Electronic Supplementary Material (ESI) for Polymer Chemistry.

Double-Site Lewis Pair for Highly Active and Living Synthesis of Sulfur-containing Polymers

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Catalogue

Part 1. Tables.

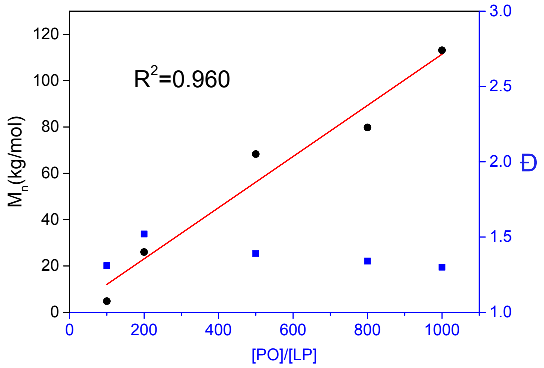
Table S1. Scanning work for TEB/**TEED** LP. [a]

Entry	Time [h]	LB	PO conv.(%)[b]	Copolymer selectivity (%) [c]	PPMTC Linkages (%)[c]	M_n [kg/mol][d]	Đ [M_w/M_n][d]
1[e]	0.1	**TEED**	88	81	>99	43.5	1.56
2	0.1	DBU	36	48[f]	>99	51.8	1.41
3	0.5	**TEED**	20	88	>99	97.5	1.44
4	0.067	**TEED**	86	88	>99	63.2	1.42
5	0.05	**TEED**	80	89	>99	61.2	1.26

[a] The reactions were performed in bulk ([COS]:[PO]:[TEB]:[LB] = 1000:500:1:0.5, molar ratio) in a 10 ml autoclave at 60 °C, no O-S ER product was found in all of the purified product confirmed by NMR spectra. [b] Conversion of PO was determined by the weight of the copolymer and copolymer selectivity. [c] Determined by ^{1}H NMR spectroscopy. The polymer selectivity is the molar ratio of the copolymer to the cyclic product. [d] Determined by using gel permeation chromatography (GPC) in THF, calibrated with polystyrene standards. [e] (***S***)-PO was used. [f] Two kinds of O-S ER products (5-methyl-1,3-oxathiolan-2-one and 4-methyl-1,3-dithiolan-2-one) were founded in the cyclic products. 1,8-Diazabicyclo[5.4.0]undec-7-ene (**DBU**):13.28;

Table S2. Ratio of PO to LP V.S. M_n in bulk. [a]

Entry	Time [h]	Feeding ratio	PO conv.(%)[b]	Copolymer selectivity (%)[c]	PPMTC Linkages (%)[c]	M_n [kg/mol] [d]	Đ [M_w/M_n][d]
1	0.1	1:0.5:100	98	58	>99	4.8	1.31
2	0.1	1:0.5:200	90	75	>99	26.0	1.52
3	0.5	1:0.5:500	95	76	>99	68.3	1.39
4	0.5	1:0.5:800	96	81	>99	79.8	1.34
5	0.5	1:0.5:1000	92	89	>99	113.1	1.30



The effect of [PO]/[LP] ratio on M_ns of PPMTCs.

[a] The reactions were performed in bulk ([COS]:[PO] = 2:1, ([LP] = [TEB]/[**TEED**](1/0.5)), molar ratio) in a 10 ml autoclave at 60 °C, no O-S ER product was found in all of the purified product confirmed by NMR spectra. [b] Conversion of PO was determined by the weight of the copolymer and copolymer selectivity. [c] Determined by ^{1}H NMR spectroscopy. The polymer selectivity is the molar ratio of the copolymer to the cyclic product. [d] Determined by using gel permeation chromatography (GPC) in THF, calibrated with polystyrene standards.

Table S3. Ratio of PO to LP V.S. M_n in solvent. [a]

Entry	[PO]:[TEB]:[TEED]	PO conv.(%)[b]	Copolymer selectivity (%)[c]	PPMTC Linkages (%)[c]	M_n [kg/mol][d]	$Đ$ [M_w/M_n][d]
1	100:1:0.5	>99	92	>99	16.1	1.22
2	200:1:0.5	>99	>99	>99	25.3	1.15
3	500:1:0.5	>99	>99	>99	62.0	1.10
4	800:1:0.5	>99	>99	>99	81.3	1.11
5[e]	1000:1:0.5	>99	>99	>99	103.1	1.09

[a] The reactions were performed in 2ml THF ([COS]: [PO] = 2:1, molar ratio) in a 10 ml autoclave at 60 °C for 2 h. No O-S ER products were found in all the purified product by NMR spectra. [b] Conversion of PO was determined by the weight of the copolymer and copolymer selectivity. [c] Determined by ^{1}H NMR spectroscopy. The polymer selectivity is the molar ratio of the copolymer to the cyclic product. [d] Determined by GPC in THF, calibrated with polystyrene standards. [e] 3h. Figures S18-S22 are the ^{1}H NMR spectra of the products.

Table S4. M_ns of the copolymers V.S. conversion. [a]

Entry	Time [h]	PO conv. (%) [b]	Copolymer selectivity (%) [c]	PPMTC Linkages (%) [c]	M_n [kg/mol][d]	PDI [M_w/M_n][d]
1	0.3	19	>99	>99	22.5	1.12
2	0.6	30	>99	>99	34.8	1.12
3	1.2	54	>99	>99	64.2	1.12
4	1.8	69	>99	>99	81.7	1.11
5	3	99	>99	>99	92.8	1.11

[a] The reactions were performed in 2mL THF ([COS]: [PO]: [TEB]:[**TEED**] = 1000:1000:1:0.5, molar ratio) in a 10 ml autoclave at 60 °C, no O-S ER product was found in all of the purified products confirmed by NMR spectra. [b] Conversion of PO was determined by the weight of the copolymer and copolymer selectivity. [c] Determined by ^{1}H NMR spectroscopy. The polymer selectivity is the molar ratio of the copolymer to the cyclic product. [d] Determined by using gel permeation chromatography (GPC) in THF, calibrated with polystyrene standards. Figures S23-S27 are the ^{1}H NMR spectra of the products.

Table S5. Impact of [COS]/[PO] ratio on the copolymerization. [a]

Entry	[COS]/[PO] (mol/mol)	PO conv. (%)[b]	COS conv. (%)[c]	Copolymer selectivity (%)[d]	PPMTC Linkages (%)[e]	M_n (kg/mol)[f]	$Đ$ (M_w/M_n)[f]
1	0.09	7	>99	>99	>99	8.9	1.11
2	0.12	11	>99	>99	>99	12.5	1.11
3	0.25	22	>99	>99	>99	21.6	1.18
4	0.47	46	>99	>99	>99	48.5	1.15
5	0.80	79	>99	>99	>99	87.3	1.11
6	1.00	>99	>99	>99	>99	103.1	1.09

[a] The reactions were performed in 2.0 ml THF in a 10 ml autoclave at 60 °C for 3 h, [TEB]: [**TEED**]: [PO] = 1:0.5:1000; no O/S ER product was found in all the purified products, confirmed by ^{1}H NMR spectra. [b] Conversion of PO was determined by the weight of the copolymer and copolymer selectivity. [c] Conversion of COS was determined by the weight of the copolymer for the adding of PO was excess. [d] ^{1}H NMR spectra of crude product. The polymer selectivity is the molar ratio of the copolymer to the cyclic product. [e] ^{1}H NMR spectra of purified product. [f] Determined by GPC using THF, calibrated with polystyrene standards.

Table S6. Scanning work for the synthesis of PPMTC-PPO di-block copolymer. [a]

Entry	[TEB]: [TEED]: [PO]: [COS]	Time [h]	PO conv. (%)[b]	COS conv. (%)[c]	PPMTC Linkages (%)[d]	M_n [kg/mol][e]	PDI [M_w/M_n][e]
1[e]	2:0.5:500:200	0.33	40	>99	>99	17.7	1.09
		12	51	>99	78	24.6	1.11
2	2:0.5:500:200	12	53	>99	75	26.3	1.08
3	1:0.5:1000:0	12	0	-	-	-	-
4	1:0.5:500:0	12	0	-	-	-	-
5	1:0.5:500:200	1	99	>99	>99	12.4	1.18

[a] The reactions were performed in bulk ([COS]: [PO] = 2:1, molar ratio) in a 10 ml autoclave at 60 °C, no O-S ER product was found in all of the purified product confirmed by NMR spectra. [b] (Mol epoxide consumed)/(mol TEB h). [c] Conversion of COS was determined by the weight of the copolymer for the adding of PO was excess. [d] Determined by ^{1}H NMR spectroscopy. The polymer selectivity is the molar ratio of the copolymer to the cyclic product. [e] Determined by using gel permeation chromatography (GPC) in THF, calibrated with polystyrene standards.

Table S7. Scanning work for different epoxides. [a]

Entry	Time [h]	Epoxide	LB	W (mg)[b]	TOF [h^{-1}][c]	Alternating degree (%)[d]	M_n [kg/mol][e]	$Đ$ [M_w/M_n][e]
1	0.5	EO	**TEED**	12	16	-	1.1	2.00
2	0.5	EO	TEA	0	-	-	-	-
3	2	EB	**TEED**	52	13	>99	4.8	1.28
4	2	EB	TEA	6	1.5	>99	8.0	1.41
5	2	CHO	**TEED**	0	-	-	-	-
6	2	CHO	TEA	0	-	-	-	-
7	0.5	PGE	**TEED**	10	6	>99	4.7	1.31
8	0.5	PGE	TEA	80	51	>99	24.3	1.24

[a] The reactions were performed in a 10 ml autoclave at 80 °C ([COS]: [epoxide]:[LP] = 4000:2000:1, [B]/[N] =1.0, molar ratio). EO: ethylene oxide; EB: 1,2-epoxybutane; CHO: cyclohexane oxide; PGE: phenyl glycidyl ether; [b] Weight of the product. [c] (Mol epoxide consumed)/(mol TEB h), TOF is used here to compare the activity of the catalyst system in the same copolymerization condition. [d] Determined by ^1H NMR spectroscopy. [e] Determined by using gel permeation chromatography (GPC) in THF, calibrated with polystyrene standards.

The applicability of the double site Lewis pairs for different epoxides was studied (Table S7). It is observed that acceleration of the copolymerization by the proximity effect of diamines strongly depends on the matching of monomers and diamine. **TEED** performed better than TEA in catalyzing the copolymerization of COS and PO (TOF: 196 h^{-1} v.s. 17 h^{-1}) or EO (ethylene oxide, TOF: 16 h^{-1} v.s. 0 h^{-1}), while this effect weakened when the epoxide was changed to EB (1,2-epoxybutane, TOF:13 h^{-1} v.s. 1.5 h^{-1}) and CHO (cyclohexane oxide, TOF: both 0 h^{-1}). Of interest, as for the copolymerization of phenyl glycidyl ether (PGE) with COS, the catalytic activity of the TEA/TEB pair was even higher than that of **TEED**/TEB pair (TOF 6 h^{-1} v.s. 51 h^{-1}, Table S7, entry7, 8). The structurTEPDerformance correlation of the catalyst and epoxide may leave enough room to regulate the catalyst performance.

Table S8. Copolymerization of PO and COS in low concentration of LPs. [a]

Entry	[TEB]: [LB]: [PO]	LB	W (mg)[b]	TOF [h^{-1}][c]	PPMTC Linkages (%)[d]	M_n [kg/mol][e]	$Đ$ [M_w/M_n][e]
1	1:1:4000	TEA	4	22	>99	-[f]	-
2	1:0.5:4000	**TEED**	69	390	>99	3.9	1.19
3	1:0.5:4000	**TEPD**	56	317	>99	6.1	1.27
4[g]	1:1:2000	TEA	5	17	>99	-[f]	-
5[g]	1:0.5:2000	**TEED**	58	196	>99	3.8	1.15
6[g]	1:0.5:2000	**TEPD**	46	152	>99	5.8	1.13

[a] The reactions were performed in a 10 ml autoclave at 60 °C ([COS]: [PO] = 2:1, molar ratio), 0. 1h, the copolymer was collected by the crude product directly to HCl in water (1mol/L). [b] Weight of the product. [c] (Mol epoxide consumed)/(mol TEB h), TOF is used here to compare the activity of the catalyst system in the same copolymerization condition. [d] ^1H NMR spectra. [e] Determined by using gel permeation chromatography (GPC) in THF, calibrated with polystyrene standards. [f] Molecule weight of the copolymer was too low to be determined. [g] Equivalent volume of THF with PO was used as solvent, and the reaction time was 0.167h.

The control experiments conducted at very low LP concentration had also suggested the effect of **TEED** (**TEPD**) on improving the activity of COS/epoxide copolymerization (Table S8). Very low TOF of 22 h^{-1} was observed from TEB/TEA pair-catalyzed copolymerization at the feeding ratio of [PO]:[TEB]:[TEA] = 4000 :1:1 (entry 1, Table S8). In contrast, the LPs involved with **TEED** and **TEPD** exhibited high TOF values of 390 and 317 h^{-1} respectively, with the [PO]/[TEB]/[LB] molar ratio of 4000/1/0.5. The produced PPMTCs had fully alternating structure without observing O-S ER products. Concurrently, M_n^{GPC}s of the copolymers from TEB/**TEED** pair was 3.9 kg/mol (entry 2, Table S8), close to the calculated molecule weight (M_n^{Cal}: 4.8 kg/mol) based on the assumption that one **TEED** molecule would produce two chains, indicating that both amine sites of **TEED** participated the initiation. However, M_n^{GPC}s of the copolymers from the TEB/**TEPD** pair was 6.1 kg/mol (entry 3, Table S8) that was clearly higher than the M_n^{Cal}s (3.9 kg/mol), suggesting only part of sites of **TEPD** participated the initiation at low LP concentration. Further decreasing the concertation of PO([PO]:[TEB]:[TEA] = 2000 :1:1, equal volumes of THF with PO was added showed the similar copolymerization results with the above bulk system (entry 4-6, Table S8).

Part 2. Figures.

2.1 ^{1}H (^{13}C) NMR spectra of products in Table 1.

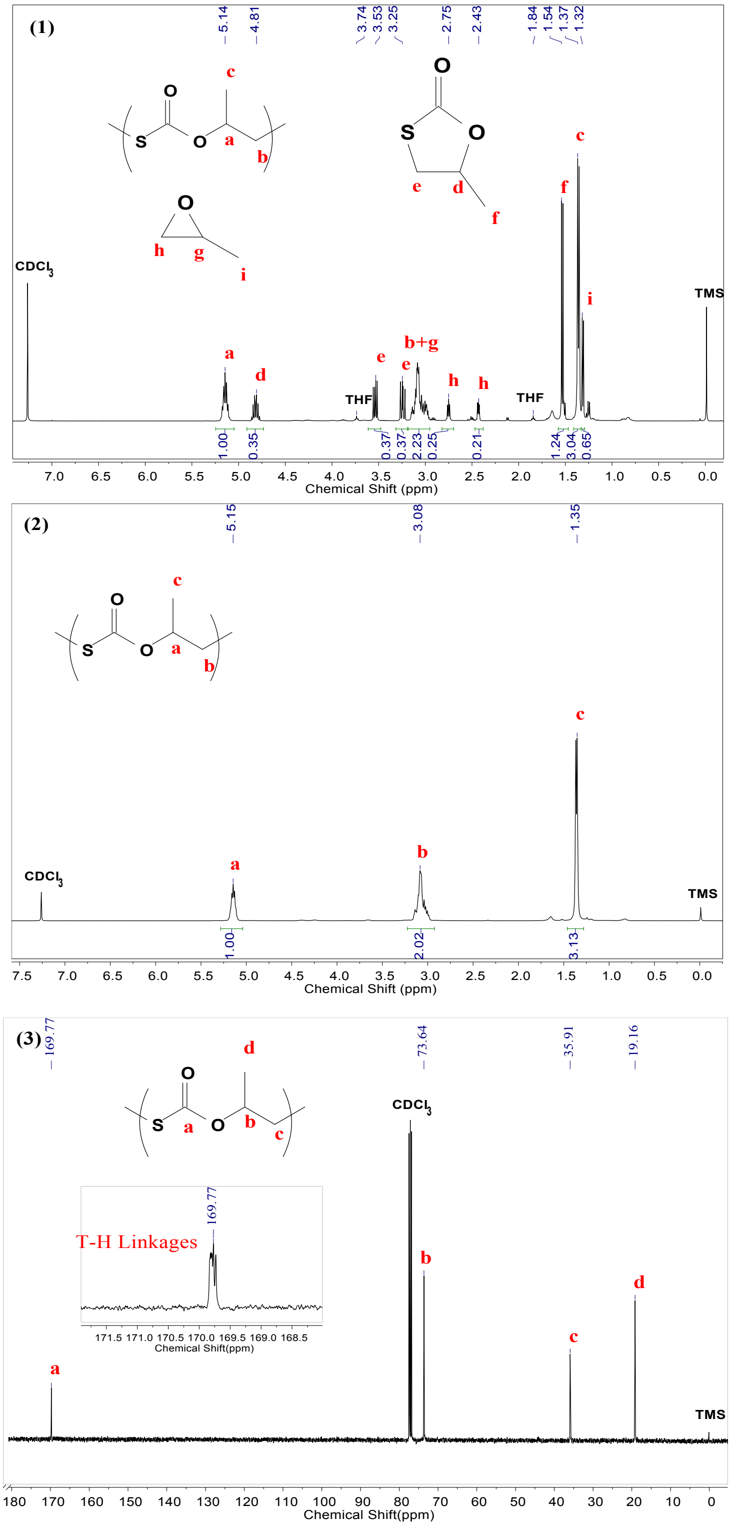


Figure S1. (1)^{1}H NMR spectrum of the crude product of entry 1, Table 1; (2) ^{1}H NMR spectrum of the purified product of entry 1, Table 1; (3) ^{13}C NMR spectrum of the purified product of entry 1, Table 1.

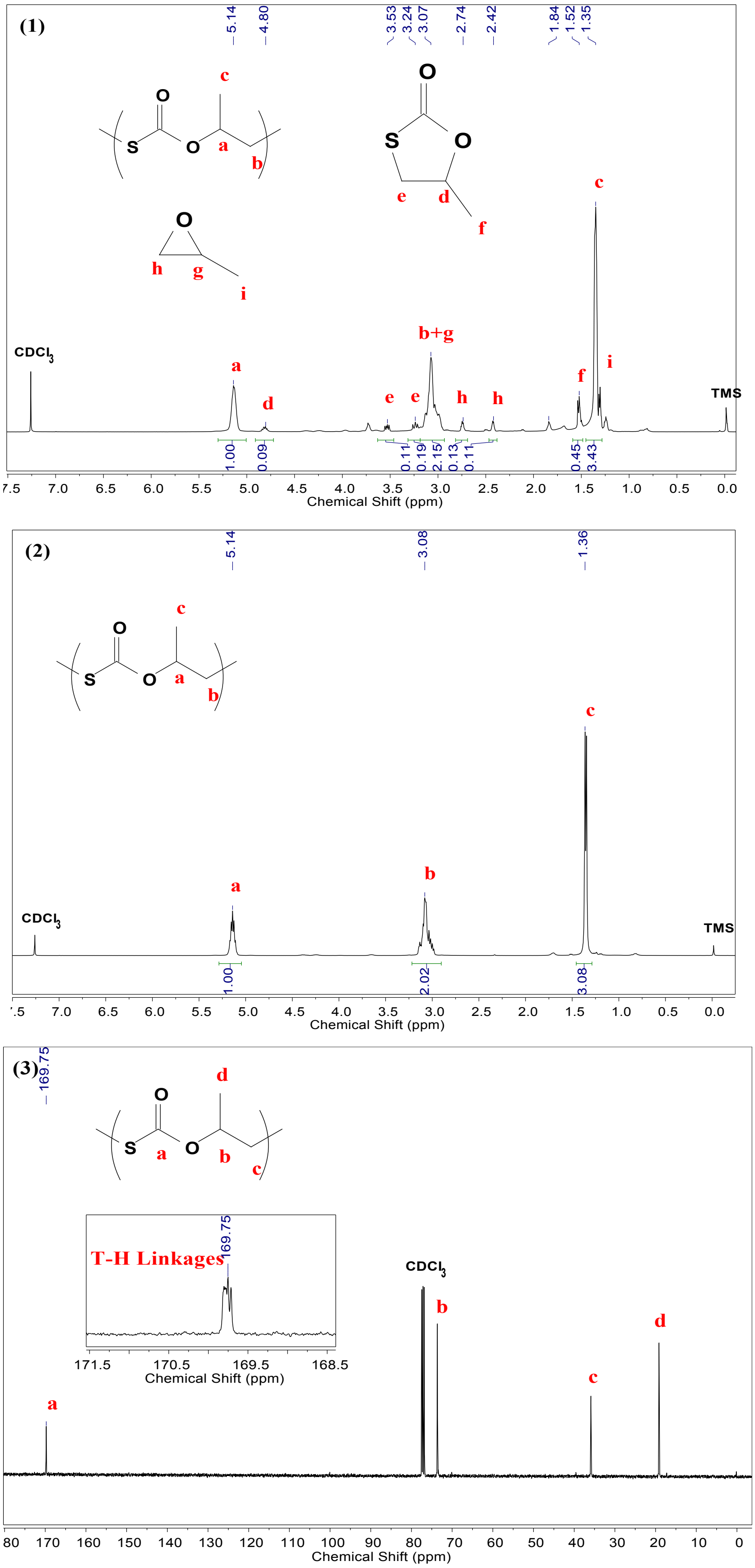


Figure S2. (1)^{1}H NMR spectrum of the crude product of entry 2, Table 1; (2) ^{1}H NMR spectrum of the purified product of entry 2, Table 1; (3) ^{13}C NMR spectrum of the purified product of entry 2, Table 1.

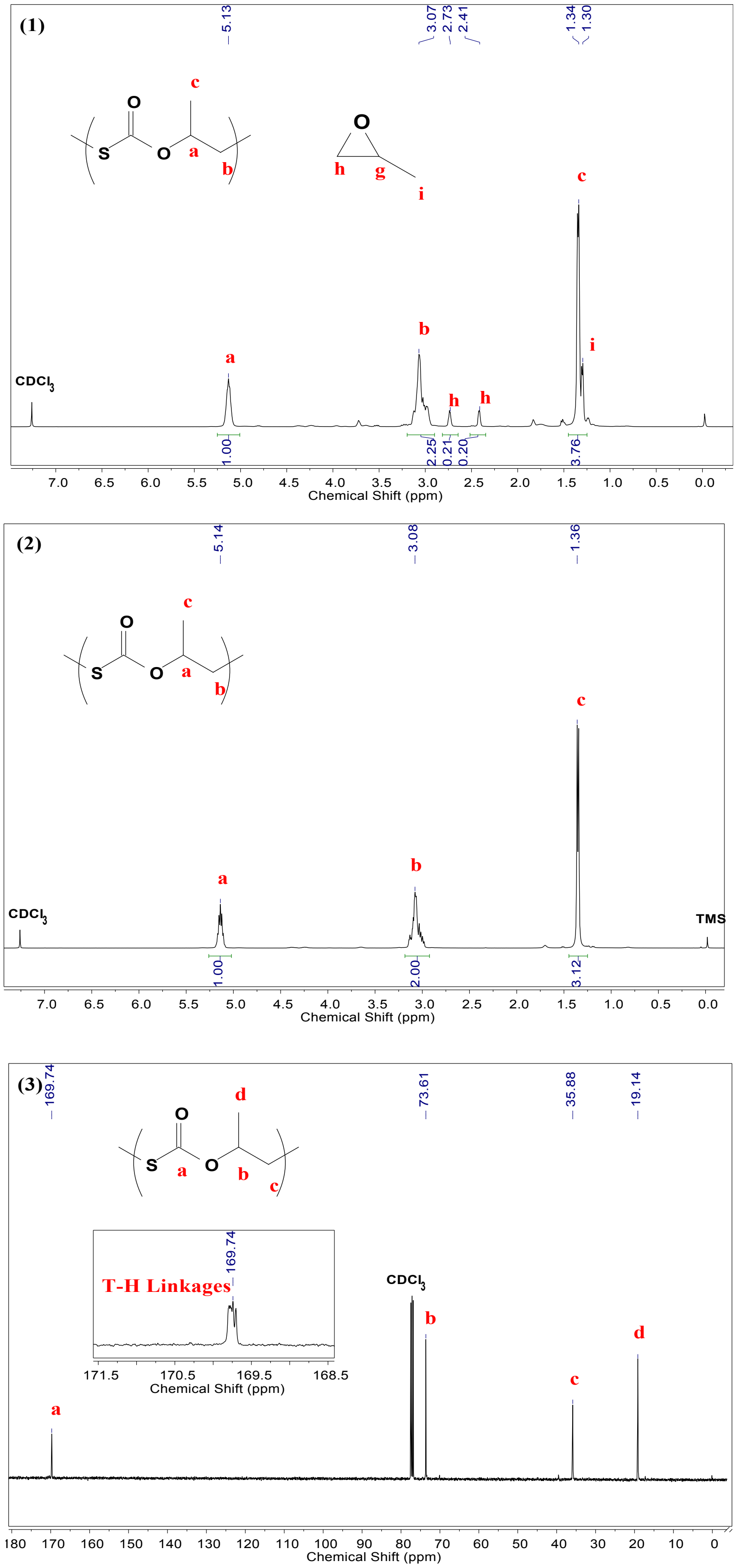


Figure S3. (1)^{1}H NMR spectrum of the crude product of entry 3, Table 1; (2) ^{1}H NMR spectrum of the purified product of entry 3, Table 1; (3) ^{13}C NMR spectrum of the purified product of entry 3, Table 1.

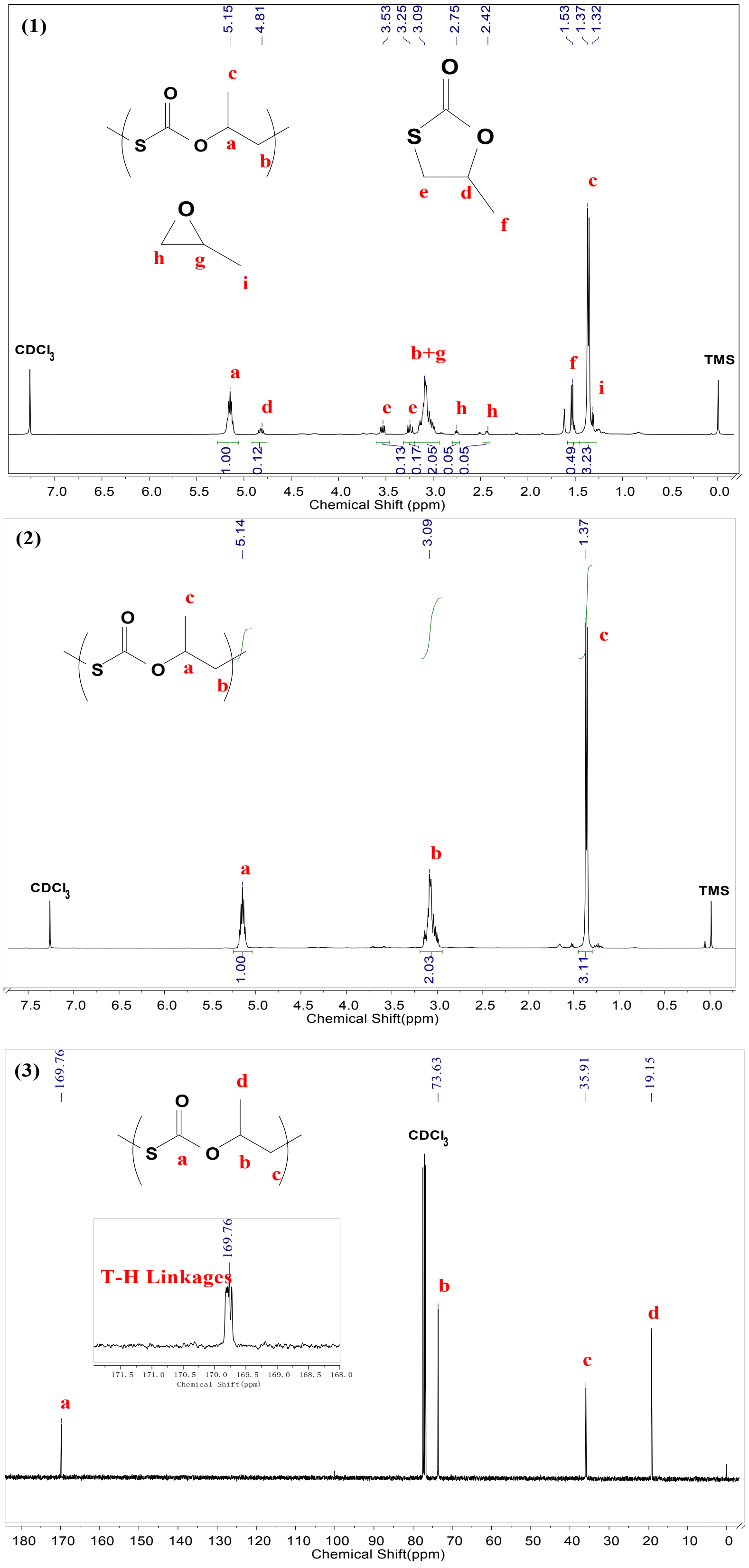


Figure S4. (1)^{1}H NMR spectrum of the crude product of entry 4, Table 1; (2) ^{1}H NMR spectrum of the purified product of entry 4, Table 1; (3) ^{13}C NMR spectrum of the purified product of entry 4, Table 1.

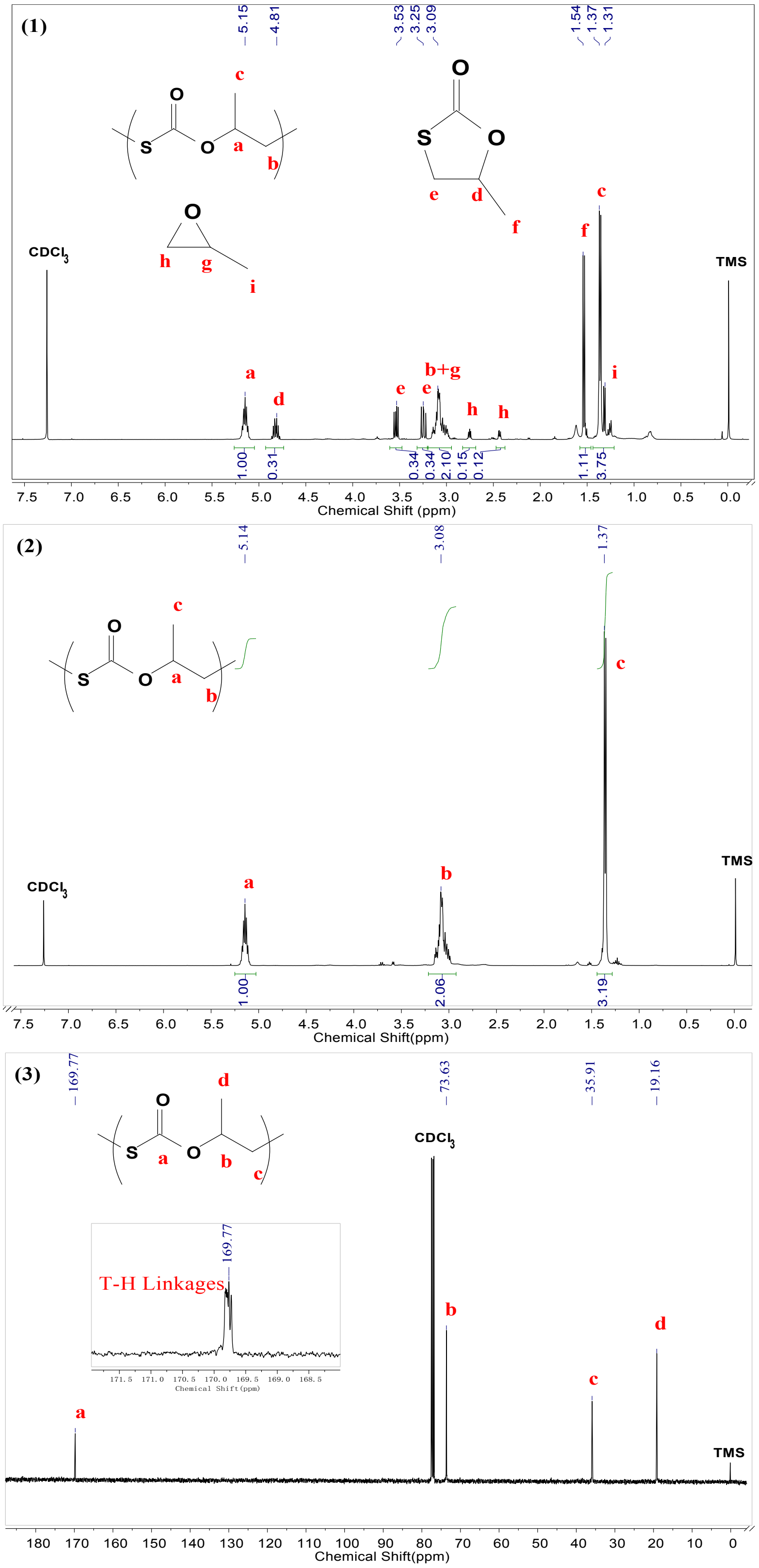


Figure S5. (1)^{1}H NMR spectrum of the crude product of entry 5, Table 1; (2) ^{1}H NMR spectrum of the purified product of entry 5, Table 1; (3) ^{13}C NMR spectrum of the purified product of entry 5, Table 1.

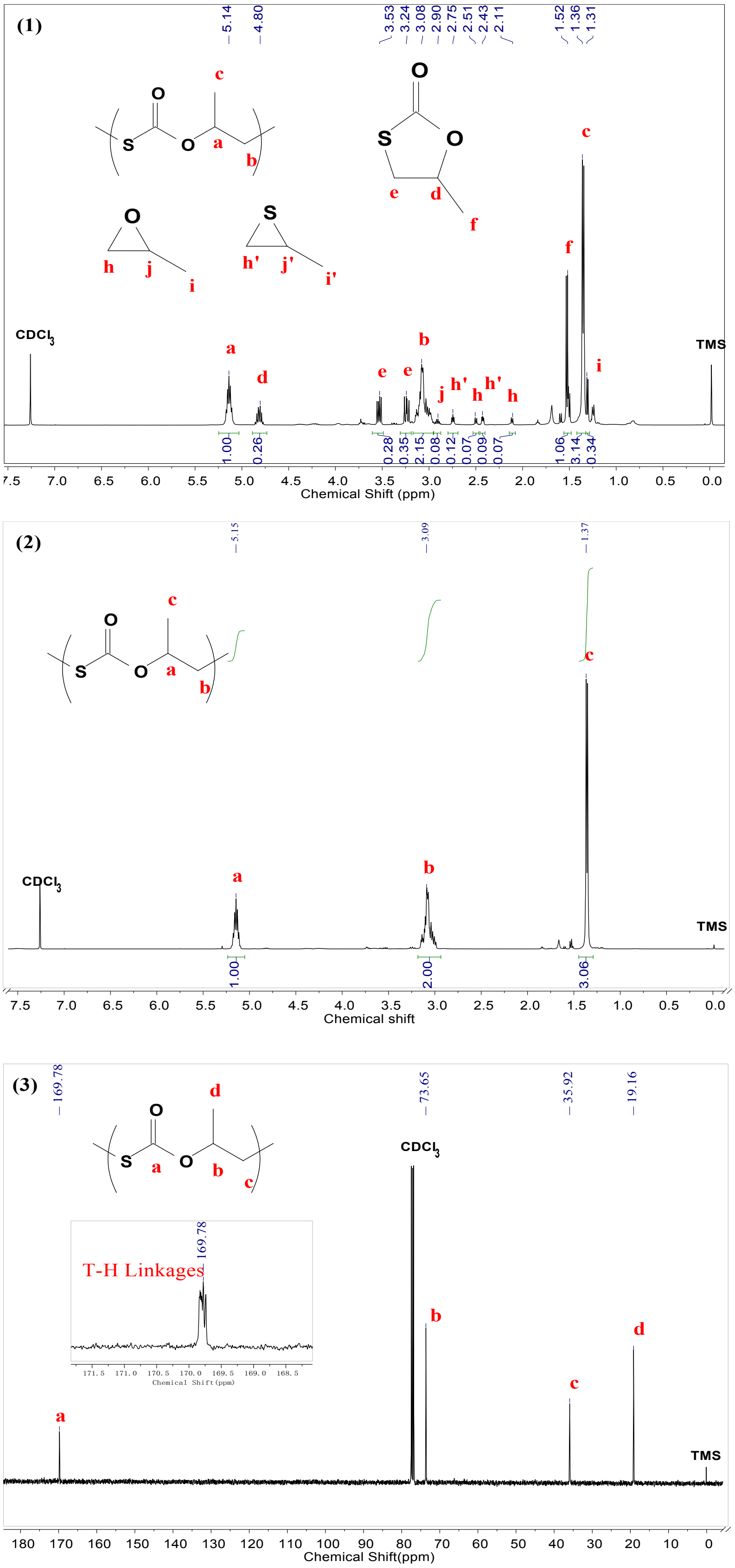


Figure S6. (1)^{1}H NMR spectrum of the crude product of entry 8, Table 1; (2) ^{1}H NMR spectrum of the purified product of entry 8, Table 1; (3) ^{13}C NMR spectrum of the purified product of entry 8, Table 1.

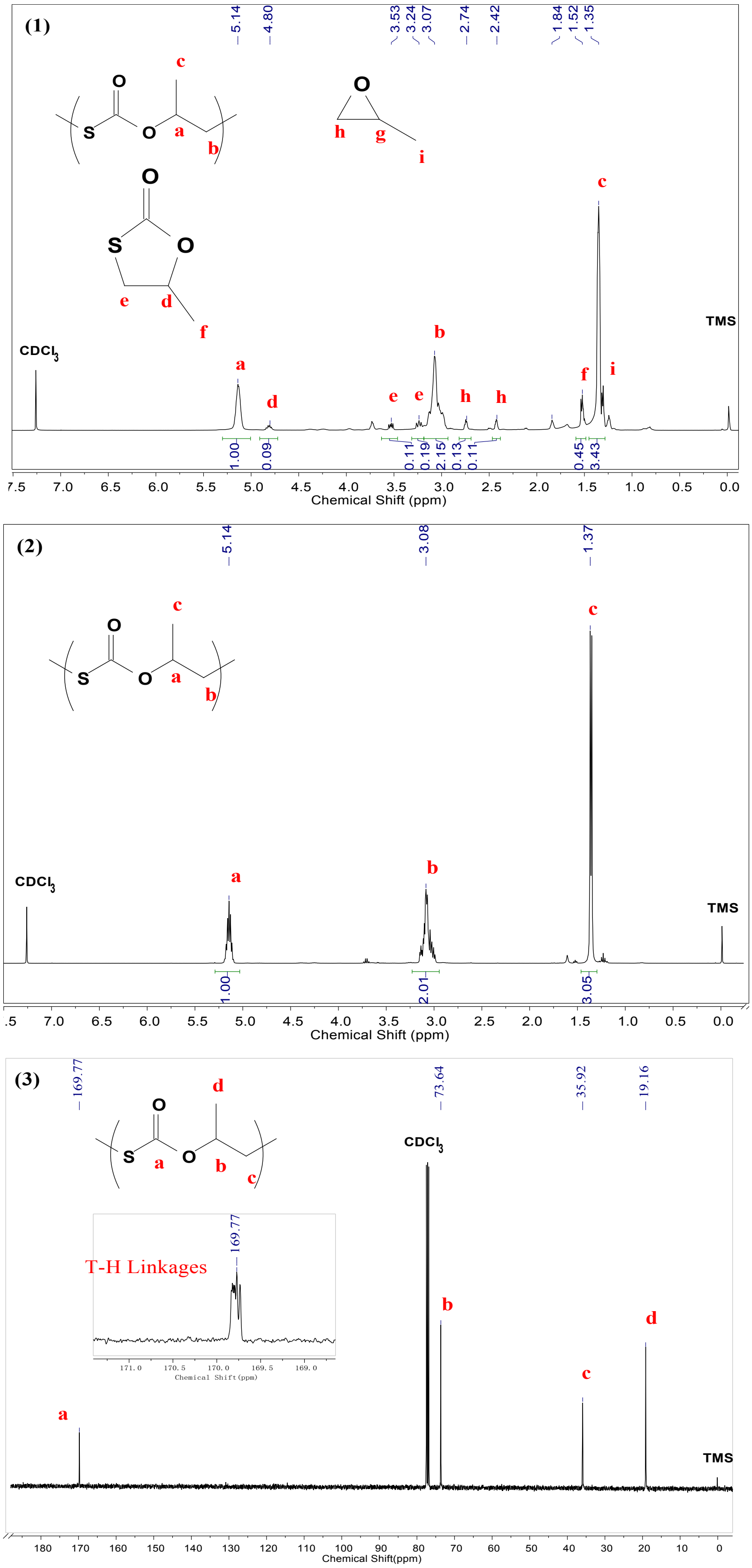


Figure S7. (1)^{1}H NMR spectrum of the crude product of entry 9, Table 1; (2) ^{1}H NMR spectrum of the purified product of entry 9, Table 1; (3) ^{13}C NMR spectrum of the purified product of entry 9, Table 1.

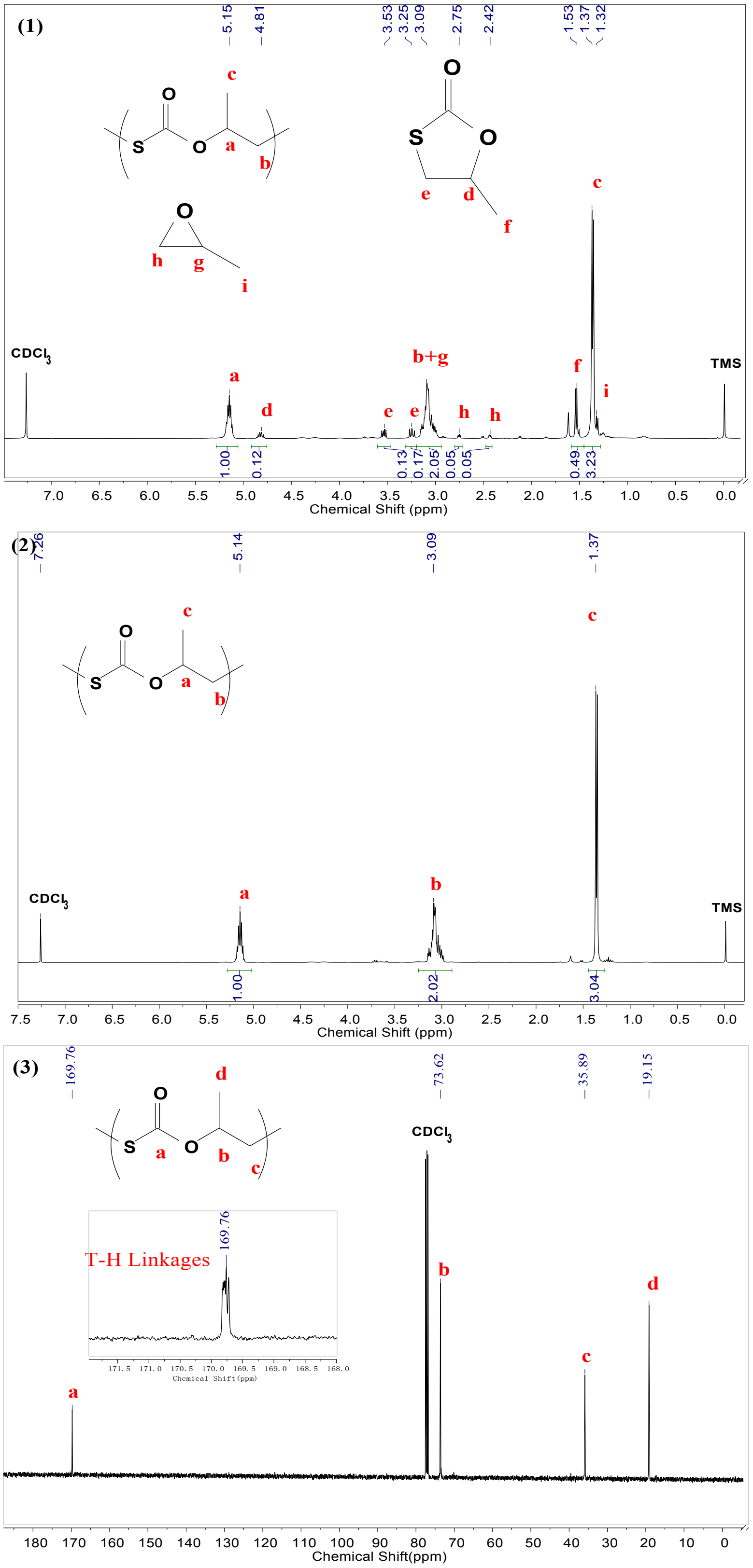


Figure S8. (1)^{1}H NMR spectrum of the crude product of entry 10, Table 1; (2) ^{1}H NMR spectrum of the purified product of entry 10, Table 1; (3) ^{13}C NMR spectrum of the purified product of entry 10, Table 1.

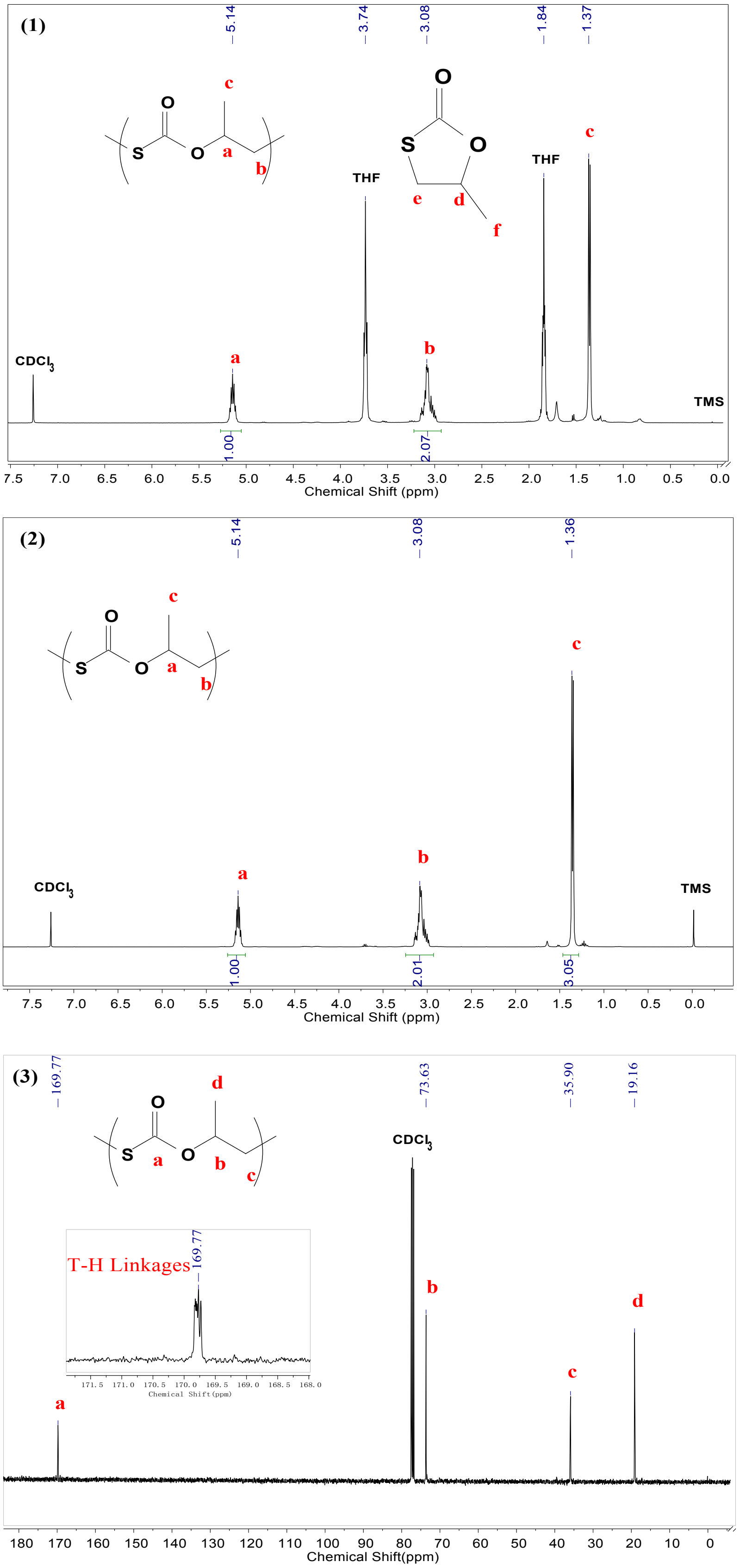


Figure S9. (1)^{1}H NMR spectrum of the crude product of entry 11, Table 1; (2) ^{1}H NMR spectrum of the purified product of entry 11, Table 1; (3) ^{13}C NMR spectrum of the purified product of entry 11, Table 1.

2.2 ^{1}H(^{13}C) NMR spectra of products in Table S1.

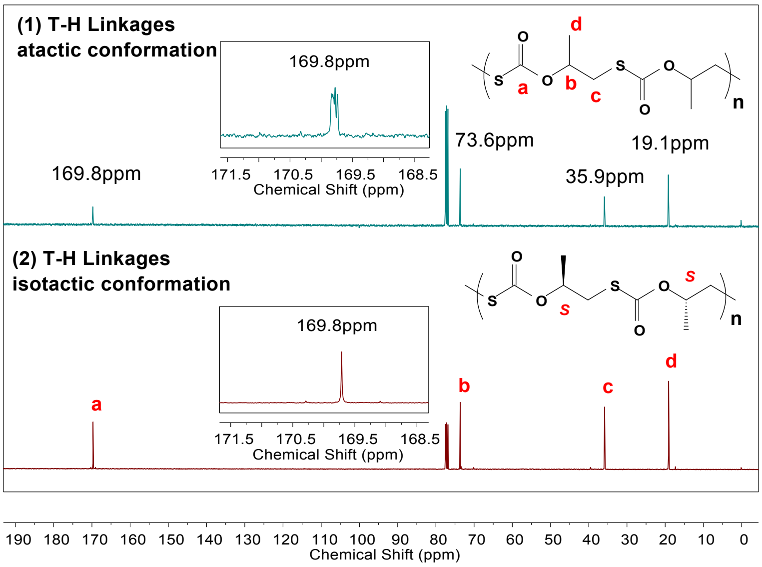


Figure S10. ^{13}C NMR spectra of the purified products, the carbonyl region was shown to confirm the T-H diad linkage. (1) Racemic PO; (2) (***S***)-PO (entry 1, Table S1).

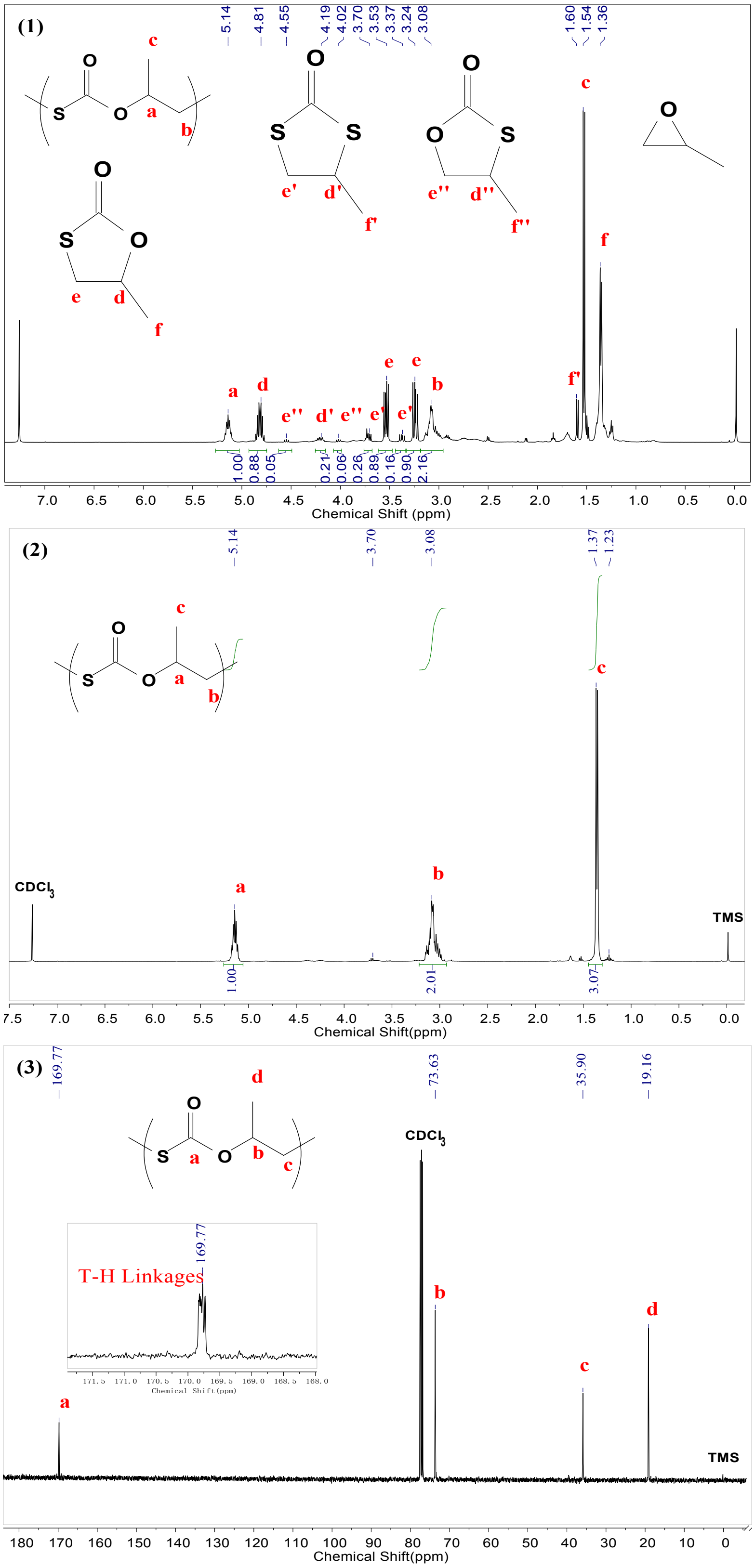


Figure S11. (1)^{1}H NMR spectrum of the crude product of entry 2, Table S1; (2) ^{1}H NMR spectrum of the purified product of entry 2, Table S1; (3) ^{13}C NMR spectrum of the purified product of entry 2, Table S1.

2.3 Interaction between TEB and different Lewis bases.

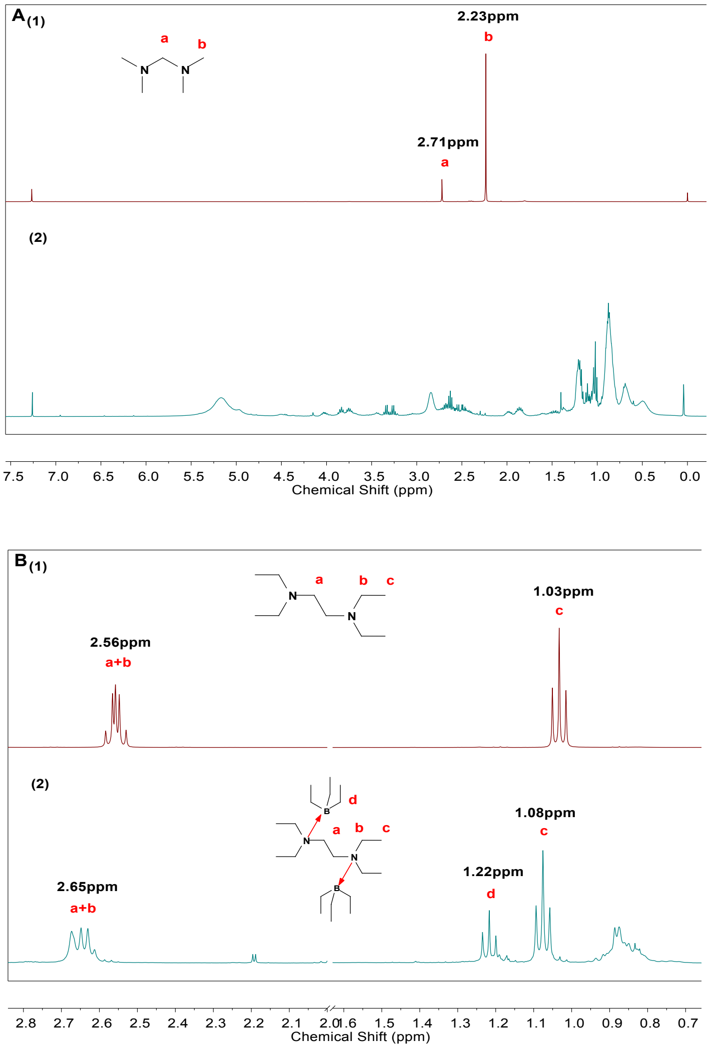


Figure S12. Interaction between TEB and different Lewis base, revealed by ^{1}H NMR spectra. A. TEB/**TMDM**; B. TEB/**TEED,** N/B 1:1 of molar ratio (LB: TEB=0.5:1) in $CDCl_3$;

Comparing with the TEB/**TEED** pair, **TMDM** converted in the presence of TEB.

2.4 ^{1}H NMR spectra of PPMTC-*b*-PPO block copolymer.

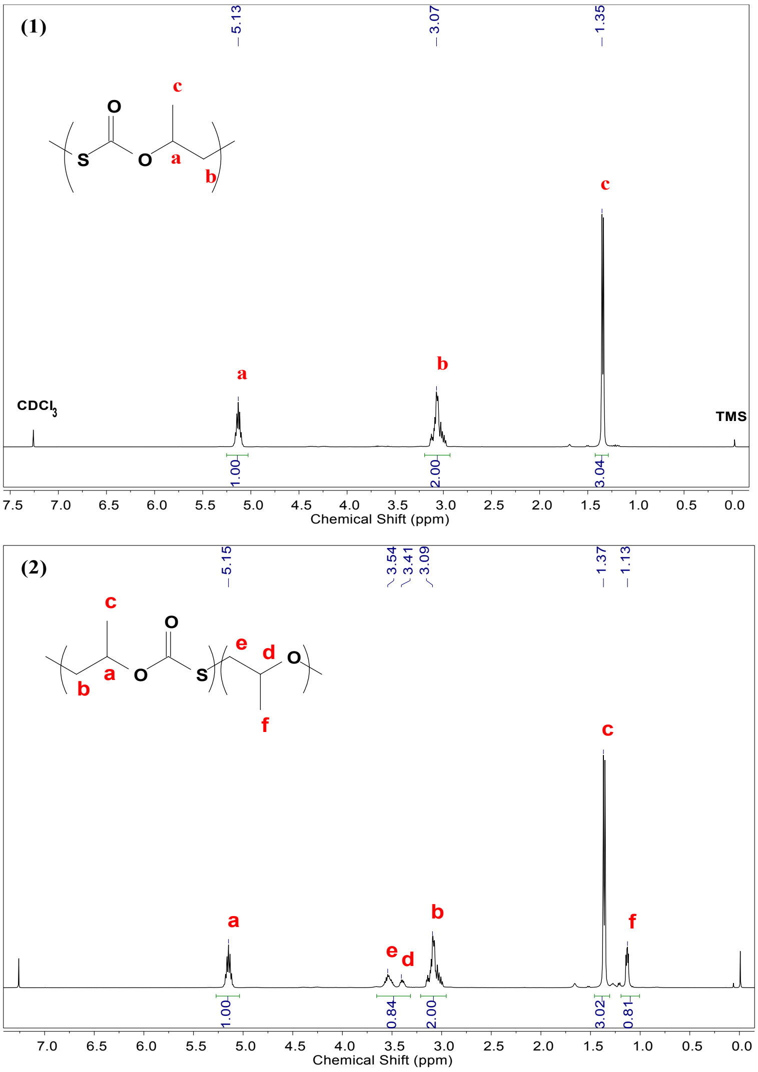


Figure S13. (1) ^{1}H NMR spectrum of the purified product of entry 1, Table S6, 0.33 h; (2) ^{1}H NMR spectrum of the purified product of entry 1, Table S6, 12h.

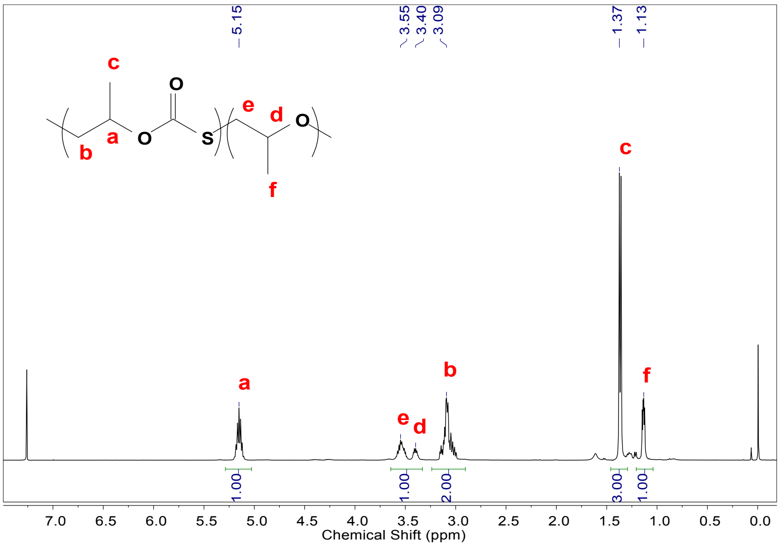
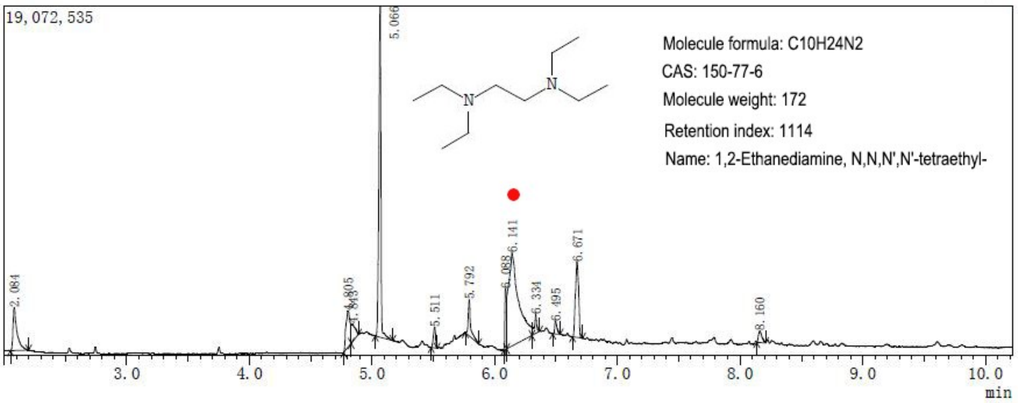
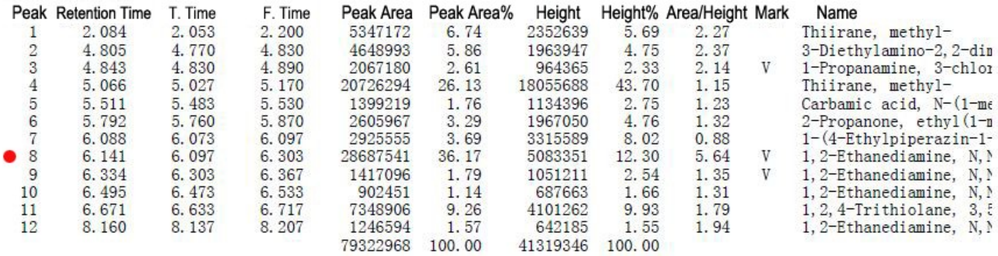


Figure S14. ^{1}H NMR spectrum of the purified product of entry 2, Table S6;

2.5 Characterization of the catalyst by GC-MS after copolymerization.





Peak	Retention Time	T. Time	F. Time	Peak Area	Peak Area%	Height	Height%	Area/Height	Mark	Name
1	2.084	2.053	2.200	5347172	6.74	2352639	5.69	2.27		Thiirane, methyl-
2	4.805	4.770	4.830	4648993	5.86	1963947	4.75	2.37		3-Diethylamino-2,2-di
3	4.843	4.830	4.890	2067180	2.61	964365	2.33	2.14	V	1-Propanamine, 3-chlo
4	5.066	5.027	5.170	20726294	26.13	18055688	43.70	1.15		Thiirane, methyl-
5	5.511	5.483	5.530	1399219	1.76	1134396	2.75	1.23		Carbamic acid, N-(1-m
6	5.792	5.760	5.870	2605967	3.29	1967050	4.76	1.32		2-Propanone, ethyl(1-
7	6.088	6.073	6.097	2925555	3.69	3315589	8.02	0.88		1-(4-Ethylpiperazin-1-
● 8	6.141	6.097	6.303	28687541	36.17	5083351	12.30	5.64	V	1,2-Ethanediamine, N,
9	6.334	6.303	6.367	1417096	1.79	1051211	2.54	1.35	V	1,2-Ethanediamine, N,
10	6.495	6.473	6.533	902451	1.14	687663	1.66	1.31		1,2-Ethanediamine, N,
11	6.671	6.633	6.717	7348906	9.26	4101262	9.93	1.79		1,2,4-Trithiolane, 3,
12	8.160	8.137	8.207	1246594	1.57	642185	1.55	1.94		1,2-Ethanediamine, N,
				79322968	100.00	41319346	100.00			

Figure S15. Matching structure of the peak with maximum abundance (at 6.141 min, 36% in all the 12 peaks) in GC-MS spectrum.

The copolymerization was conducted with the feeding ratio of [COS]:[PO]:[TEB]:[**TEED**] = 400:200:1:0.5, molecule weight of the produced copolymer (25.3 kg/mol) was close to the calculated value (23.6 kg/mol). After participating the produced copolymer in HCl/ethanol (1.0 mol/L), the solvent was evaporated in vacuum. Then, the residue was collected by ethyl alcohol and characterized by GC-MS.

2.6 Conversion V.S. time of COS/PO copolymerization by different LPs.

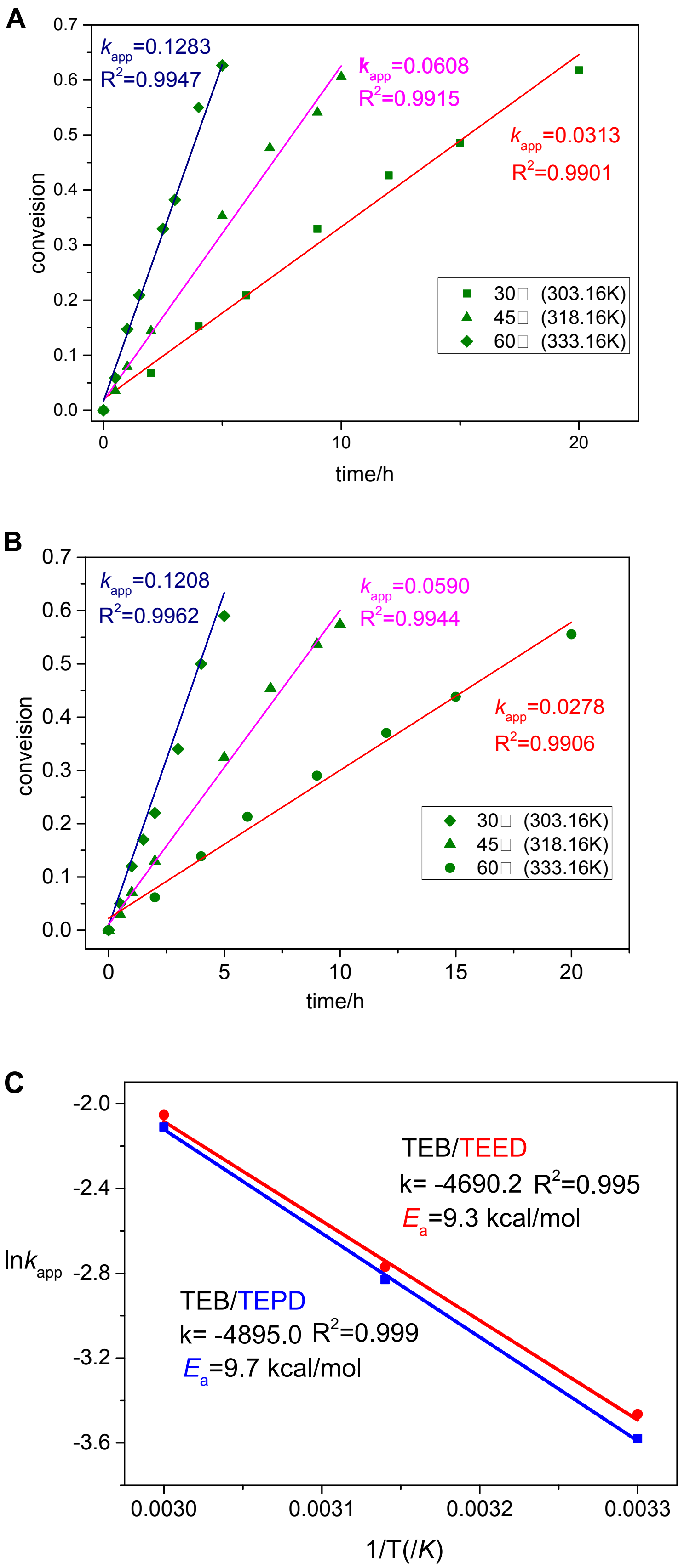


Figure S16. A. the plot of the conversion *vs*. time, [TEB]: [**TEED**]: [PO]: [COS] =1: 0.5: 2000: 2000, in 2.0 ml THF at 30 °C, 45 °C, 60 °C; B. the plot of the conversion *vs*. time, [TEB]: [**TEPD**]: [PO]: [COS] =1: 0.5: 2000: 2000, in 2.0 ml THF at 30 °C, 45 °C, 60 °C.

Determination of the activation energy for chain growth.

Conversion of PO was determined for different copolymerization time in these two catalyst systems at 30, 45 and 60 °C. Then we used linear regression analysis to get the rate constant (k_{app}, h^{-1}) of each catalyst at different reaction temperature. After that, k value was defined as the slop of the fitted curve '($\ln k_{\text{app}}$) v.s. (1/T)', and was calculated. Basing on Arrhenius equation, we could get the apparent activation energy for chain growth (E_a) by such an equation.

$$E_a = -k * R$$

R is the Gas constant, 8.314 J/(mol °C)

2.7 Interaction between TEED and TEB and the activation of COS.

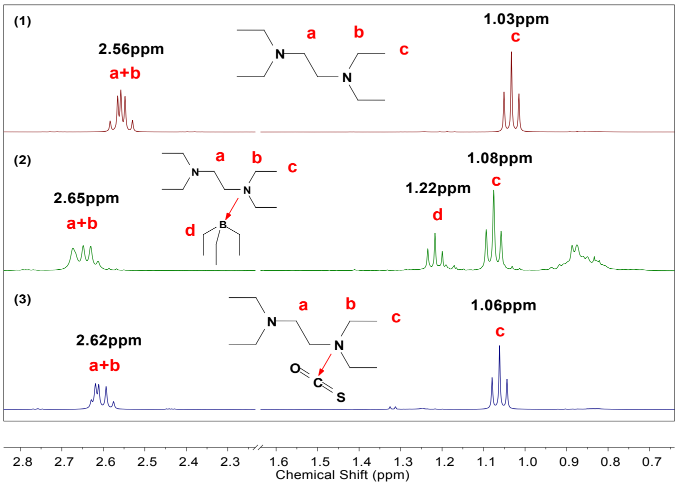


Figure S17. ^{1}H NMR spectra of (1) **TEED**; (2) **TEED**/TEB (0.5:1) pair; (3) **TEED**/COS (0.5: excess)

^{1}H NMR traces were performed to reveal the interaction of **TEED**/TEB pair and the activation of COS by **TEED**. Formation of the TEB/**TEED** pair was proved by a clear deshielding effect of TEB on **TEED** in the ^{1}H NMR spectra, where the chemical shift of the protons of neat **TEED** at 2.56 and 1.03 *ppm* changed to 2.65 and 1.08 *ppm* respectively upon adding TEB ([**TEED**]:[TEB] = 0.5:1, molar ratio) (spectra 1 and 2, Figure S17). A similar deshielding effect on **TEED** was observed by adding COS because it can also act as a Lewis acid (spectrum 3, Figure S17).

Part 3. Figures for tables in SI.

3.1 ^{1}H NMR spectra of products in Table S3.

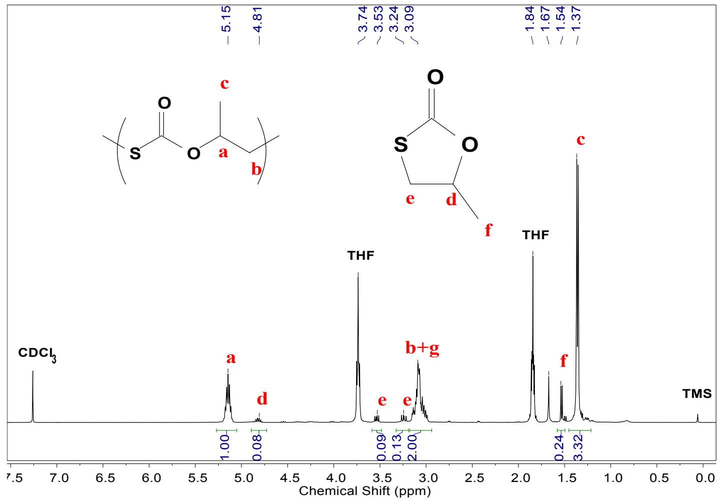


Figure S18. ^{1}H NMR spectrum of the crude product of entry 1, Table S3.

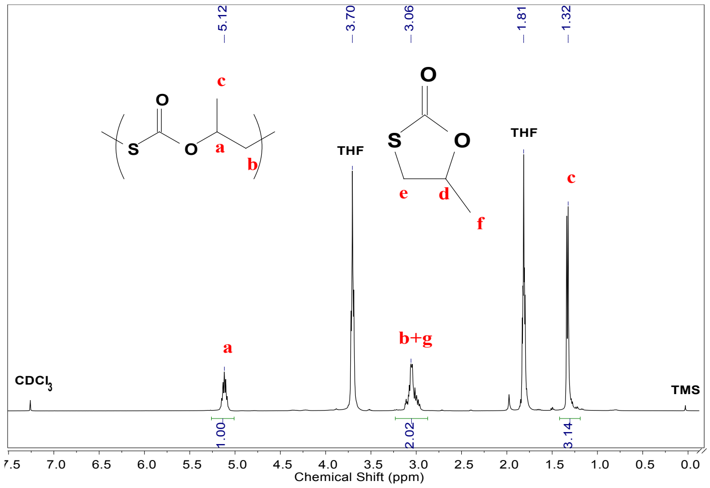


Figure S19. ^{1}H NMR spectrum of the crude product of entry 2, Table S3.

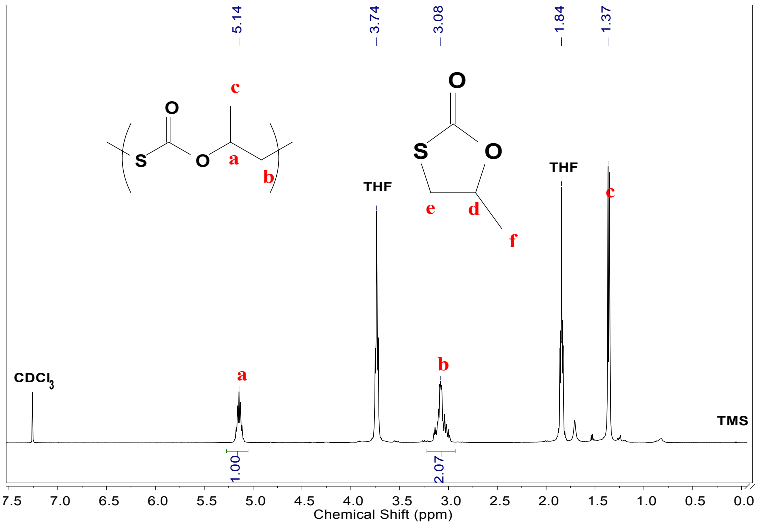


Figure S20. ^{1}H NMR spectrum of the crude product of entry 3, Table S3.

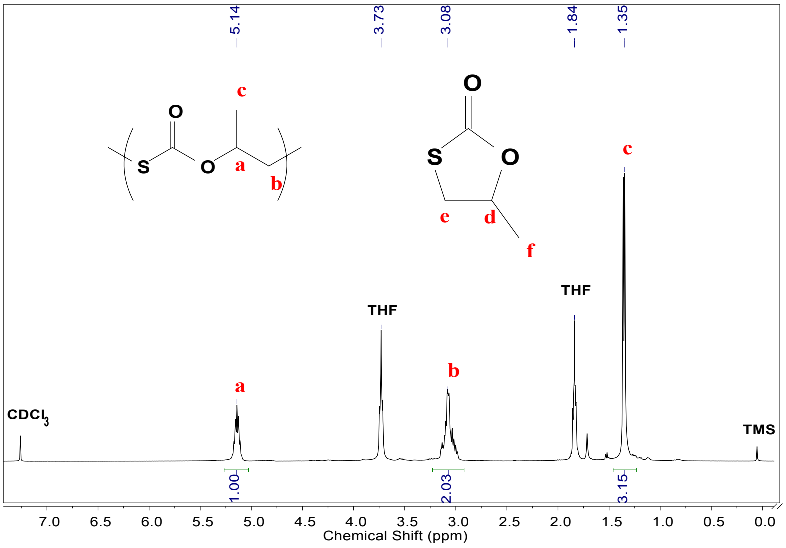


Figure S21. ^{1}H NMR spectrum of the crude product of entry 4, Table S3.

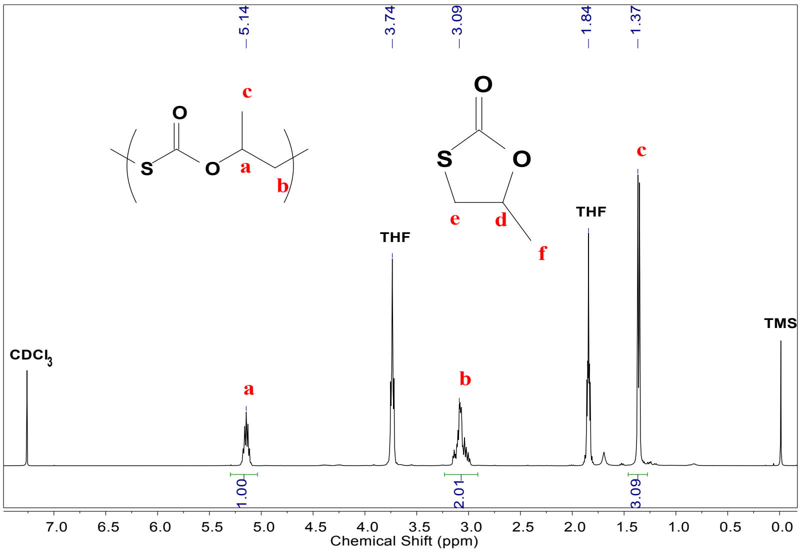


Figure S22. ^{1}H NMR spectrum of the crude product of entry 5, Table S3.

3.2 ^{1}H NMR spectra of products in Table S4.

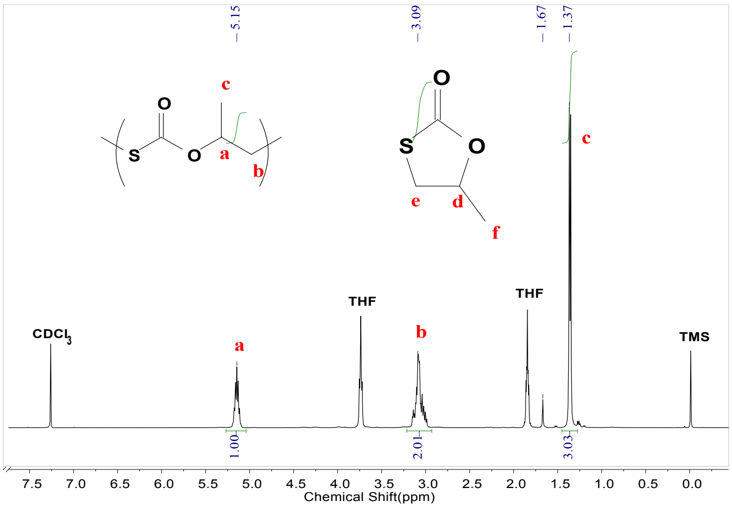


Figure S23. ^{1}H NMR spectrum of the crude product of entry 1, Table S4;

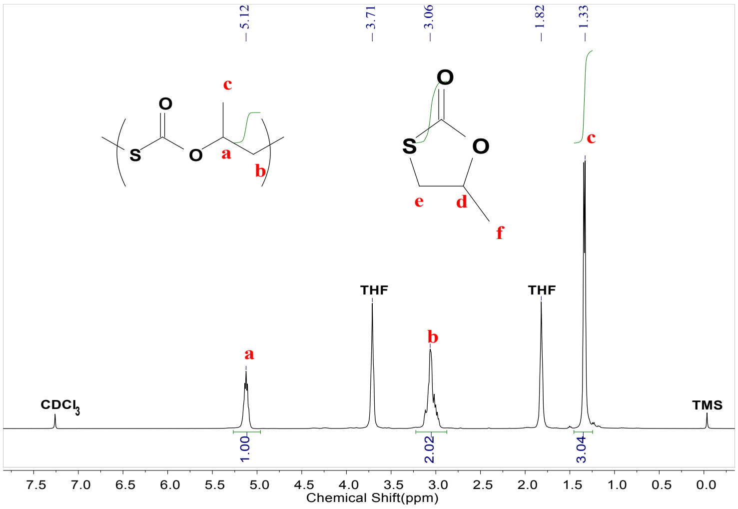


Figure S24. ^{1}H NMR spectrum of the crude product of entry 2, Table S4;

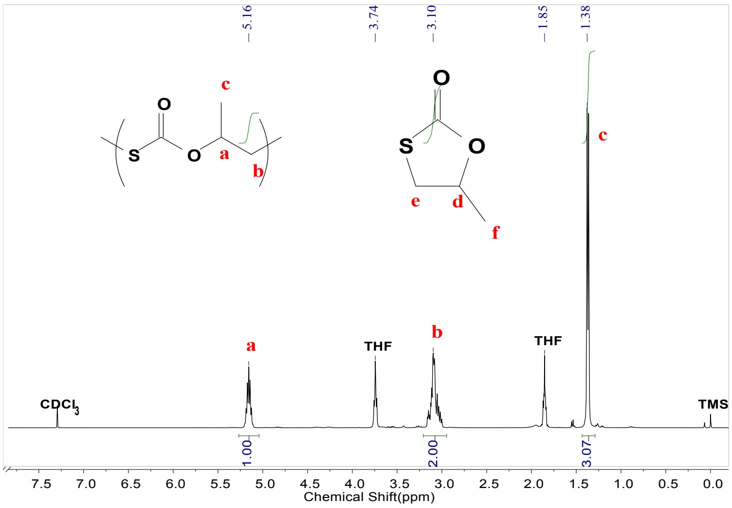


Figure S25. ^{1}H NMR spectrum of the crude product of entry 3, Table S4.

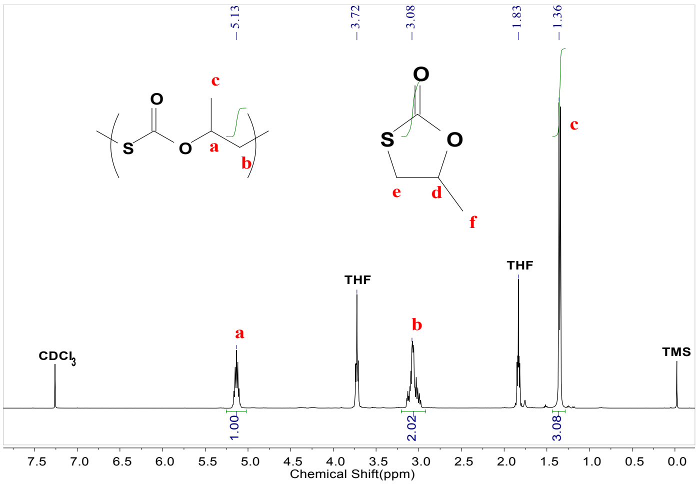


Figure S26. ^{1}H NMR spectrum of the crude product of entry 4, Table S4.

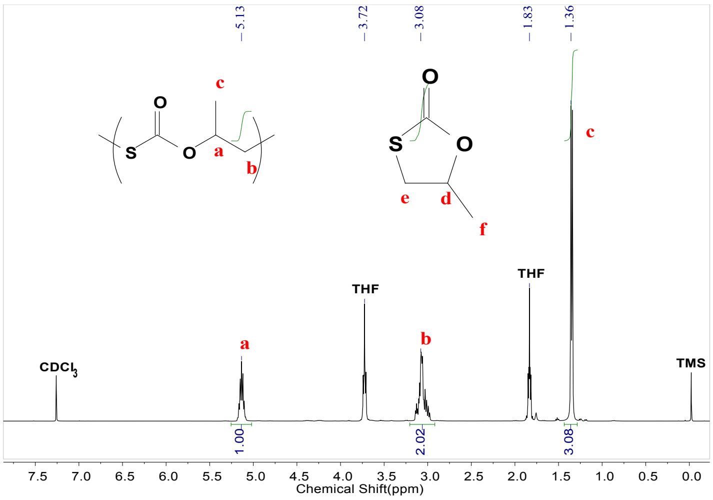


Figure S27. ^{1}H NMR spectrum of the crude product of entry 5, Table S4.

Part 4. Materials and methods.

4.1 Materials.

Unless otherwise specified, all syntheses and manipulations were carried out on a double-manifold Schlenk vacuum line under nitrogen atmosphere or in a nitrogen-filled glovebox. Following purification, materials were stored in a nitrogen-filled glovebox prior to use unless otherwise specified. Triethyl borane (TEB) in tetrahydrofuran solution (1.0 mol/L), N,N,N',N'-Tetra***e***thyl***e***thylenediamine (**TEED**), and N,N,N',N'-Tetra***e***thyl***m***ethylenediamine (**TEMD**) was purchased from Sigma-Aldrich. Triethylamine (TEA**)**, 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU), N,N,N',N'-Tetra***e***thyl-1,3-***p***ropanediamine (**TEPD**), N,N,N',N'-Tetra***m***ethyl***e***thylenediamine (**M-E**), N,N,N',N'-Tetra***e***thyl***m***ethylenediamine (**TEMD**) and N,N,N',N'-Tetra***m***ethyldiamino***m***ethane (**TMDM**) was bought from J&K Chemical. TEB was used without further purification and other Lewis bases were purified by distillation after stirring with calcium hydride for 3 days in nitrogen. Propylene oxide (PO) was purified by distillation after stirring with calcium hydride for 3 days. Tetrahydrofuran (THF) was distilled from sodium/benzophenonemixture before used. Carbonyl sulfide (COS) (99.9%, ACS Grade, Alfa Aesar) was purchased from the APK (Shanghai)Gas Company LTDand used directly.

4.2 Copolymerization of COS with PO.

A 10 mL autoclave with magnetic stirrer was first dried in an oven at 120 °C overnight, then immediately placed into the glove box chamber. After keeping under vacuum for 2-3 h, the reaction vessel was moved into the glove box with nitrogen atmosphere. The copolymerization of COS with PO described below is taken from entry 11 in Table 1 as an example. **TEED** (2.9 μL, 28.6 μmol) was firstly added into the reactor and dissolved in 2 mL of THF. PO (1.0 mL, 14.3 mmol) was carefully added into the vessel after the introduction of an appropriate amount of triethyl borane (21 μL, 0.021 mmol). The reactor was sealed and taken out from the glove box and charged with appropriate weight of COS (ca. 1.72 g, by weighting). The copolymerization was carried out at 25 °C for 8 h. At the end of the copolymerization, the reactor was cooled in ice-water bath, then the unreacted COS was released, and an aliquot was then taken from the resulting crude product for the determination of the ratio of copolymer/cyclic products by the ^{1}H NMR spectrum. The other solution was quenched with HCl in ethanol (1.0 mol/L). The crude product was dissolved with CH_2Cl_2 and then precipitated in cold ethanol. The product was collected by centrifugation and dried in vacuum at 40 °C until constant weight. For the copolymerization conducted in mins (i.e. 1 min), the autoclave filled with PO and LP was put into the preheated oil bath, a timer was started once COS was pushed in. COS was quickly vented as soon as the reaction time was over. Then the copolymer was collected together to weigh. For the copolymerization with multi-steps, we cooled the autoclave in ice-water bath and transferred it into the glovebox, then an aliquot was then taken from the resulting crude product for characterization and the other was remained for further reaction.

4.3 Characterization.

All ^{1}H and ^{13}C NMR spectrawere recorded on a Bruker AVANCE DMX 400Hz instrument in $CDCl_3$. Chemical shift values were referenced to $CHCl_3$ at 7.26 ppm for

^{1}H NMR and 77.16 for ^{13}C NMR. GC-MS spectra were taken on a GC/MS-QP2010 chromatograph. Molecular weights and molecular weight distributions of the resultant copolymers were determined with a PL-GPC220 chromatograph (Polymer Laboratories) equipped with an HP 1100 pump from Agilent Technologies. The GPC columns were eluted with THF with 1.0 mL/min at 40 °C. The sample concentration was 0.4 wt %, and the injection volume was 50 μL. Calibration was performed using monodisperse polystyrene standards covering the molecular-weight range from 500 to 5000 000Da.

4.4 Calculation of Copolymer Selectivity and TOF.

Copolymer Selectivity was calculated based on the ^{1}H NMR spectrum of the crude product. Taking Entry 1 in Table 1 as an example, spectrum of the crude product was showed in Figure S1. Protons with chemical shift of 4.80, 3.52, 3.26 and 1.51 ppm belong to the methine methylene, and methyl respectively, the corresponding peaks in 5.13, 3.08 and 1.36ppm belongs to these groups in the backbone of the copolymer. And the area ratio of these two parts was taken as the copolymer selectivity.

TOF was calculated by using the mass of pure product and feeding ratio, together with the reaction time, we can get the TOF values. For the reaction time, we started the timer when we put the autoclave into the oil-bath with set value and ended it when we got the autoclave out and vented the COS.