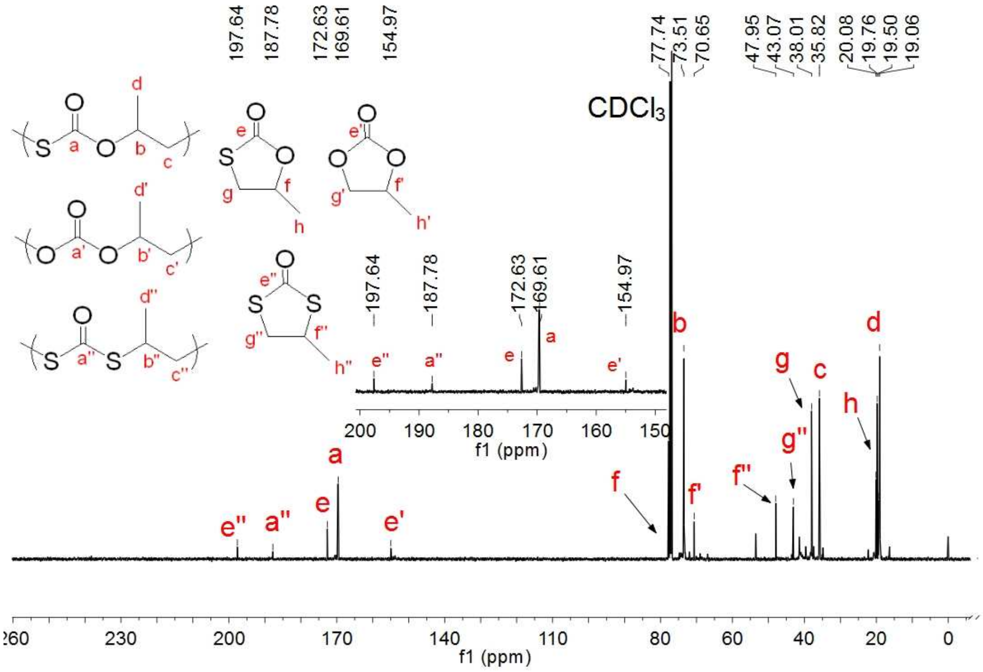


Figure S4. (a) ^{1}H NMR spectrum of the purified copolymer of entry 6 in Table 1. (b) ^{13}C NMR spectrum of the crude product of entry 6 in Table 1.

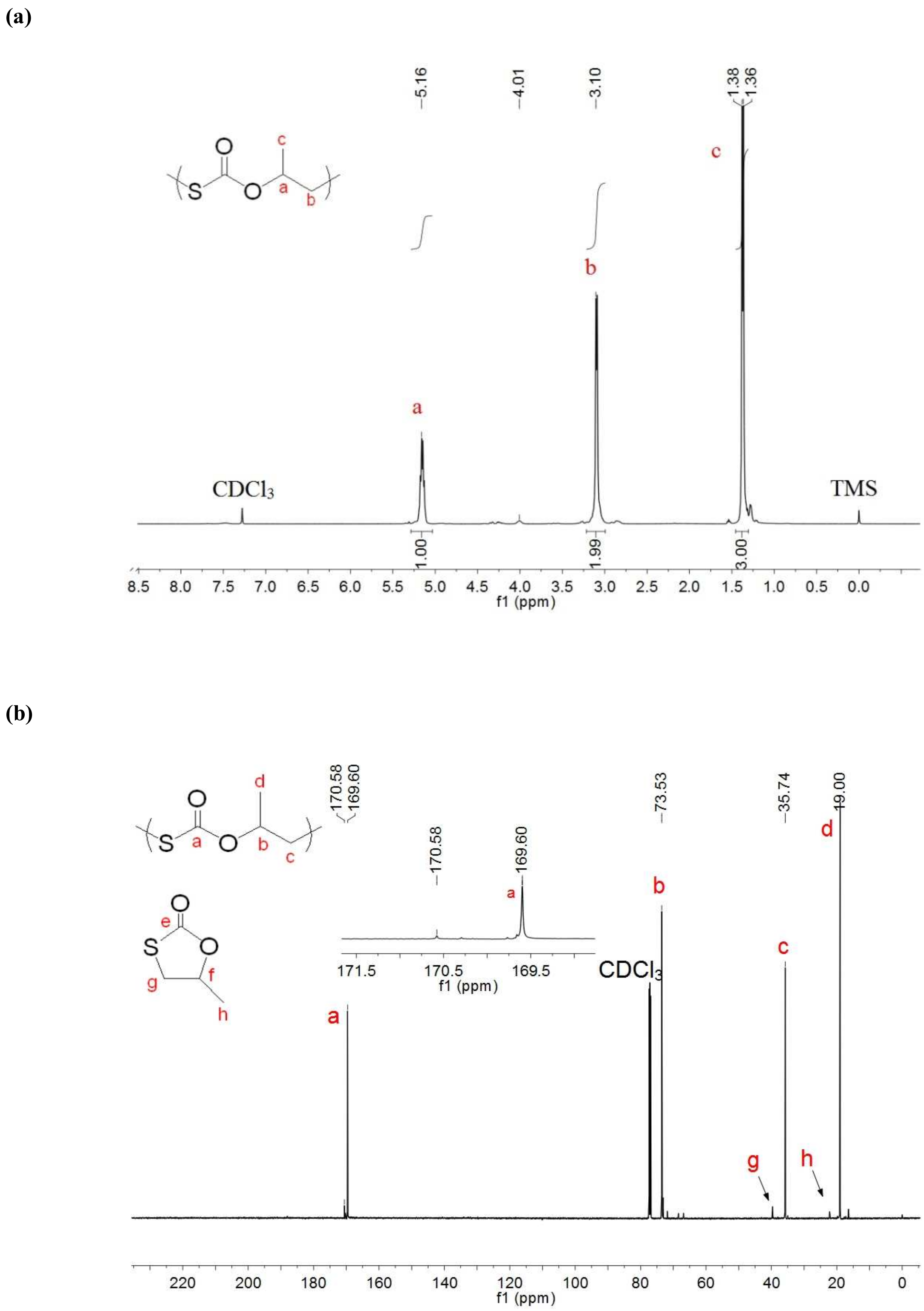


Figure S5. (a) ^{1}H NMR spectrum of the purified copolymer of entry 7 in Table 1. (b) ^{13}C NMR spectrum of the crude product of entry 7 in Table 1.

The Influencing Factors of TOF and product selectivity (1/1').

[PPN]Cl made a better performance in TOF and product selectivity than DMAP and DTMeAB. An increase in reaction temperature or a decrease in COS/PO molar ratio made a significant reduction in TOF and product selectivity (Table 1, entry 6; Table S2, entry 3).

Variation of diamine backbone in (Salen)CrCl complex had a neglected effect on TOF and product selectivity. The copolymerization via the catalysis of binary (Salen)CrCl (**a**, **b**, **c**)/[PPN]Cl systems at 25°C for 3.0 h resulted in nearly complete conversion of PO (yield of **1** + **1'** ≈ 100%), affording copolymer **1** with perfect selectivity (**1**/**1'** > 99), high M_n and narrow PDI (Table 1, entry 1, 4, 5).

The Influencing Factors of Alternating Degree.

The binary catalyst system exhibited superior selectivity for COS/PO copolymerization; all entries had alternating monothiocarbonate linkages. The alternating degrees decreased when the catalyst system exhibited very low activity (Table S2, entry 1, 2). For example, the alternating degree of entry 1 in Table S2 was 77% because M_n of the resultant copolymer was very low (< 1kDa) and the signal of the end groups in ^{1}H NMR spectrum distorted the calculation of the alternating degree. Low MW copolymer was also fully alternating, which was confirmed by the ESI-MS results (see Figure S16). In addition, a decrease of COS/PO molar ratio made a slight reduction in monothiocarbonate linkages (Table S2, entry 3).

The **a(b, c)**/DTMeAB system caused relative low activity and copolymer selectivity (Table S2, entries 2, 8 and 14). The ^{13}C NMR spectra of entries 8 and 14 in Table S2 (A, B in Figure S6) showed clearly resonances of the dithiocarbonate linkage (188.04 *ppm*), carbonate linkage (153.48 *ppm*). That is, O/S ER occurred when DTMeAB was used as the cocatalyst. We considered that O/S ER in **a(b, c)**/DTMeAB catalyst system might be caused by the contained water in the commercial DTMeAB. Note that DTMeAB was easier to absorb water than [PPN]Cl.

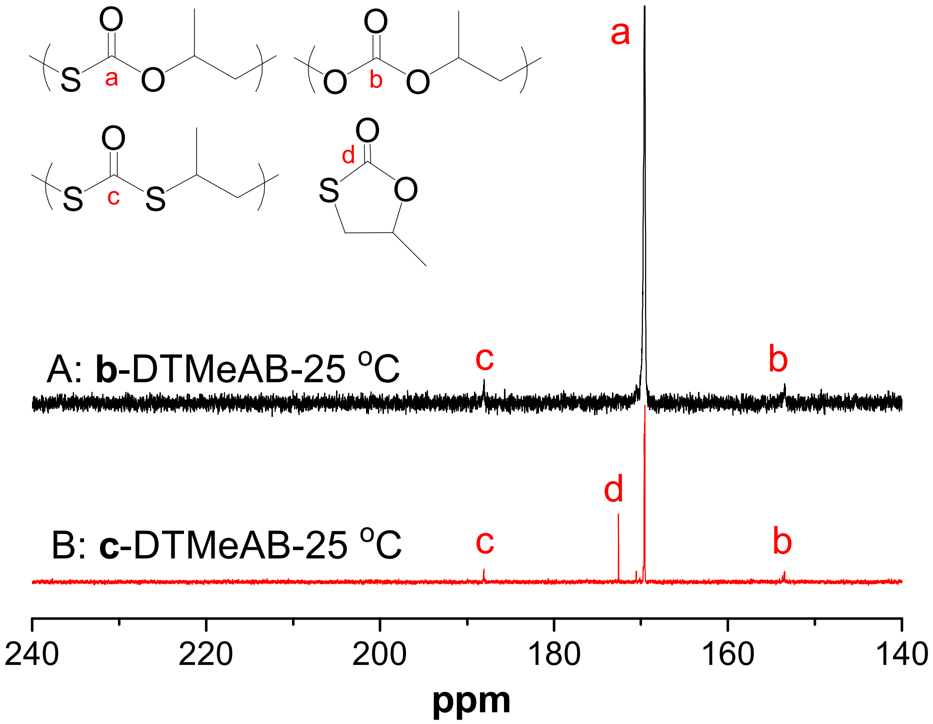
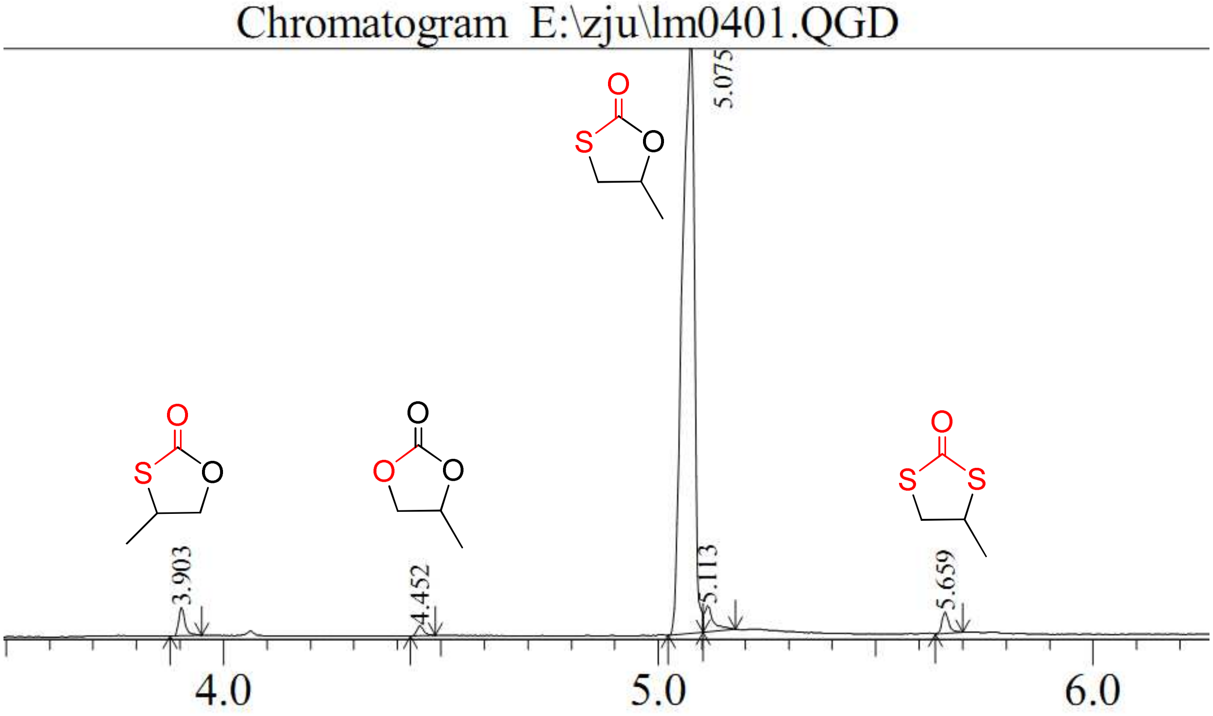


Figure S6. ^{13}C NMR spectra of carbonyl region of the crude products resulted from different reaction conditions.

GC-MS analysis for the cyclic products of COS-PO copolymerization.



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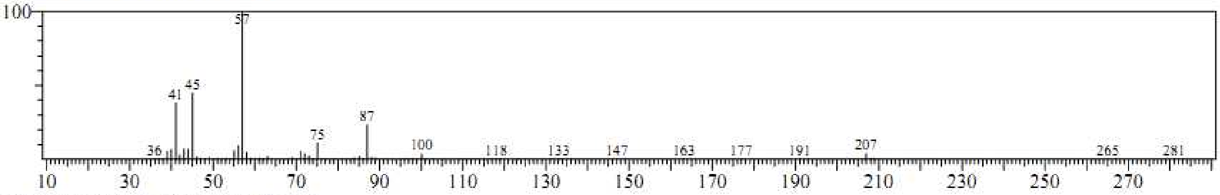
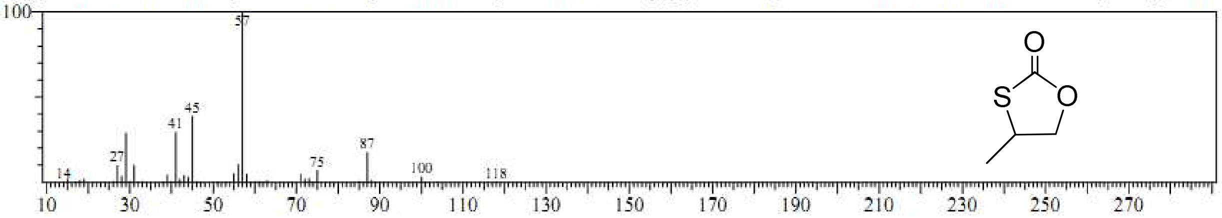
RawMode:Single 3.903(572) BasePeak:57.05(952761)
BG Mode:None Group 1 - Event 1



Hit#:1 Entry:4873 Library:NIST05.LIB
SI:93 Formula:C6H14O2 CAS:111-76-2 MolWeight:118 RetIndex:936
CompName:Ethanol, 2-butoxy- $$ .beta.-Butoxyethanol $$ Butyl cellosolve $$ Butyl glycol $$ Butyl oxitol $$ BuCs $$ Dowanol EB $$ Ethylene glycol bu



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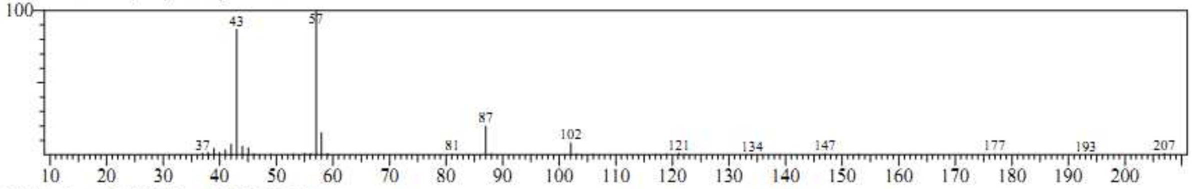
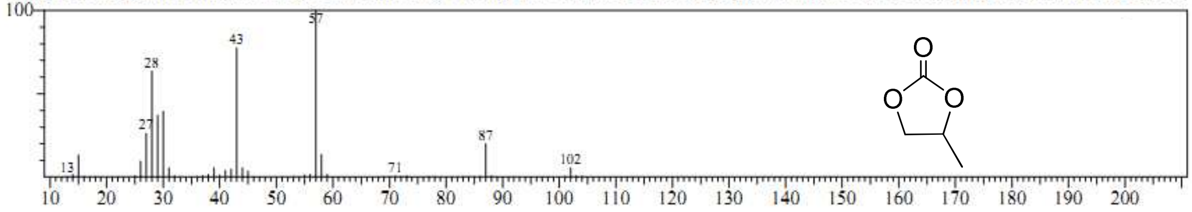
RawMode:Single 4.447(735) BasePeak:57.05(267481)
BG Mode:4.650(796) Group 1 - Event 1



Hit#:1 Entry:2177 Library:NIST05.LIB
SI:96 Formula:C4H6O3 CAS:108-32-7 MolWeight:102 RetIndex:875
CompName:Propylene Carbonate $$ 1,3-Dioxolan-2-one, 4-methyl- $$ Carbonic acid, cyclic propylene ester $$ Cyclic methylethylene carbonate $$ Cyclic p



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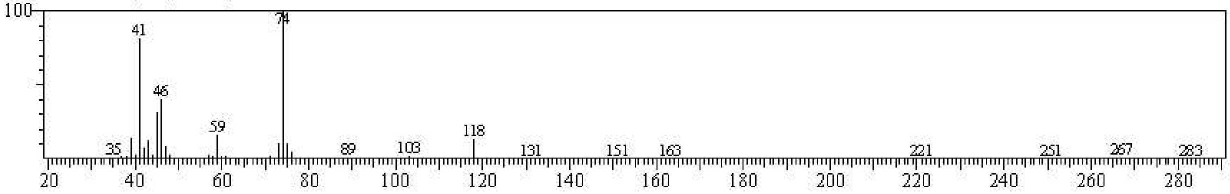
BG Mode:4.840(853) Group 1 - Event 1



Hit#:3 Entry:4792 Library:NIST05.LIB
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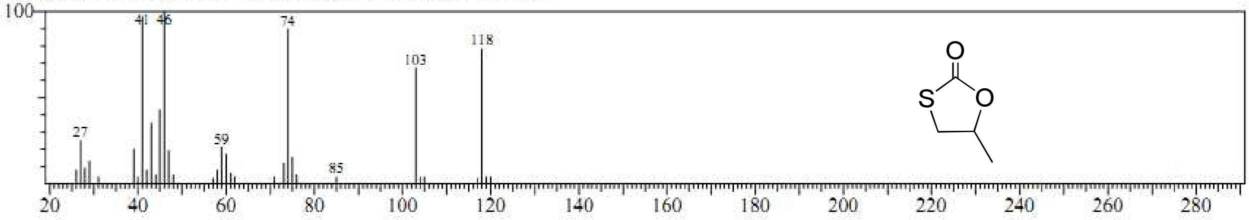
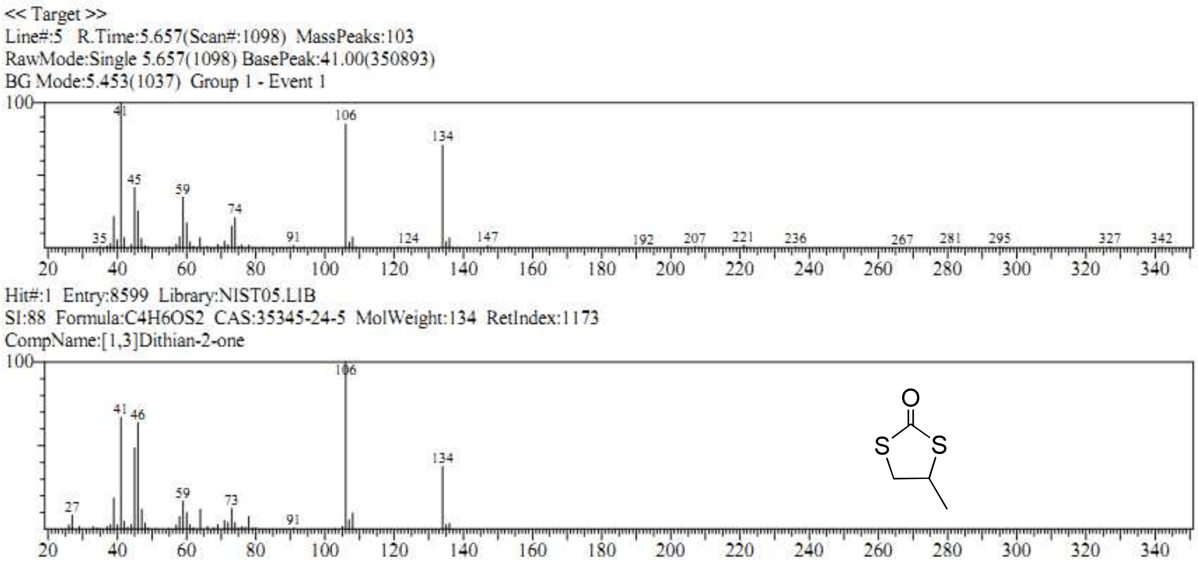
CompName:1,3-Oxathiane, 2-methyl- $$ 2-Methyl-1,3-oxathiane $$





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RawMode:Single 5.657(1098) BasePeak:41.00(350893)
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Hit#:1 Entry:8599 Library:NIST05.LIB
SI:88 Formula:C4H6OS2 CAS:35345-24-5 MolWeight:134 RetIndex:1173
CompName:[1,3]Dithian-2-one

Figure S7. GC-MS spectrum of the cyclic products of entry 6 in Table 1.

Table S3. Four cyclic five-membered compounds with m/z values (Figure S7, entry 6 in Table 1).

R.Time	m/z	Area%	Cyclic product
3.903	118, 74, 59, 45, 41	2.31	4-methyl-[1,3]oxathiolan-2-one
4.452	102, 87, 57, 43	0.90	4-methyl-[1,3]dioxolan-2-one
5.075	118, 74, 59, 46, 41	92.12	5-methyl-[1,3]oxathiolan-2-one
5.659	134, 106, 74, 59, 45, 41	1.84	4-methyl-[1,3]dithiolan-2-one

The effect of reaction time on the copolymerization of COS/PO.

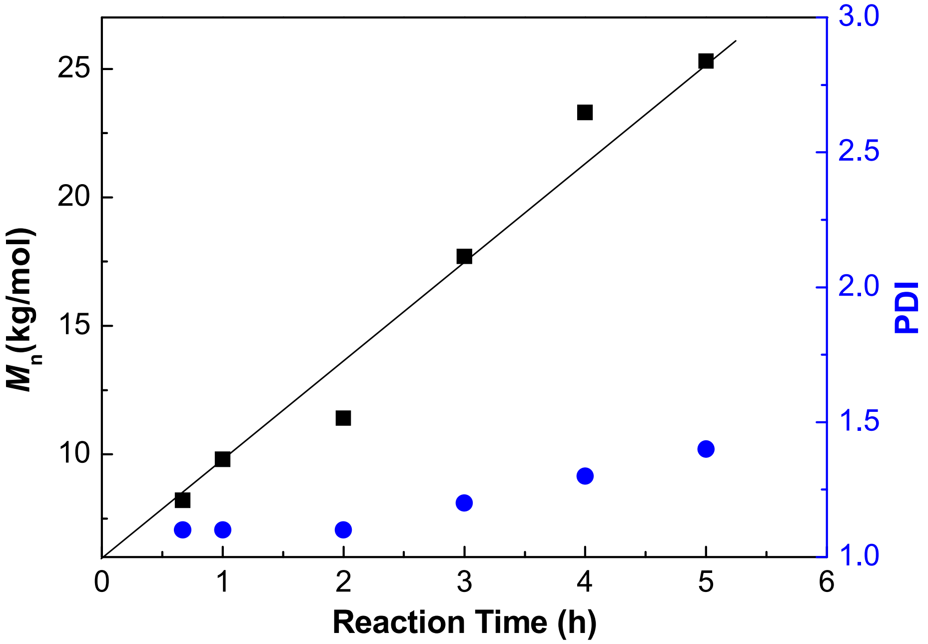


Figure S8. Plots of M_n (■) and PDI (●) vs reaction time, other reaction conditions were same as entry 5 in Table 1.

PDIs in the late polymerization stage became wide because high monomers' conversion and high viscosity of the reaction system.

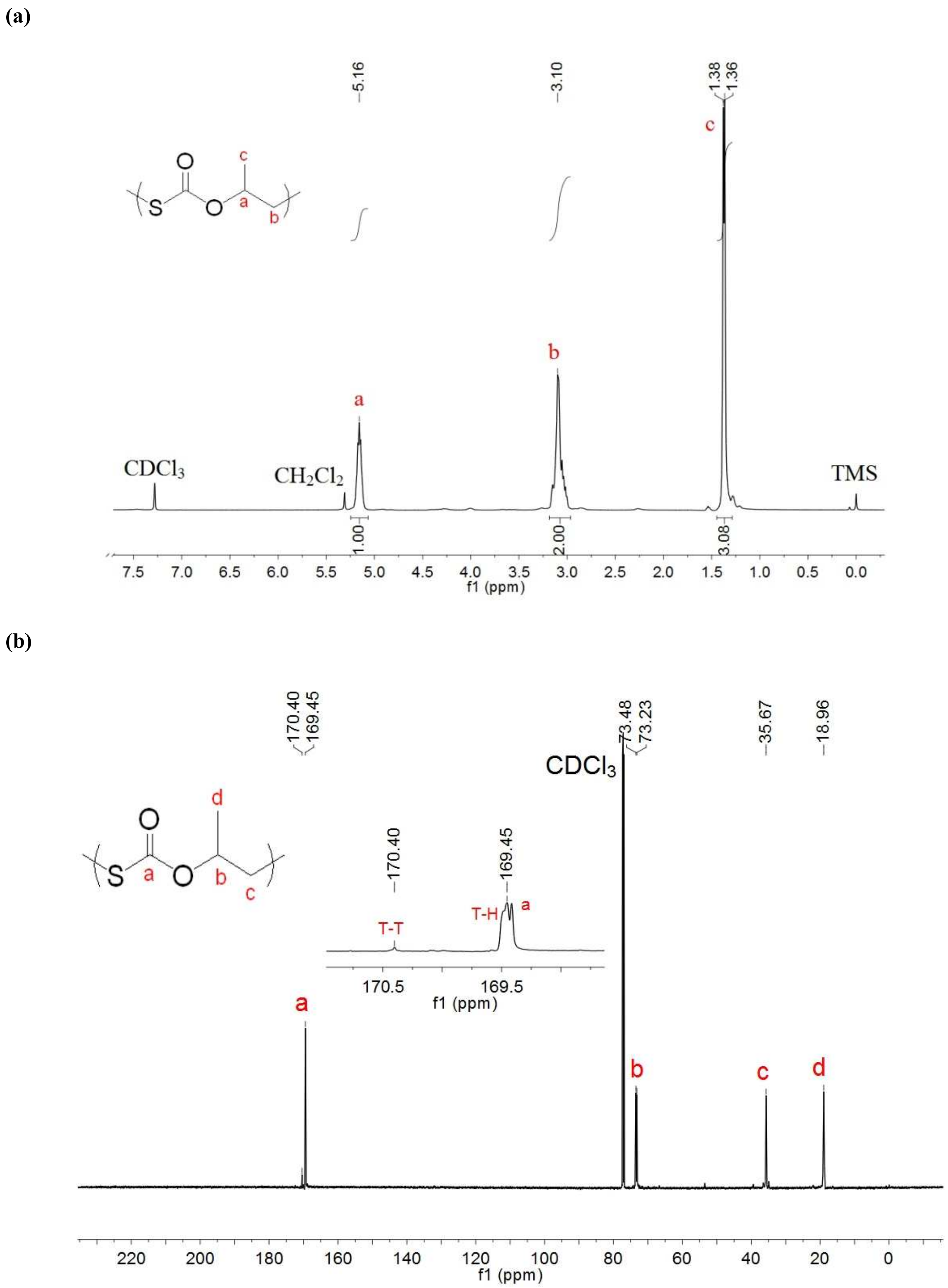
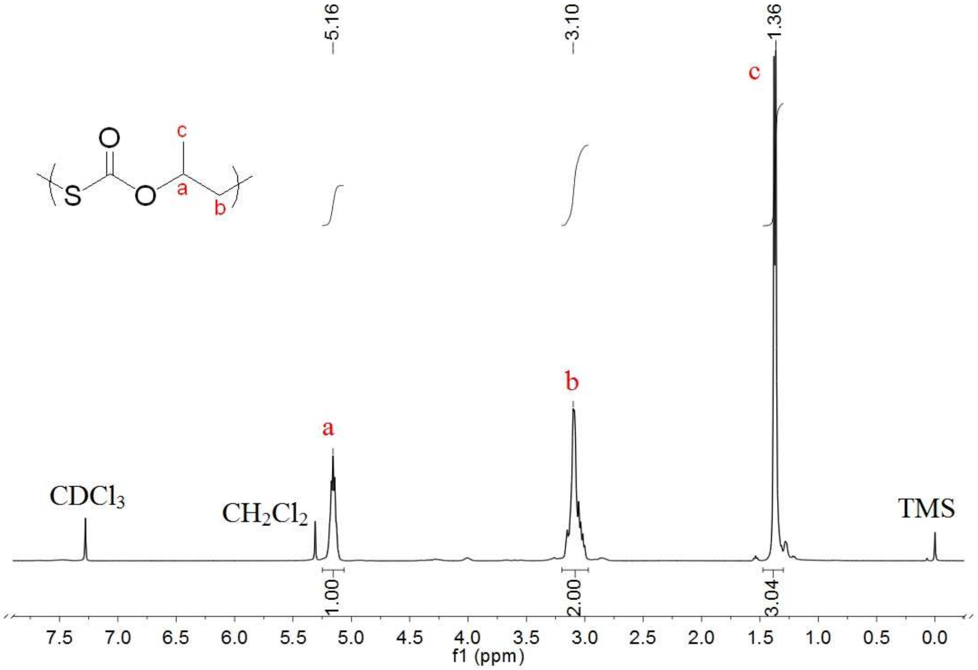


Figure S9. (a) ^{1}H NMR spectrum of the crude product (entry 1 in Table 2). (b) ^{13}C NMR spectrum of the crude product (entry 1 in Table 2).

(a)



(b)

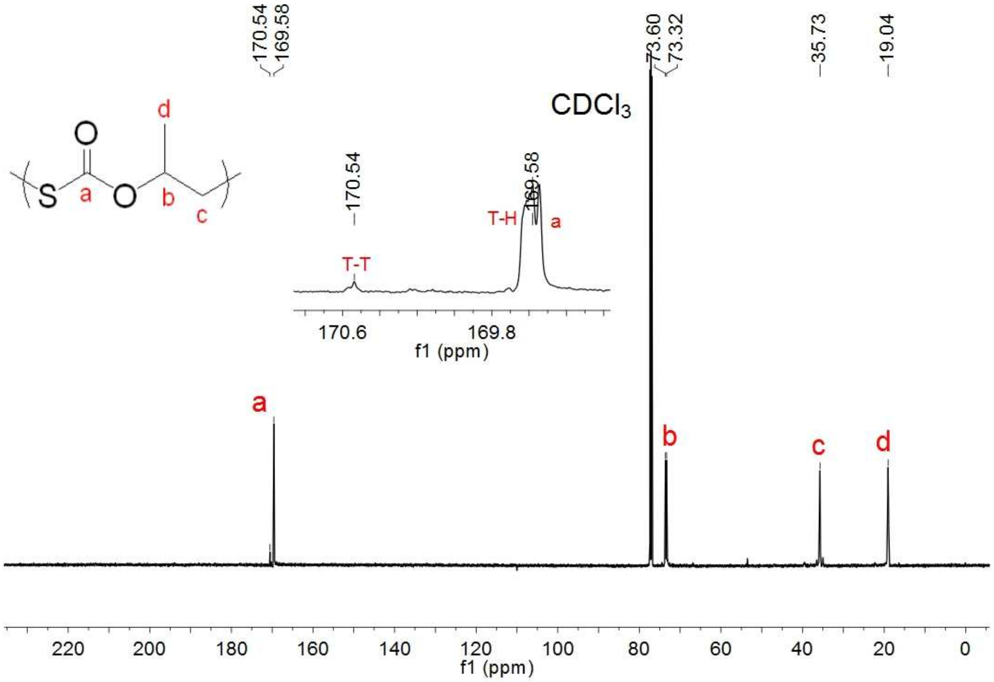


Figure S10. (a) ^{1}H NMR spectrum of the crude product (entry 2 in Table 2). (b) ^{13}C NMR spectrum of the crude product (entry 2 in Table 2).

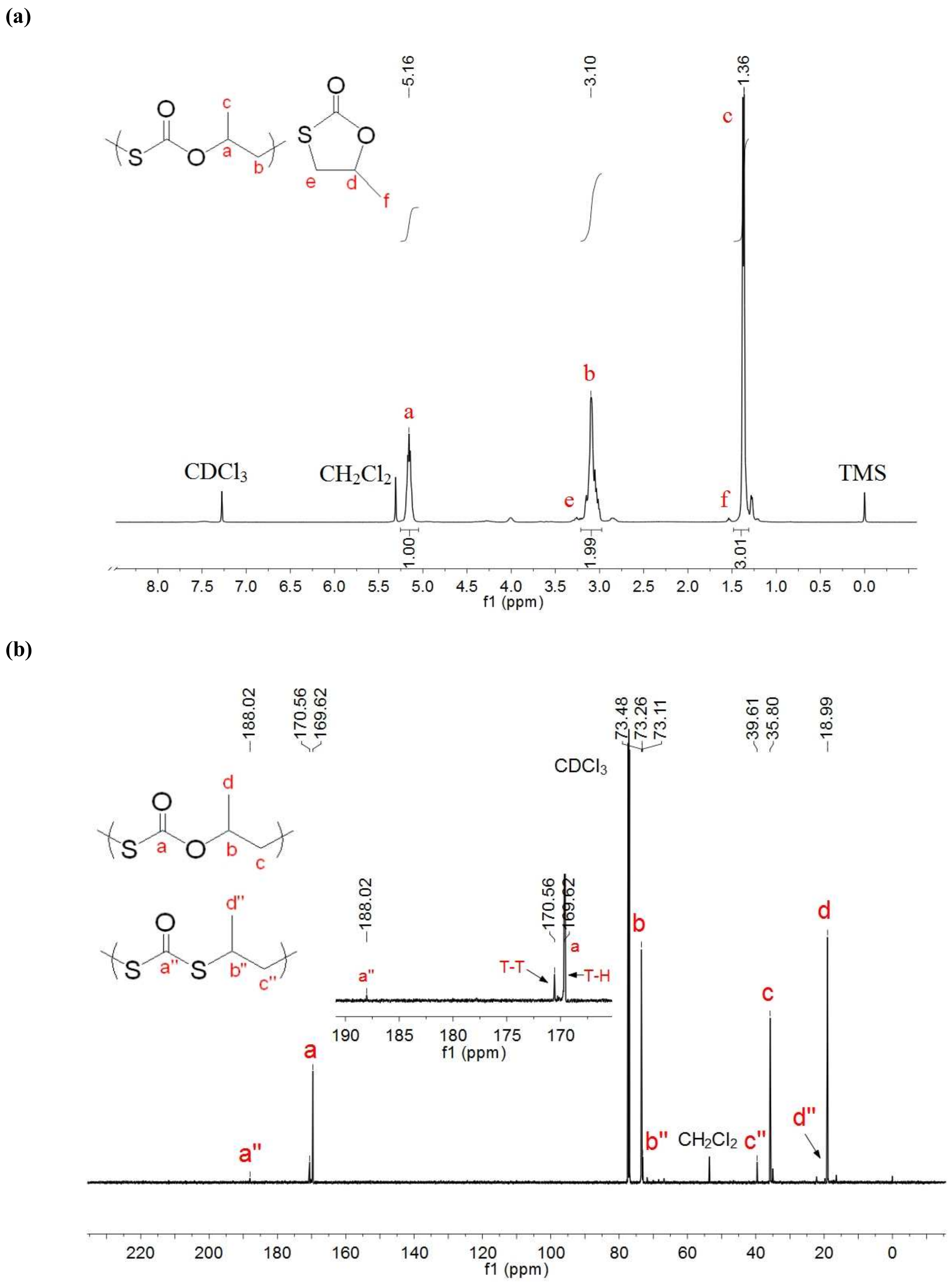
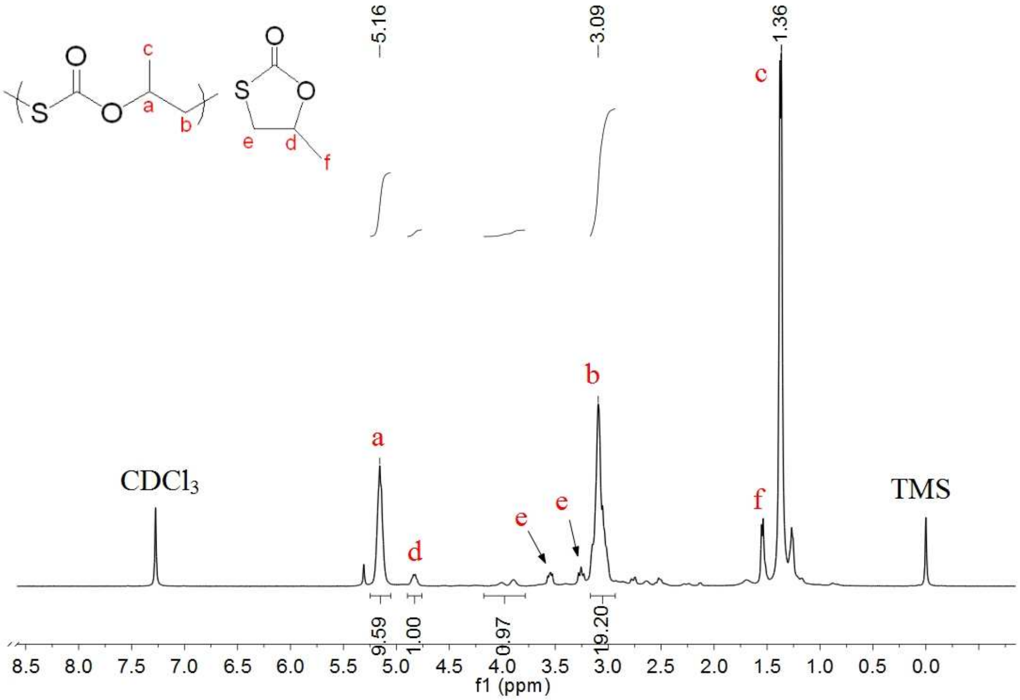


Figure S11. (a) ^{1}H NMR spectrum of the crude product (entry 3 in Table 2). (b) ^{13}C NMR spectrum of the crude product (entry 3 in Table 2).

(a)



(b)

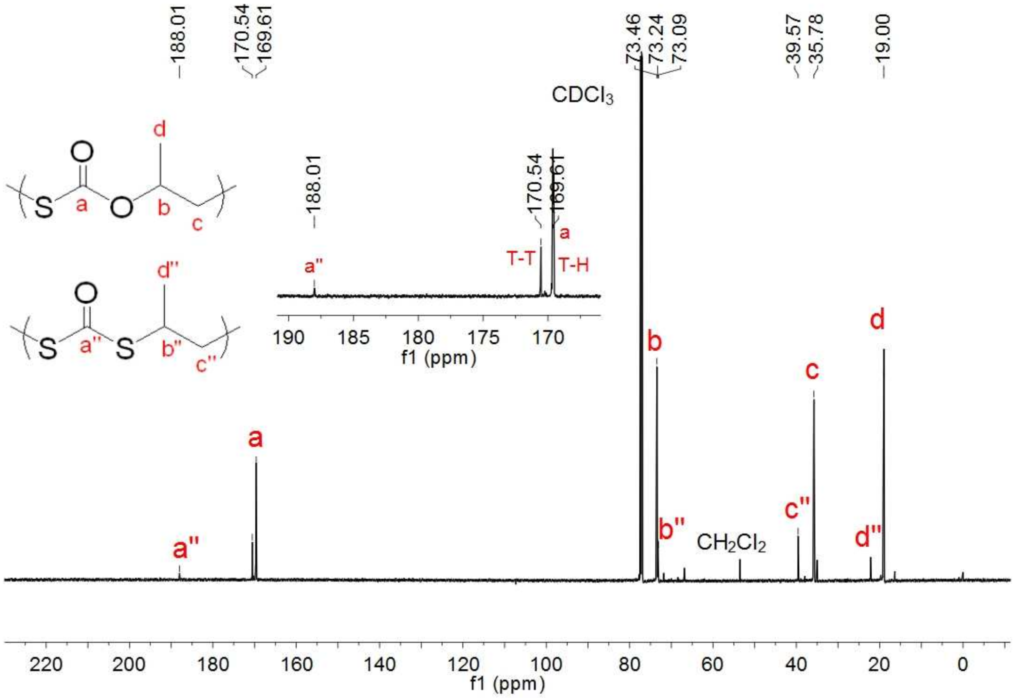


Figure S12. (a) ^{1}H NMR spectrum of the crude product (entry 4 in Table 2). (b) ^{13}C NMR spectrum of the crude product (entry 4 in Table 2).

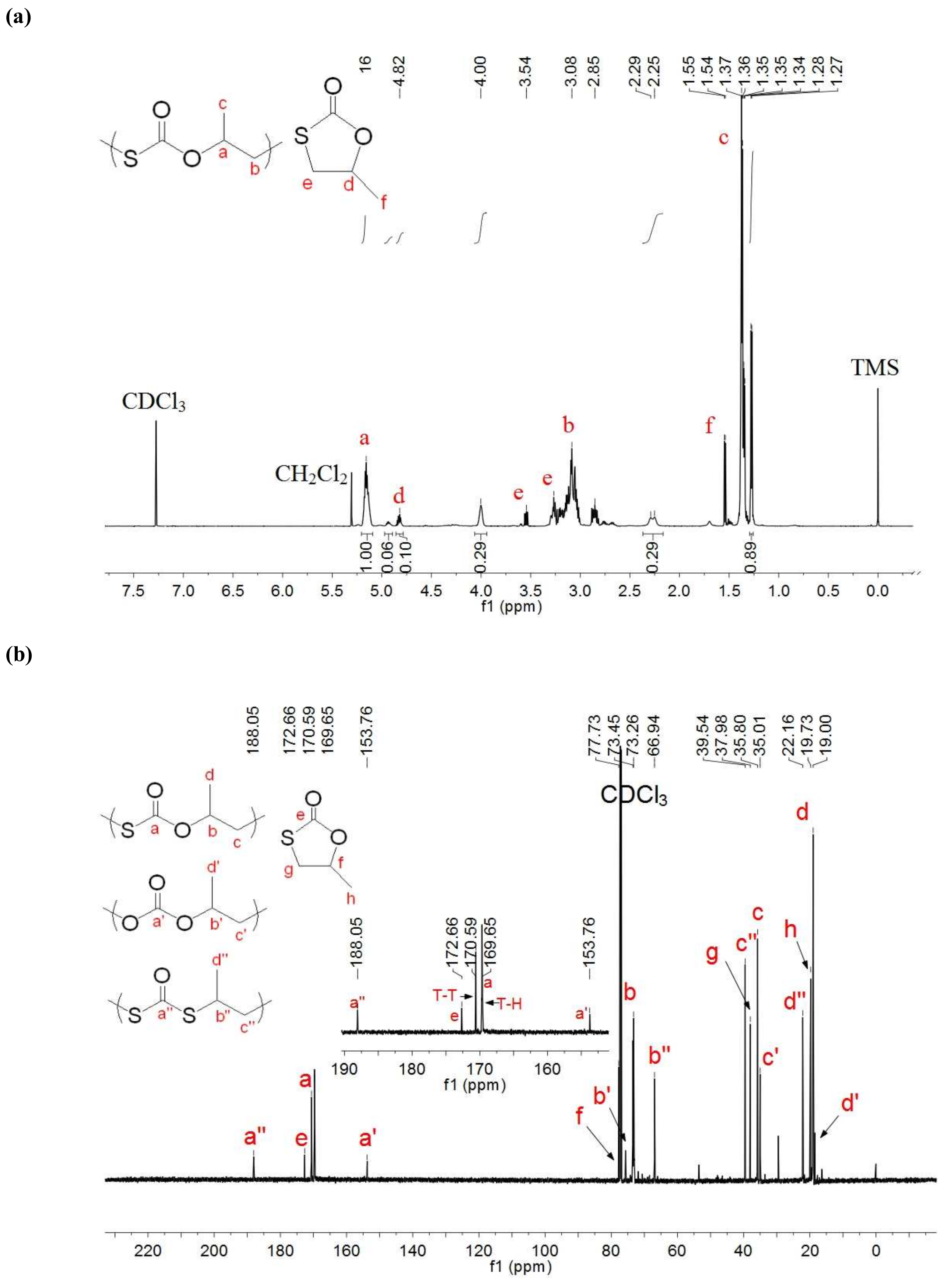
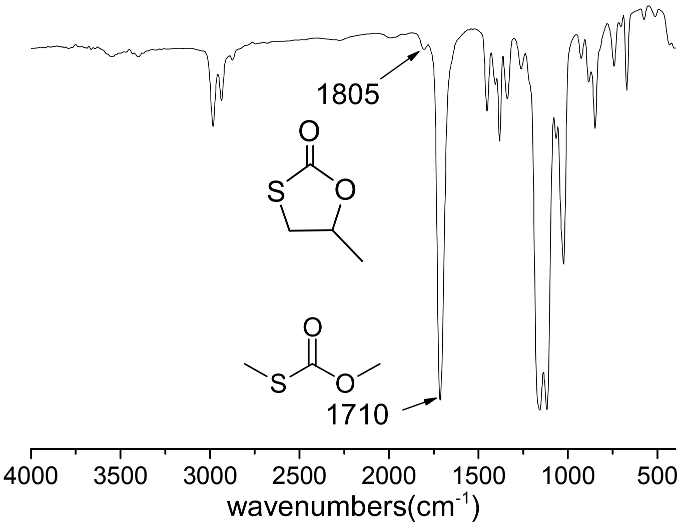


Figure S13. (a) ^{1}H NMR spectrum of the crude product (entry 5 in Table 2). (b) ^{13}C NMR spectrum of the crude product (entry 5 in Table 2).

FT-IR and Raman spectra.

(a)



(b)

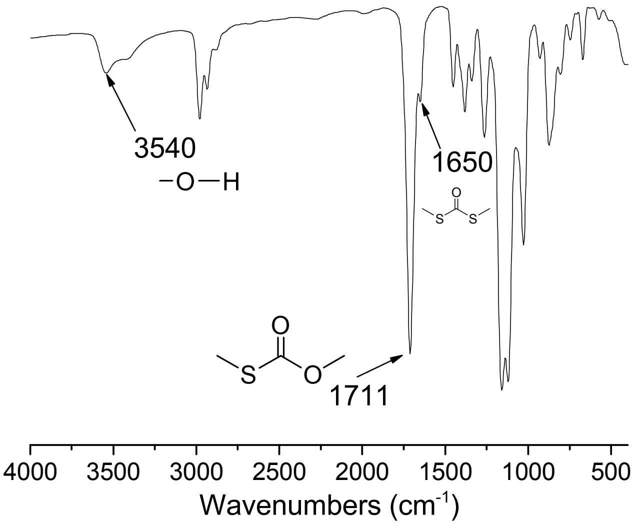


Figure S14. FT-IR spectra of (a) the crude product of entry 5 in Table 1 and (b) the purified polymer of entry 5 in Table 2.

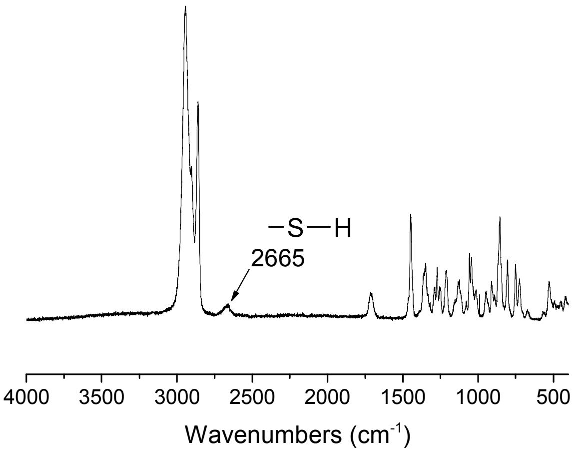


Figure S15. Raman spectrum of the purified polymer of entry 5 in Table 2.

ESI-MS analysis for the products of COS-PO copolymerization

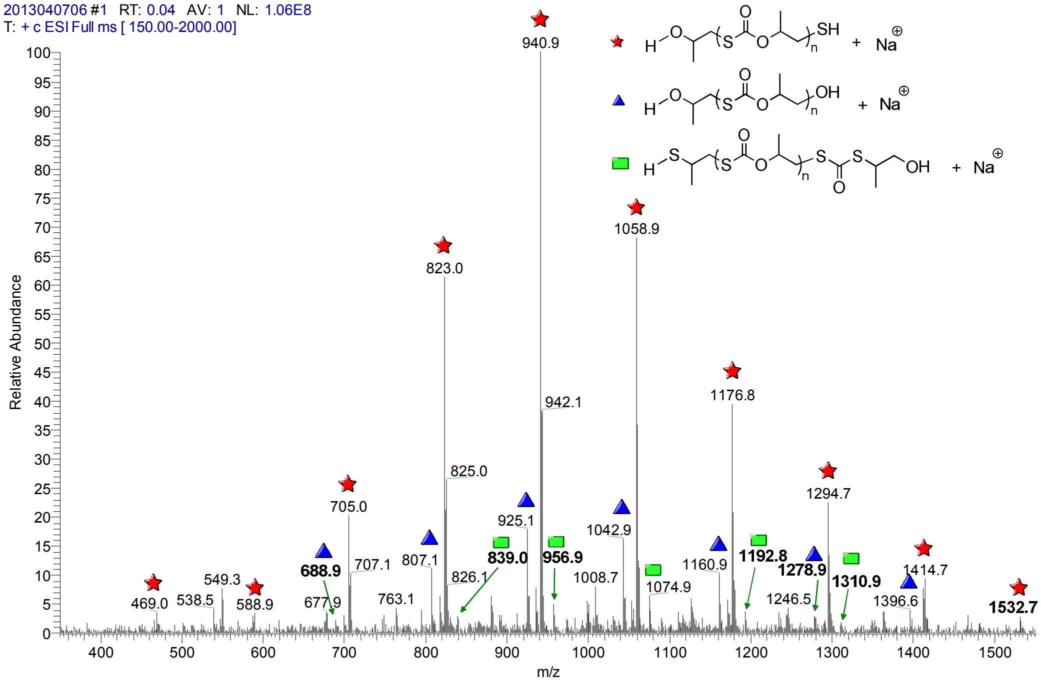
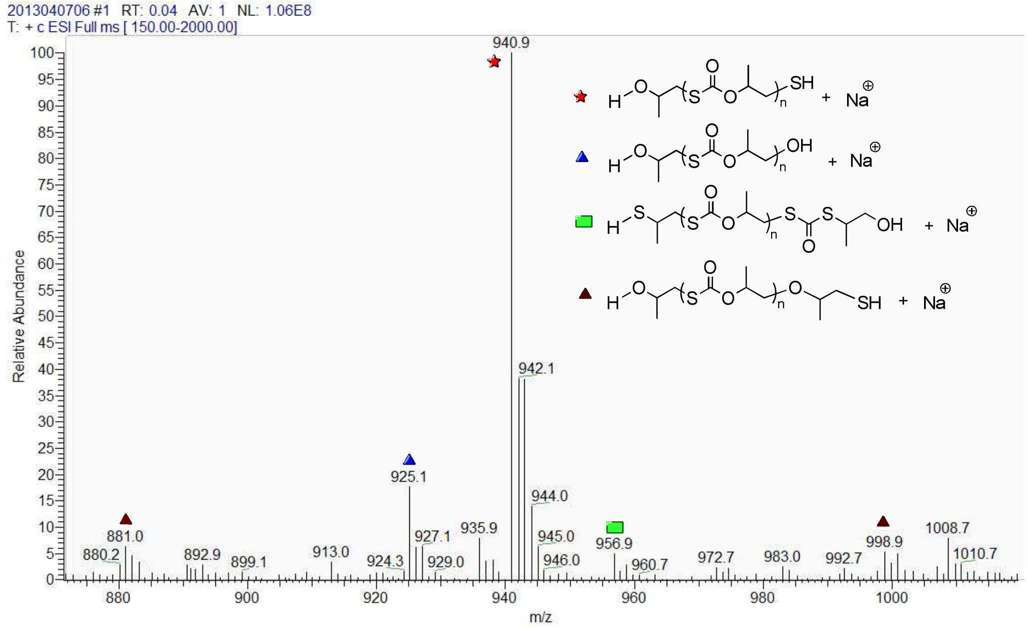


Figure S16. (a) ESI-MS analysis for the products of COS-PO copolymerization (entry 5, Table 2).

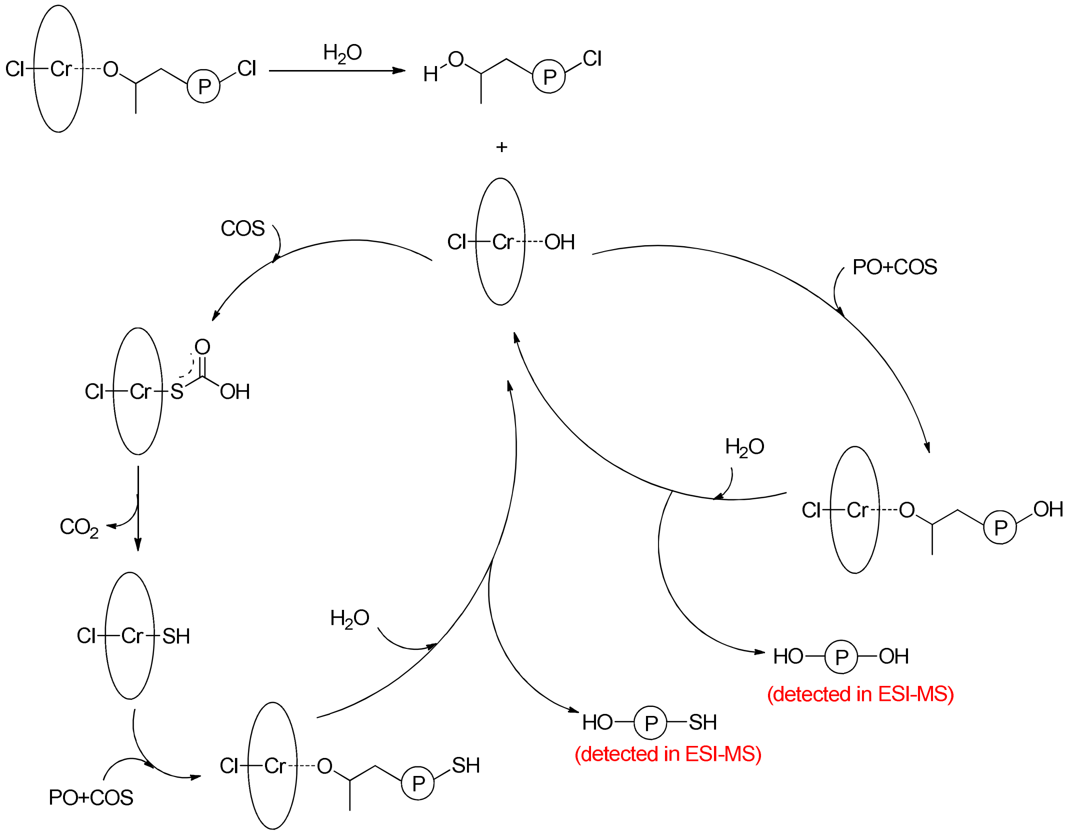
H-PO-(COS-PO)$_n$-SH + Na$^+$	469, 587, 705, 823, 941, 1059, 1177, 1295, 1413, 1531
H-PO-(COS-PO)$_n$-OH + Na$^+$	689, 807, 925, 1043, 1161, 1279, 1397, 1515
H-PO-(COS-PO)$_n$+(COS-PS)-SH + Na$^+$	839, 957, 1075, 1193, 1311



(b) ESI-MS spectrum (880 ~1010 m/z) of the products of COS-PO copolymerization (entry 5, Table 2).

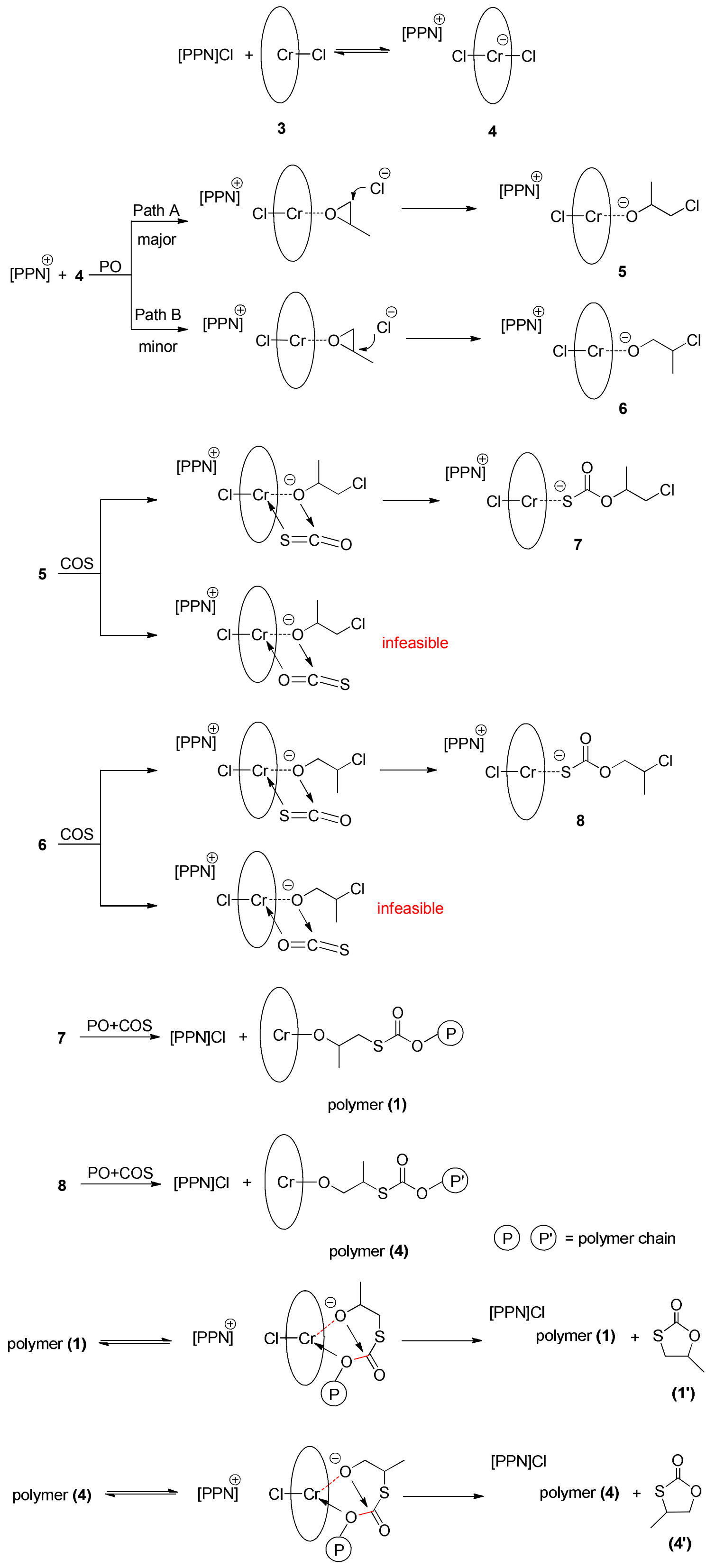
The ESI-MS spectrum (880 ~ 1010 m/z) showed above was ascribed to four species (insert scheme). A species with one more PO unit (▲) was captured with rather small relative abundance. Such small amounts of consecutive ether unit could not found by ^{1}H NMR spectrum (Note that this is a copolymer with rather small MW), so we can say that the alternating degree of COS-PO copolymers (esp. that with high MWs) were > 99%.

Scheme S2. H_2O acted as a chain transfer agent in the reaction.



H_2O acted as a chain transfer agent in this reaction, it could terminate the copolymerization and gave a copolymer with one -OH chain end and the other -Cl chain end. Meanwhile, the Cr-OH became a new initiating center. The Cr-OH center could initiate PO/COS copolymerization and lead to a copolymer with both two -OH chain ends. The Cr-OH could also react with a COS so that a O/S ER occurred, which offered a new initiating center : Cr-SH. Similar with Cr-OH, the Cr-SH could initiate PO/COS copolymerization and lead to a copolymer with one -OH chain end and the other -SH. These two copolymers were both detected in ESI-MS spectrum. When the system was well water-removed, the Cr-Cl would be the only initiating center, as reported elsewhere, and the copolymers with -Cl chain end were in majority. However, when a large amounts of H_2O were added (entry 5, Table 2), the copolymer with one –Cl end group was not observed by ESI-MS spectrum because the chain transfer reaction of propagating species to water was very fast. The Cr-OH became the major initiating center and the copolymer with two -OH chain ends was in large abundance (Figure S16).

Scheme S3. Plausible reaction mechanism of the copolymerization of PO-COS.



The Thermal Performance of the Copolymer

The copolymer **1** of entry 1 in Table 1 (PPMTC linkages = 100%, M_n= 24 400 Da) was chosen for DSC and TGA measurements. The T_g of the copolymer **1** was 19.5 °C and the T_d of the copolymer **1** was137.3 °C.

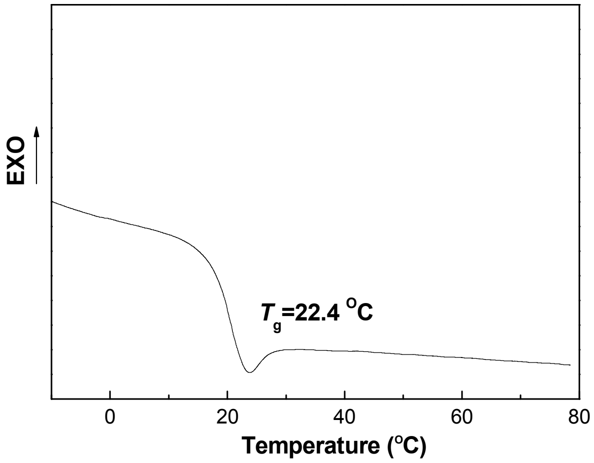


Figure S17. The DSC curve of the copolymer (entry 1, Table 1).

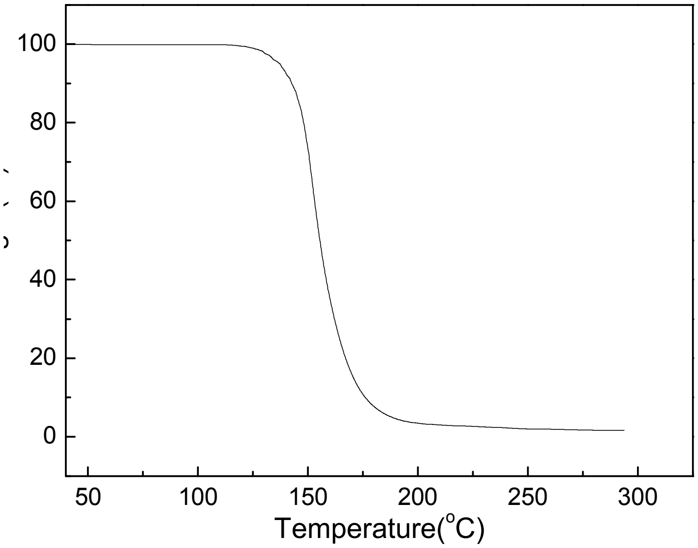


Figure S18. The TGA curve of the copolymer (entry 1, Table 1).

References:

1. (a) You, Y. Z.; Hong, C. Y.; Pan, C. Y. *Macromol. Rapid Commun.* **2002**, *23*, 776. (b) Leung, L. M.; Chan, W. H.; Leung, S. K. *J. Polym. Sci., Part A: Polym.Chem.* **1993**, *31*, 1799. (c) Berti, C.; Marianucci, E.; Pilati, F. *Makromol Chem-Macromol Chem Physic* **1988**, *189*, 1323.
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3. (a) Zhang, X. H.; Liu, F.; Sun, X. K.; Chen, S.; Du, B. Y.; Qi, G. R.; Wan, K. M. *Macromolecules* **2008**, *41*, 1587. (b) Nakano, K.; Tatsumi, G.; Nozaki, K. *J. Am. Chem. Soc.* **2007**, *129*, 15116. (c) Darensbourg, D. J.; Andreatta, J. R.; Jungman, M. J.; Reibenspies, J. H. *Dalton Trans* **2009**, 8891. (d) Stephen W. Osborn, Y. US patent 3213108, 1965.