Electronic Supplementary Material (ESI) for Polymer Chemistry.

Unprecedentedly high active organocatalysts for the copolymerization of carbonyl sulfide and propylene oxide: Steric hindrance effect of tertiary amines

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Experiment

1. General details

Unless otherwise specified, all operations were carried out under a dry nitrogen atmosphere using standard Schlenk-line and glovebox techniques. TEB solution 1.0 M in THF was purchased from Sigma-Aldrich and used as received. 1,4-Diazabicyclo-[2.2.2]-octane (**DABCO**) was purchased from a commercial supplier and purified by sublimation before use. *N,N*-diethylcyclohexylamine (**DECHA**), and *N,N*-dimethylcyclohexylamine (**DMCHA**) were purchased from commercial suppliers. N^1,N^1,N^4,N^4-tetraethylcyclohexane-1,4-diamine (**1,4 TECHDA**) and N^1,N^1,N^2,N^2-tetraethylcyclohexane-1,2-diamine (**1,2 TECHDA**) were synthesized following a literature procedure.[1] ^{1}H NMR and ^{13}C NMR spectra of **1,2 TECHDA** and **1,4 TECHDA** were shown in Figure S1 and S2, respectively. All Lewis bases were purified by distillation over calcium hydride under nitrogen and stored in a freezer in a glove box. *Rac*-propylene oxide (PO) was purified by distillation after stirring with calcium hydride overnight. Carbonyl sulfide (COS) (99.9%, ACS Grade, Alfa Aesar) was purchased from the APK (Shanghai) Gas Company LTD and used as received. It was noted that purity of COS is very important for the successful reactions. New bottle of COS was used for all polymerizations in this study. pK_a values of all Lewis bases are calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994-2018 ACD/Labs).

2. Measurement

All ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE DMX 500Hz 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. 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. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometric measurements were performed on a Bruker Ultraflex MALDI TOF mass spectrometer, equipped with a nitrogen laser delivering 3 ns laser pulses at 337 nm. trans-2-[3-(4- tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB, 99%, Alfa) was used as the matrix. The refractive index (*n*) was measured by spectroscopic ellipsometer. The polymer was dissolved in dichloromethane (5 mg/mL) and then spin-coated at 3000 rpm on a silicon wafer for 30 s, then the coated film was measured by spectroscopic ellipsometer. The thickness of the prepared thin film was 74 nm. Differential Scanning Calorimetry (DSC) was determined using a TA Q200 instrument under nitrogen atmosphere with cooling and heating rate of 10^{o}C/min, temperature in the range of -50^{o}C -200^{o}C. Thermogravimetric Analysis (TGA) was determined using a TA Q200 instrument under nitrogen atmosphere with heating rate of 10^{o}C/min, room temperature to 400^{o}C.

3. Copolymerization of COS with PO

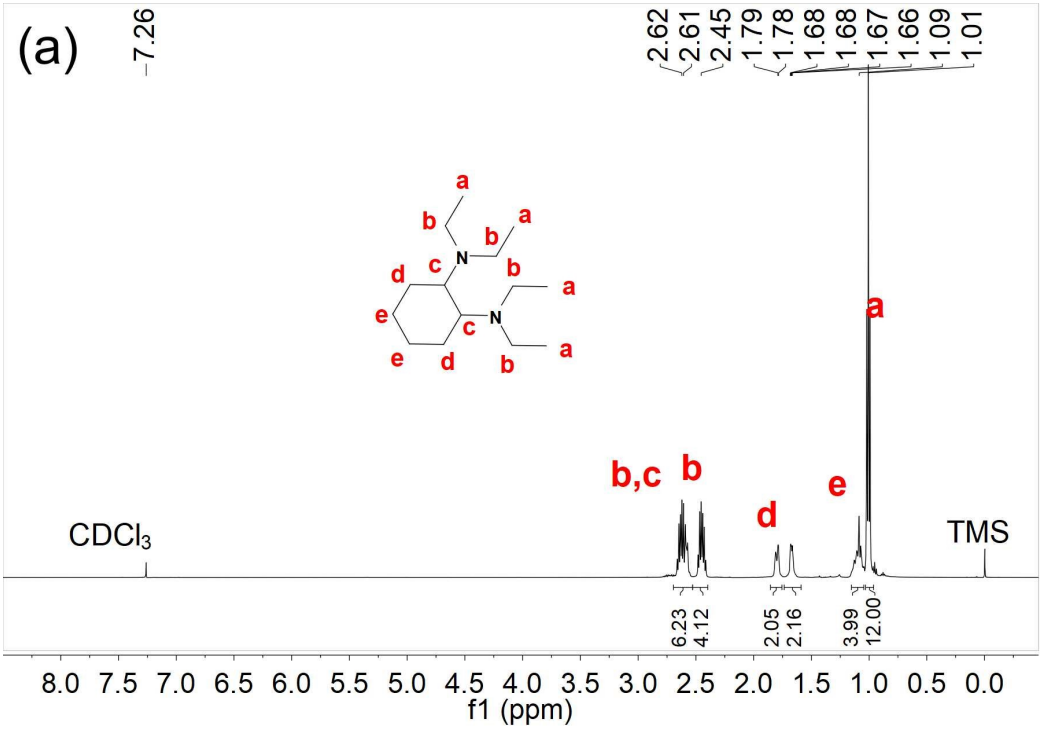
A 10 ml autoclave with a magnetic stirrer was first dried in an oven at 110 °C overnight, then immediately placed into the glove box. The copolymerization of COS with PO described below is taken from entry 7 in Table 1 as an example. **DMCHA** (3.6 mg, 0.0286 mmol) was firstly added into the reactor. PO (2.0 mL, 28.6 mmol) and triethyl borane (TEB) (29 μL, 0.0286 mmol) were added into the vessel, respectively. The reactor was sealed and taken out from the glove box and charged with the appropriate weight of COS (ca. 2.06 g, by weight). The autoclave was immediately put into the preheated oil bath at 60^{o}C. The copolymerization was carried out at 60^{o}C for 1 min. At the end of the copolymerization, the reactor was cooled in an ice-water bath, then the unreacted COS was quickly released and an aliquot was then taken from the resulting crude product for ^{1}H NMR spectroscopy determination. 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.

entry	PO/LA/LB	LB	time (min)	PO Conv. (%) [b]	selectivity (%) [b]	alternating degree (%) [b]	TOF (h^{-1})[c]	M_n (kg/mol) [d]	$Đ$ (M_w/M_n) [d]
1	100/1/0.5	1,2TECHDA	10	28	99	>99	170	4.4	1.27
2	100/1/0	-	10	0	-	-	-	-	-
3	100/0/1	DMCHA	10	0	-	-	-	-	-
4	10000/1/1	DMCHA	5	9	>99	>99	10800	26.0	1.14

Table S1. COS/PO copolymerization catalyzed by TEB/Lewis bases.[a]

[a)] The reactions were performed in the bulk ([COS]/[PO] = 1.2/1, molar ratio) at 60°C in a 10 ml autoclave; [b)] determined by ^{1}H NMR spectroscopy. The copolymer selectivity is the molar ratio of the copolymer/cyclic product; The alternating degree is the molar percentage of the monothiocarbonate unit in the polymer chain. [c)] (mol epoxide consumed)/(mol TEB h); [d)] determined by gel permeation chromatography in THF at 40°C, calibrated with polystyrene standards.



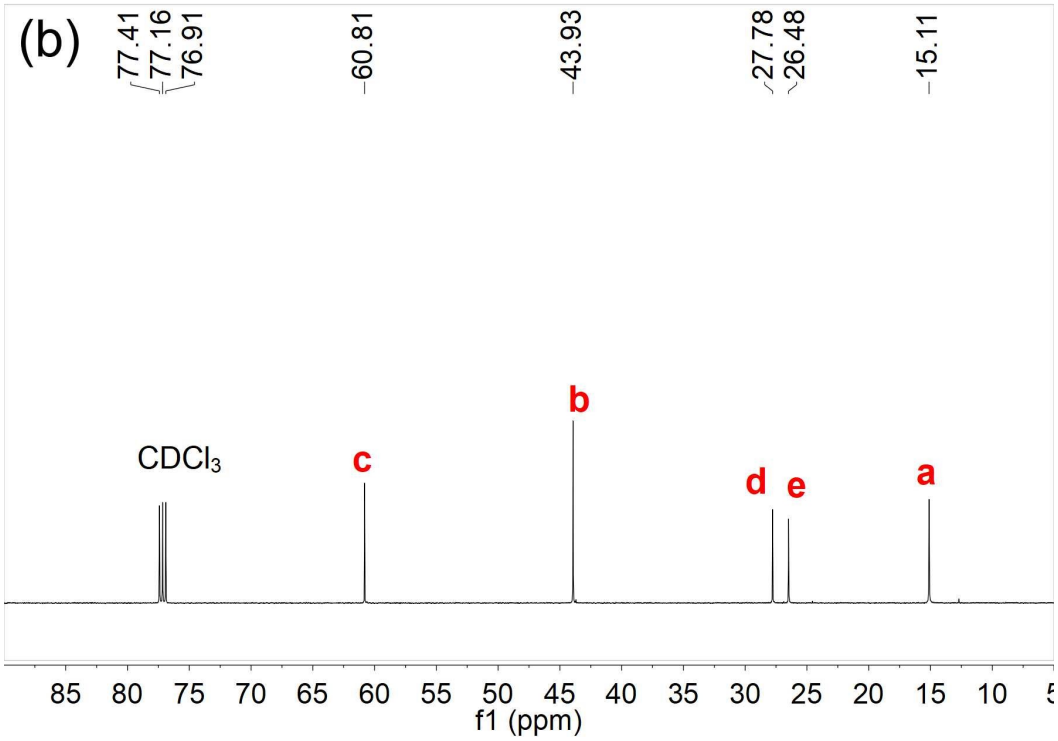
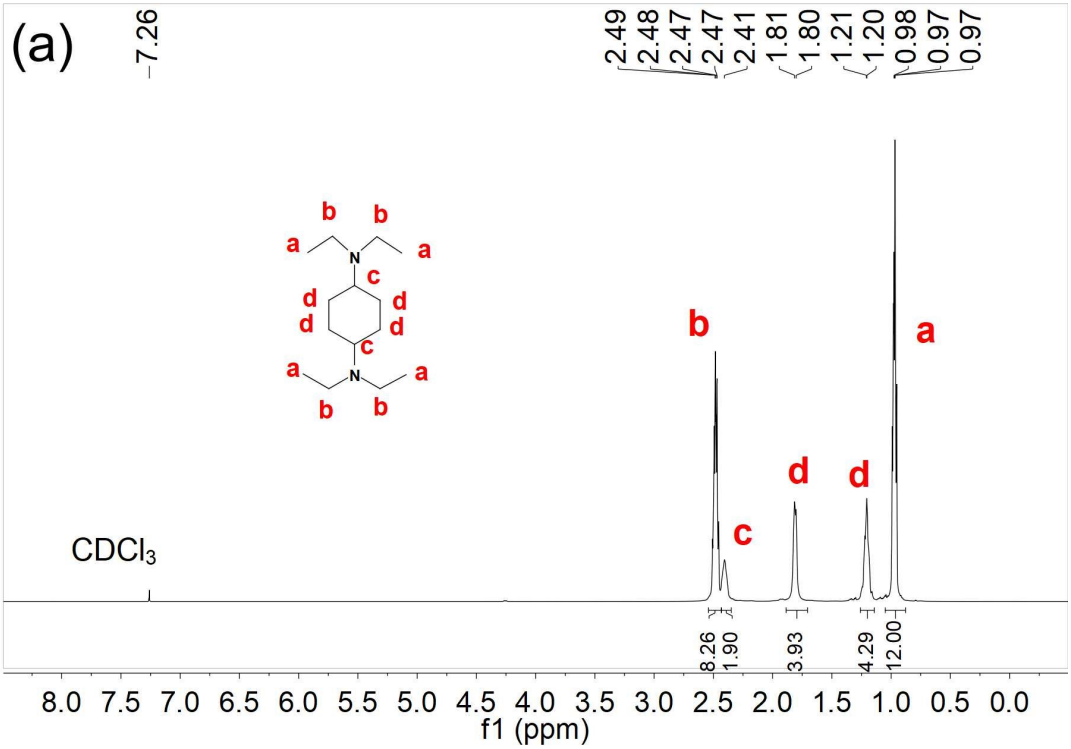


Figure S1. (a) ^{1}H NMR and (b) ^{13}C NMR spectra ($CDCl_3$) of 1,2 TECHDA



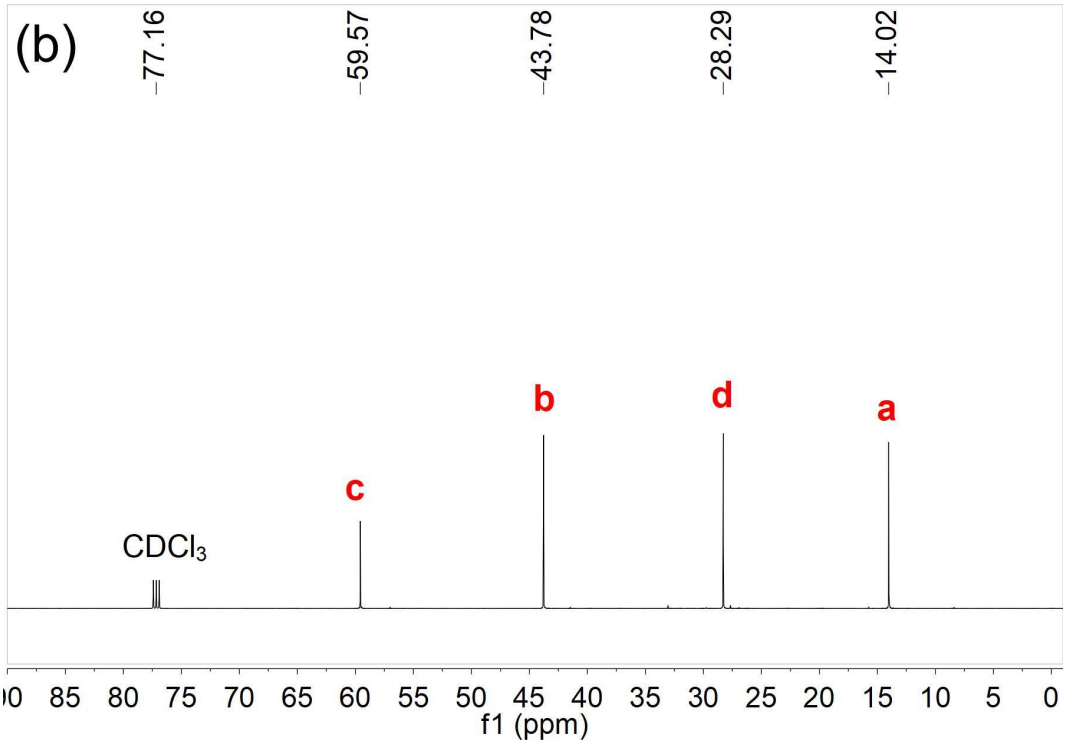


Figure S2. (a) ^{1}H NMR and (b) ^{13}C NMR spectra ($CDCl_3$) of 1,4 TECHDA

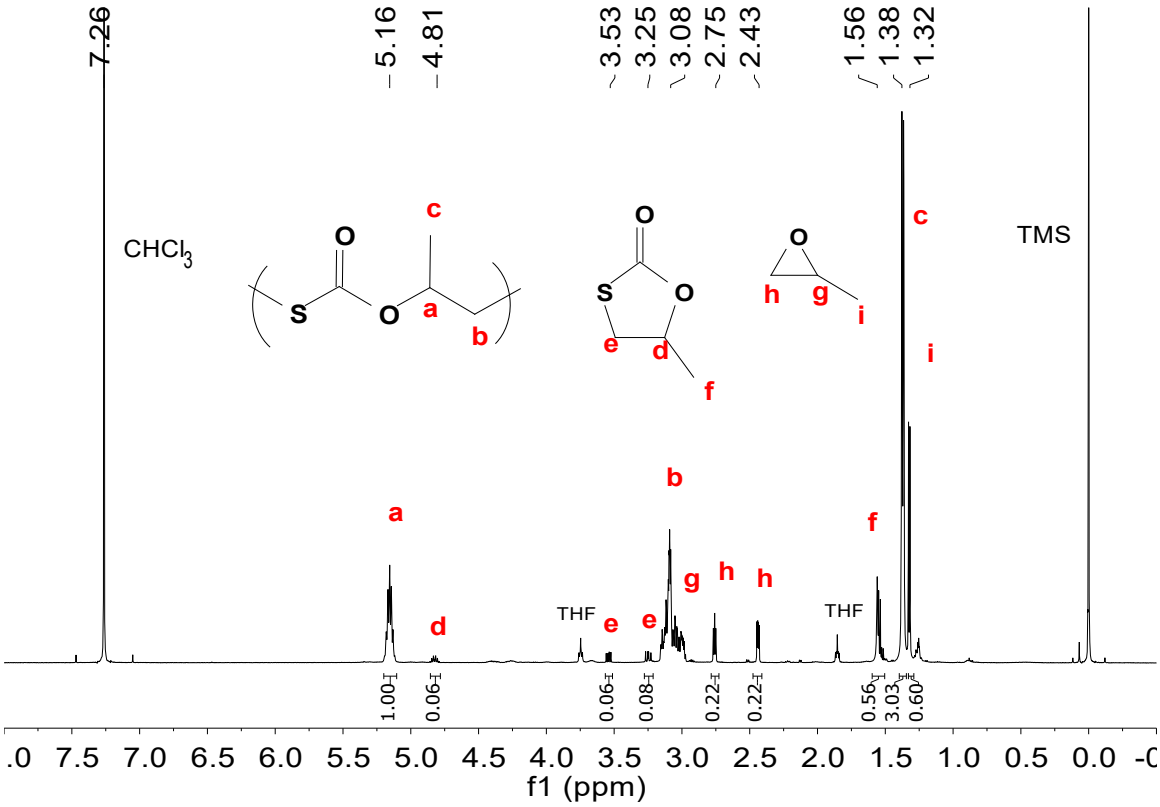


Figure S3. ^{1}H NMR ($CDCl_3$) of the crude product (entry 1, Table 1)

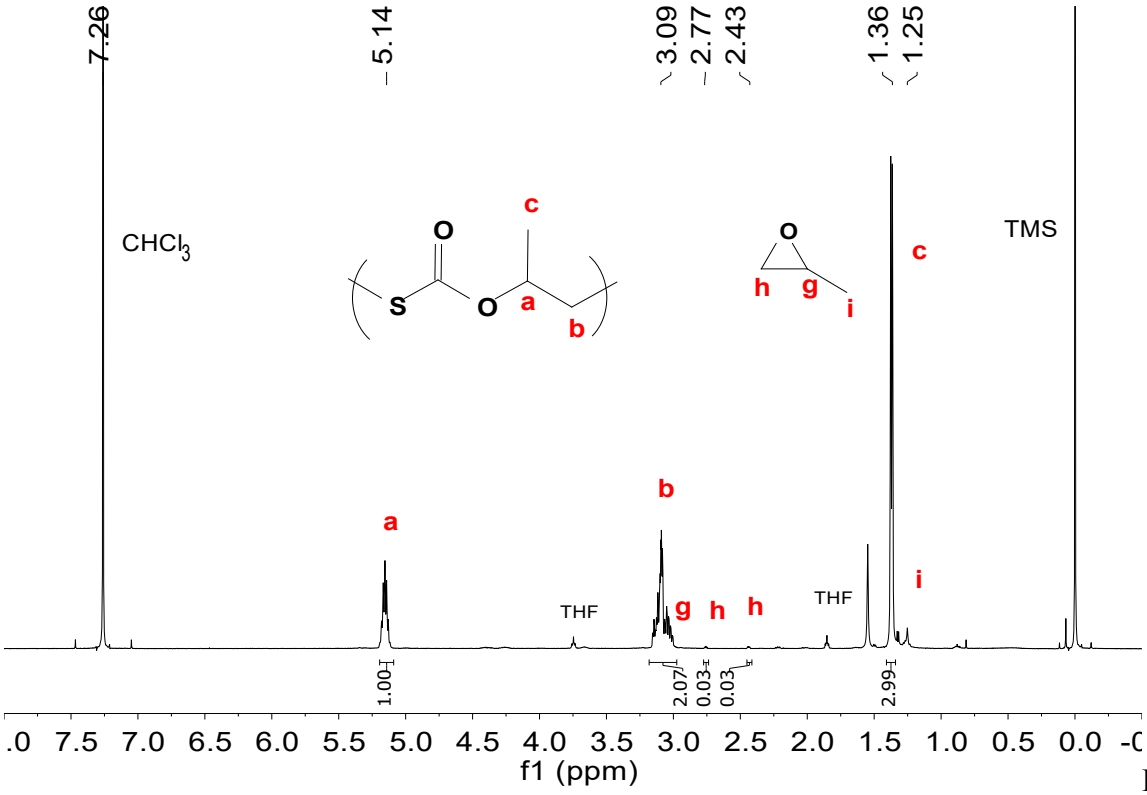


Figure S4. ^{1}H NMR ($CDCl_3$) of the crude product (entry 2, Table 1)

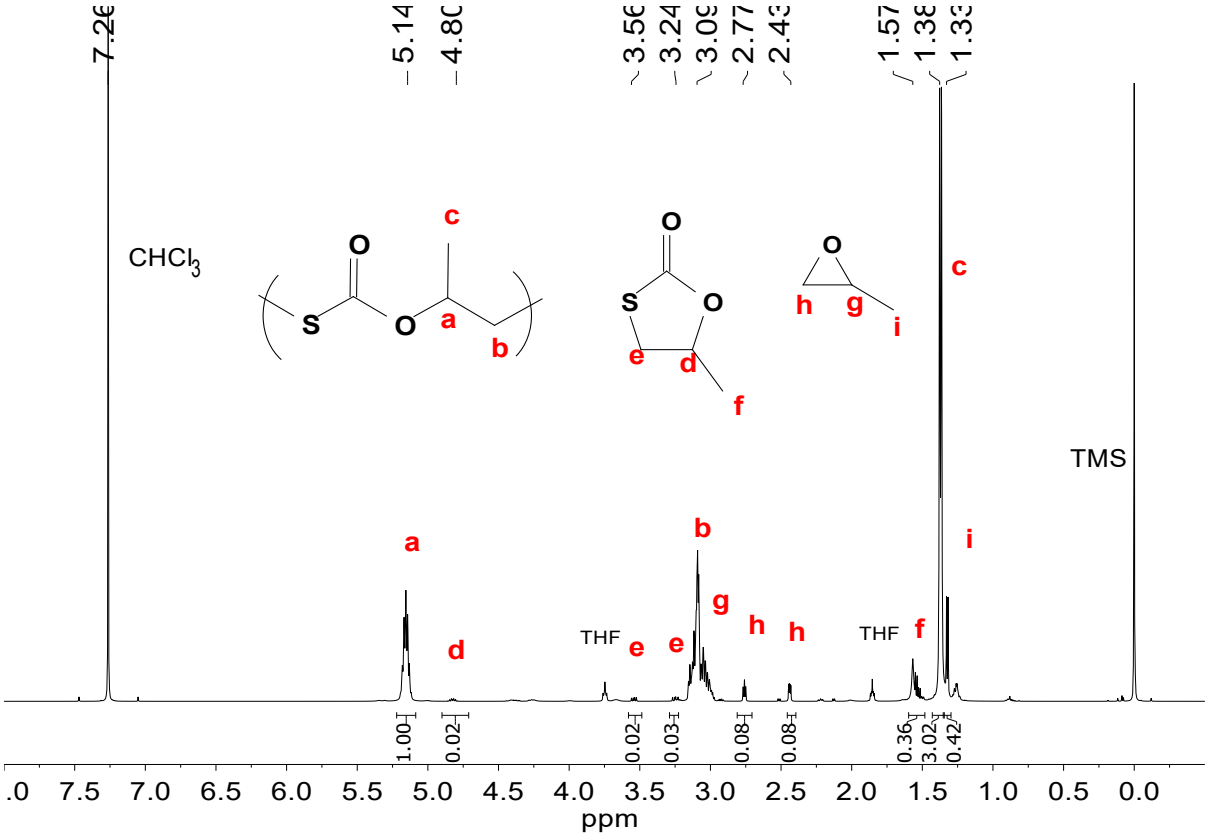


Figure S5. ^{1}H NMR ($CDCl_3$) of the crude product (entry 4, Table 1)

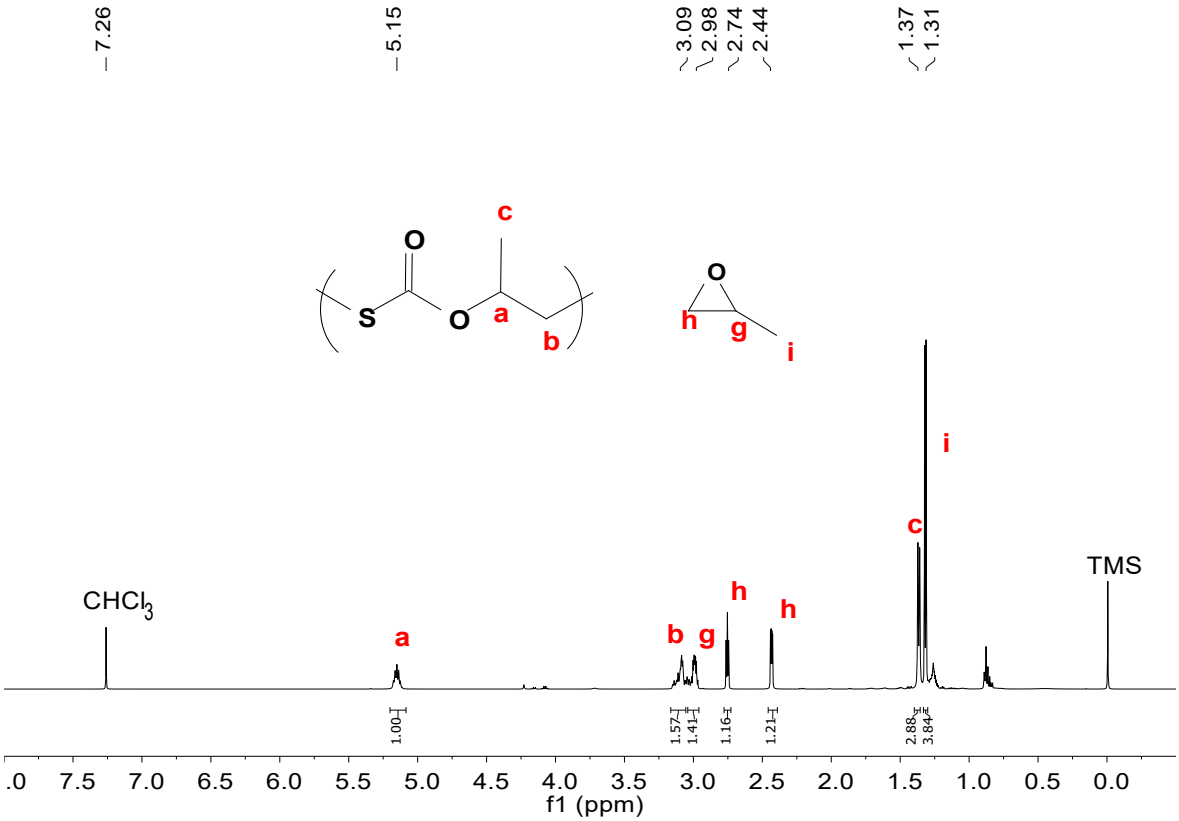


Figure S6. ^{1}H NMR ($CDCl_3$) of the crude product (entry 5, Table 1)

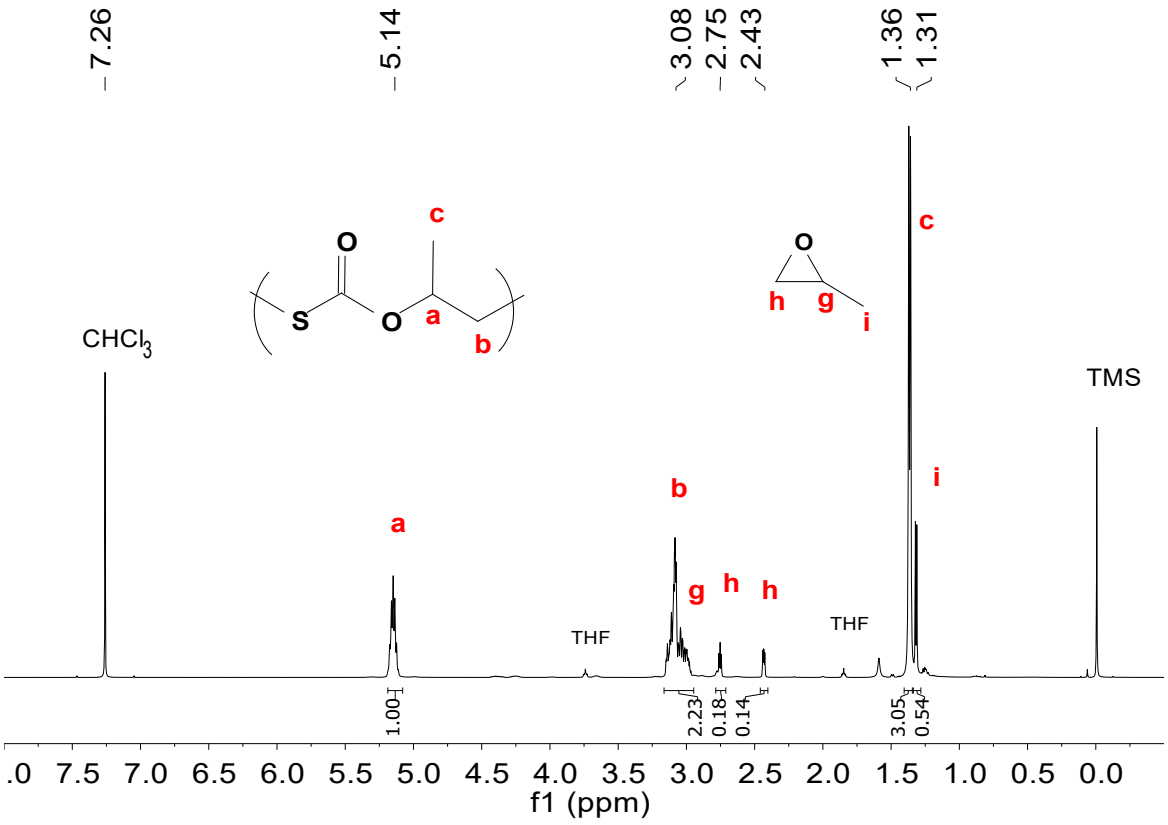


Figure S7. ^{1}H NMR ($CDCl_3$) of the crude product (entry 6, Table 1)

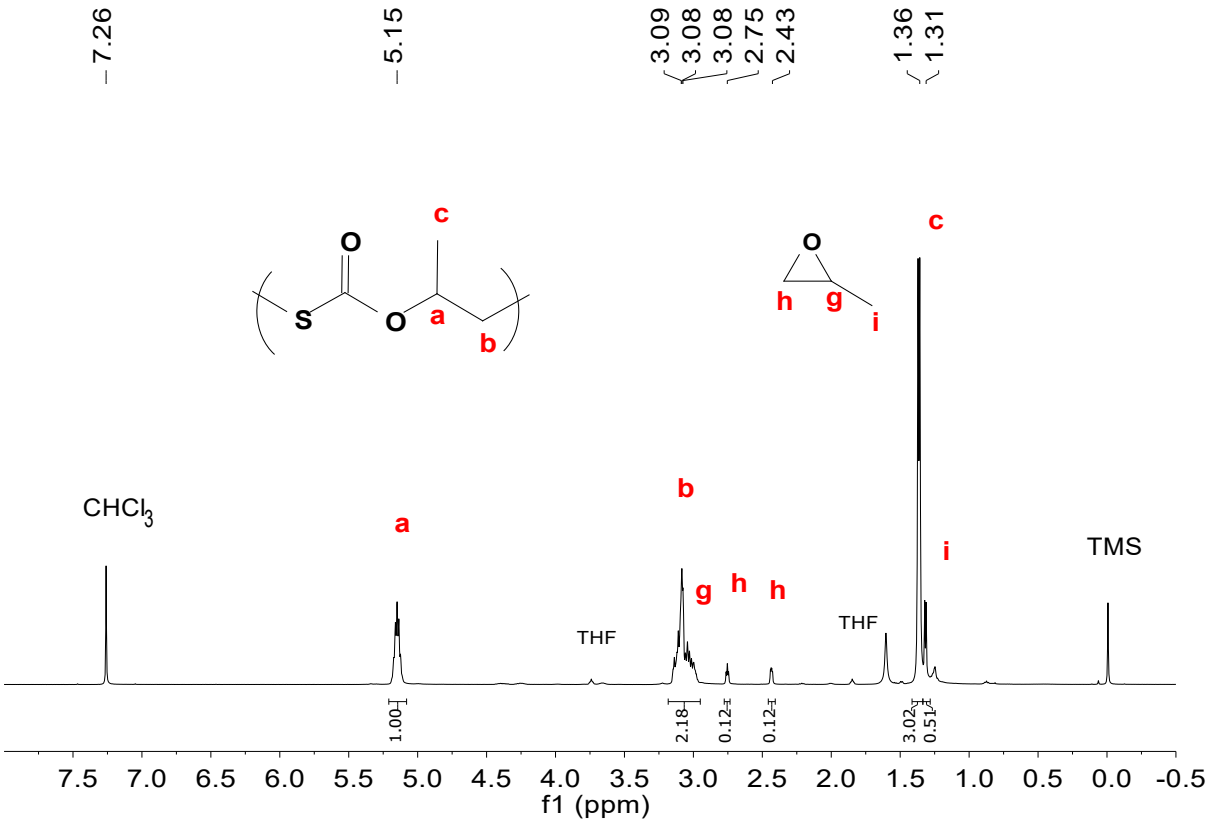


Figure S8. ^{1}H NMR ($CDCl_3$) of the crude product (entry 7, Table 1)

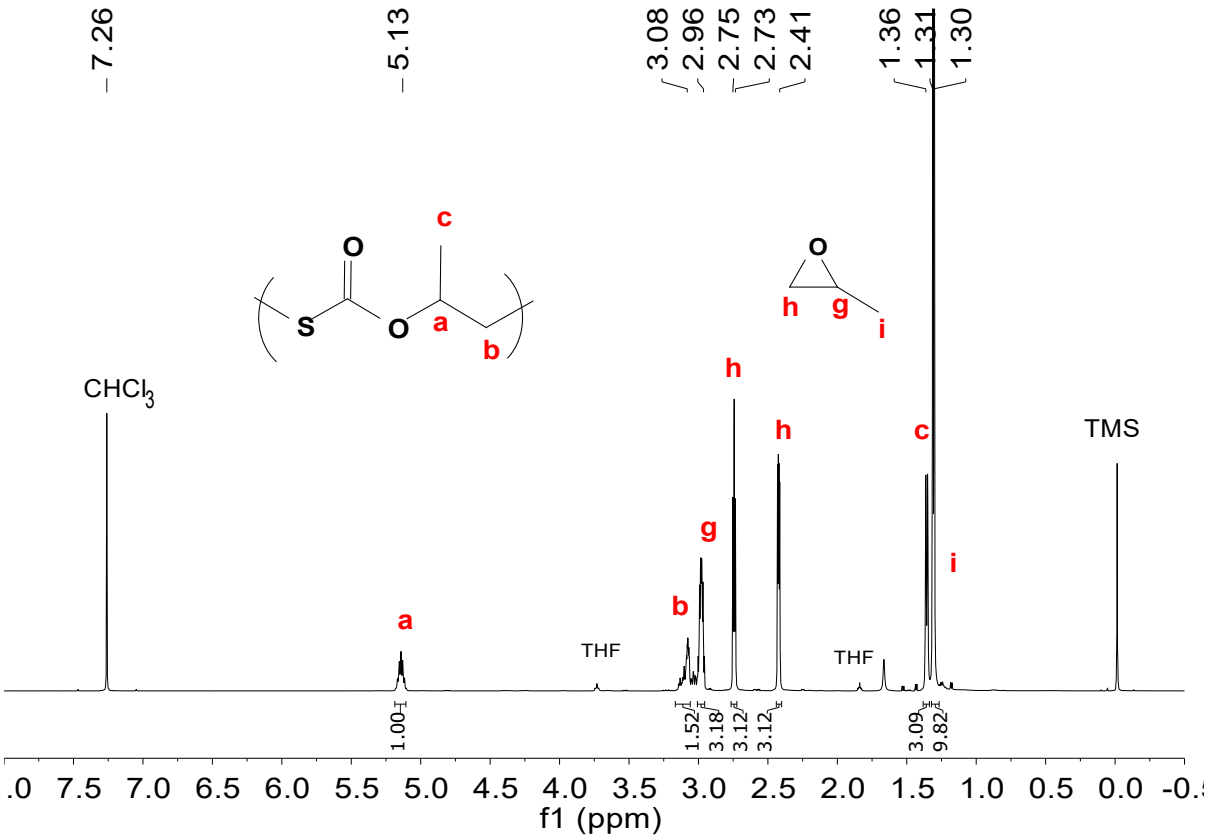


Figure S9. ^{1}H NMR ($CDCl_3$) of the crude product (entry 8, Table 1)

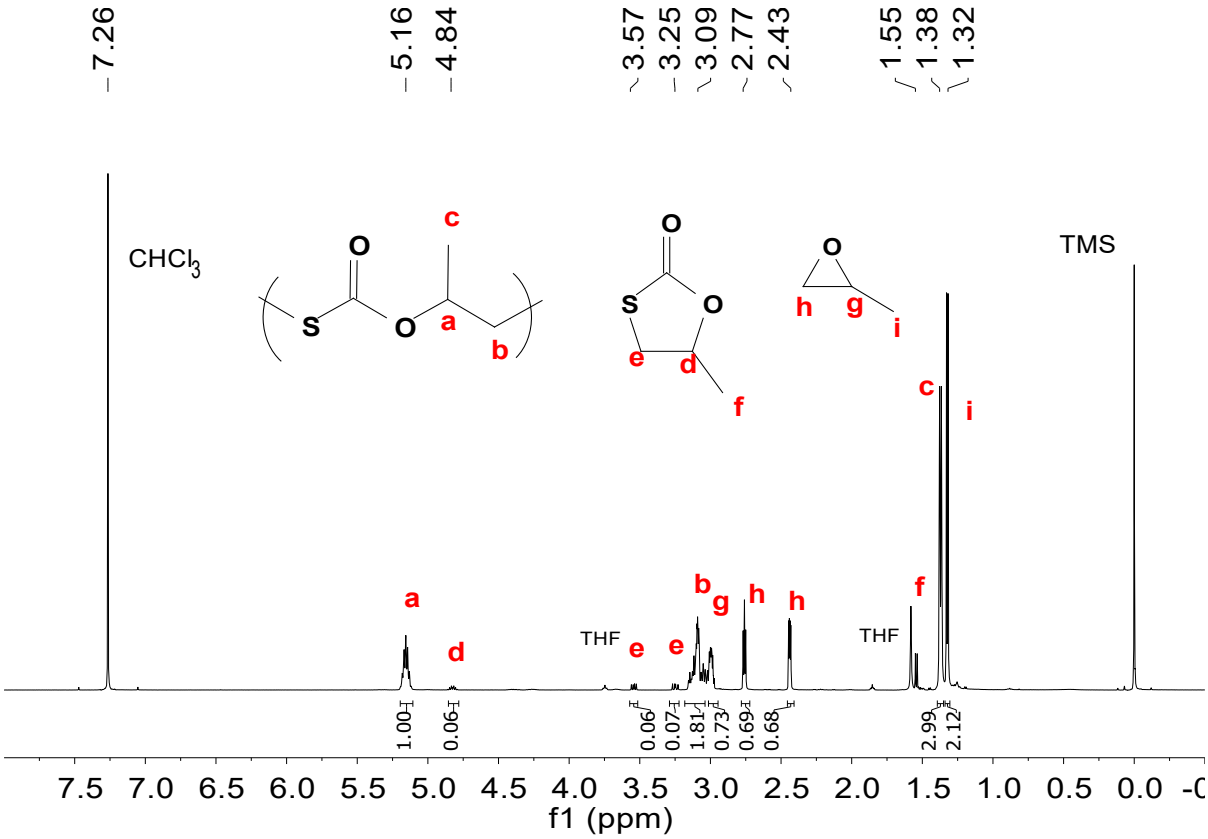


Figure S10. ^{1}H NMR ($CDCl_3$) of the crude product (entry 9, Table 1)

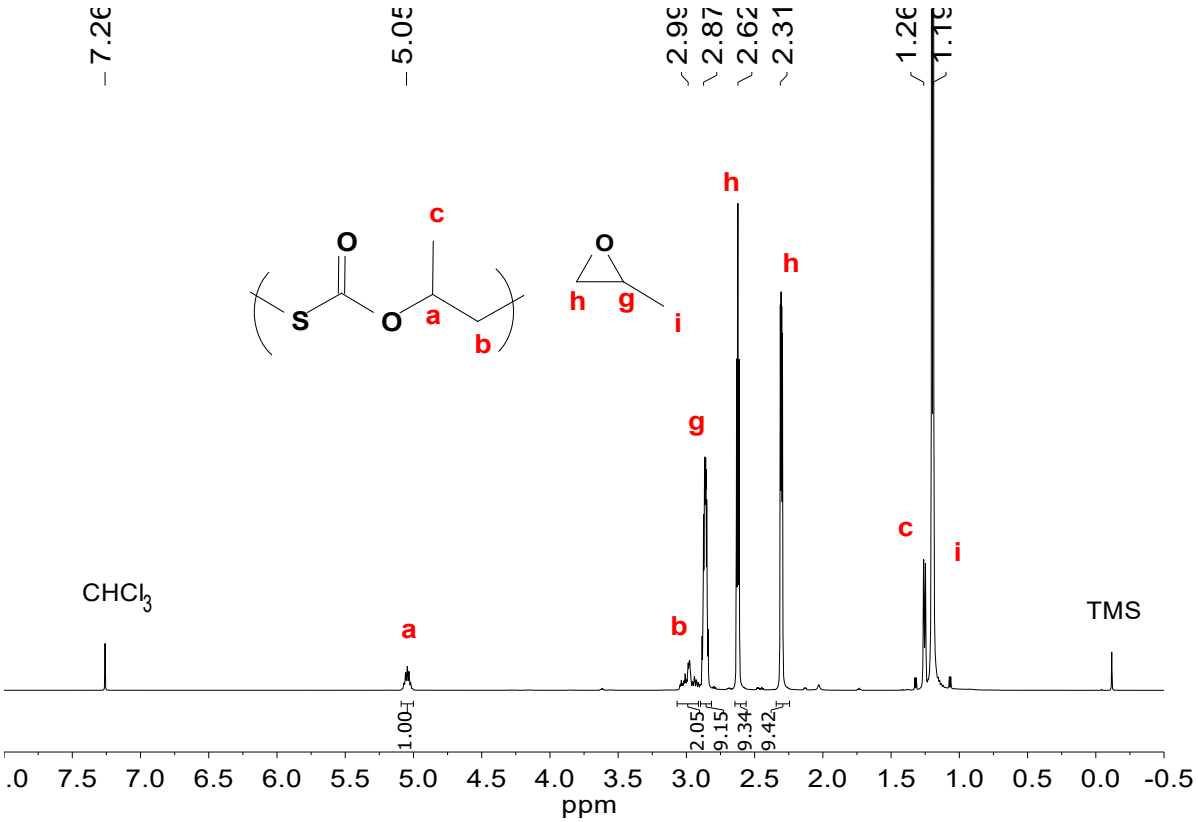


Figure S11. ^{1}H NMR ($CDCl_3$) of the crude product (entry 10, Table 1)

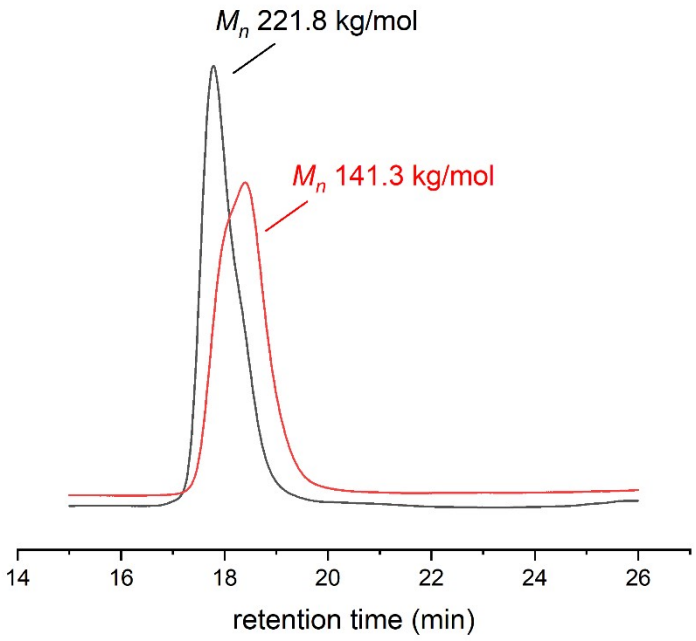


Figure S12. GPC chromatogram of the obtained PPMTCs catalyzed by TEB/**DMCHA** and 1,4**TECHDA** pairs (entry 6-7, Table 1)

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	Name	Method	Weight [mg]	N Area	C Area	H Area	N [%]	C [%]	H [%]
23	S75l	2mgChem70s	1.954	21	16 502	7 372	0.04	40.79	5.15
24	S75l	2mgChem70s	2.091	19	17 660	7 910	0.03	40.80	5.19

Figure S13. The elemental analysis result of PPMTC catalyzed by TEB/**DMCHA** pair (M_n = 30.6 kg/mol, terminated by dilute 1.0 M HCl in ethanol).

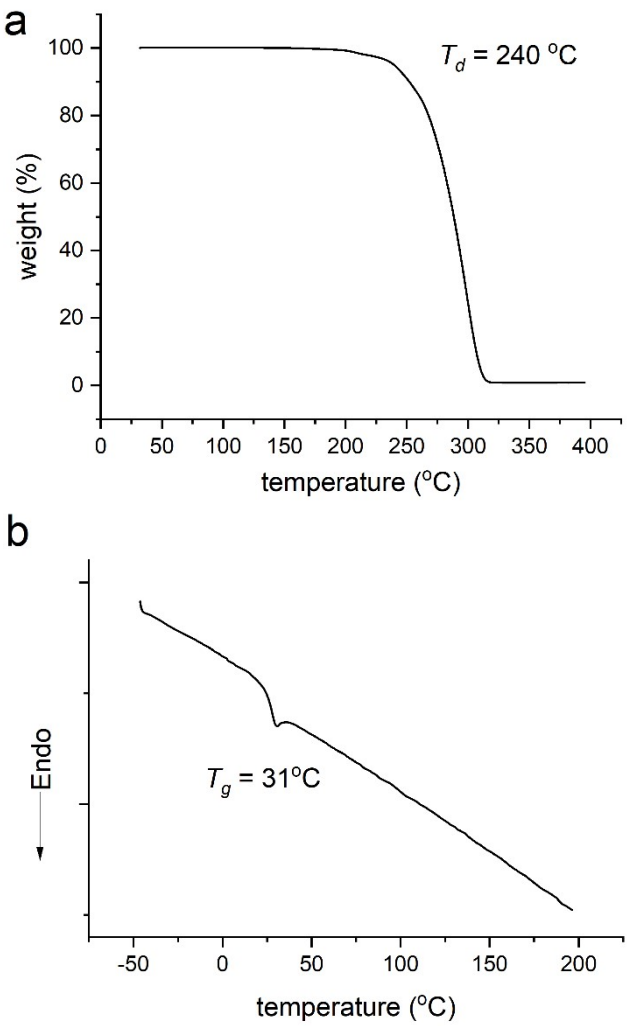

Figure S14. a) TGA and b) DSC curves of the selected PPMTC sample (entry 7, Table 1). T_d is temperature at polymer decomposition of 5% in mass fraction.

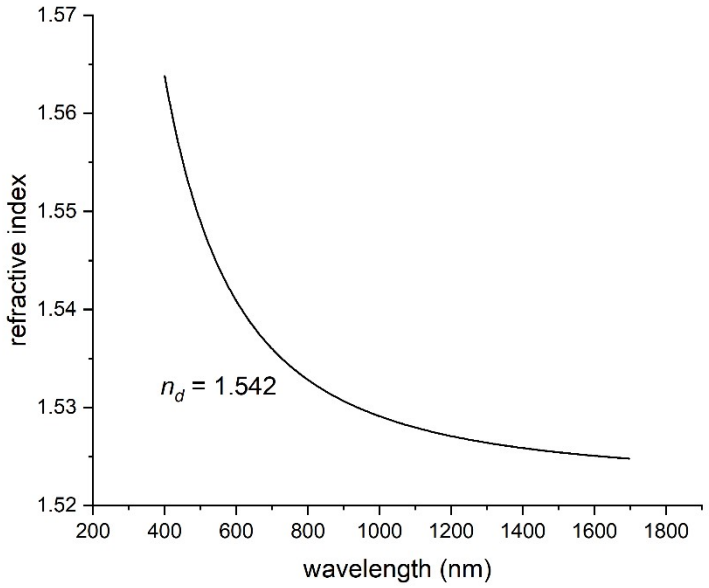

Figure S15. The refractive index (n_d) of the selected PPMTC sample (entries 7, Table 1), n_d is the refractive index at wavelength 589.9 nm determined by spectroscopic ellipsometer.

References

1. A. P. Cole, V. Mahadevan, L. M. Mirica, X. Ottenwaelder and T. D. P. Stack, *Inorg. Chem.*, 2005, **44**, 7345-7364.