Supporting Information

for

Repurposing Poly(monothiocarbonate)s to Poly(thioether)s by Organic Bases

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Materials

Various hydroxyl-terminated poly(monothiocarbonate)s were synthesized according to published procedures.[1-6] 1,2,4-Trichlorobenzene (TCB, 99 %) and 1-methylimidazole (NMI, 99 %) were purchased from J&K Scientific LTD and used directly. 1,5,7-Triazabicyclo[4,4,0]dec-5-ene (TBD, 98%), 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU, 99 %), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN, 99 %) and dimethylaminopyridine (DMAP, 98 %) were purchased from Sigma-Aldrich Chemical Co. and used as received. *N*-methyl-1,5,7-triazabicyclododecene (MTBD, 98 %) was purchased from Alfa Aesar Chemical Co. and used directly.

Characterization

^{1}H NMR and ^{13}C NMR spectra were performed on a Bruker Advance DMX 400 MHz or 600 MHz spectrometer. And chemical shift values were referenced to TMS at 0 ppm for ^{1}H NMR and ^{13}C NMR. The number-average molecular weight (M_n) and molecular weight distribution ($Đ = M_w/M_n$) of the resultant products 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. Solid state NMR measurements of the product were performed on Bruker Avance III HD 400 MHz spectrometers using 3.2 mm magicangle spinning probes. The samples were packed in 3.2 mm rotors in an argon-filled glovebox and were spun at 15 kHz or 10 kHz during NMR measurements. The thermal properties of samples were characterized by thermal gravity analysis (TGA) on a TA Q50 instrument and differential scanning calorimetry (DSC) on a TA Discovery DSC25 instrument. In TGA experiments,

the samples were heated from room temperature to 500 °C at a rate of 10 °C min^{-1} under nitrogen atmosphere. The thermal decomposition temperatures (T_d) were defined as the temperature at which the mass loss was the fastest. In DSC experiments, the samples of 3-5 mg encapsulated in an aluminum pan were first heated to 100 °C and held for 3 min to eliminate thermal history. Subsequently, the samples were cooled to -80 °C, and reheated to 100 °C to obtain DSC curves. Both the heating and cooling rates were 10 °C min^{-1}. Glass transition temperature (T_g) was determined from the second run. The refractive index (n) was measured by Spectroscopic Ellipsometer, and the polymer was dissolved in toluene (10 mg/mL) and then spin-coated at 3000 rpm on a silicon wafer for 60 s, then the coated film was measured by Spectroscopic Ellipsometer. The thicknesses of the prepared thin films were in the range 300-800 nm.

General Procedures of Repurposing PMTCs to Poly(thioether)s

All repurposing of PMTCs were carried out in the N$_2$ atmosphere unless otherwise specified. Using PPMTC and DBU as an instance, PPMTC (propylene monothiocarbonate repeating units = 1 mmol) and DBU (3.05 mg, 0.02 mmol) were dissolved in 0.5 mL of TCB in a closed vial (10 mL). Then, the vial was heated to 100 °C. The reactions were performed in a closed-system without venting of gas during whole reaction. The contents of the intermediates and products were determined by comparison of the integrals of signals arising from the protons in ^{1}H NMR spectra.

Repurposing PPMTC to PPS with DBU

Table S1. Repurposing PPMTC to PPS with different molecular mass using DBU[a]

Entry	M_n of PPMTC (kg/mol)[b]	$Đ$ (M_w/M_n) of PPMTC[b]	M_n of PPS (kg/mol)[b]	$Đ$ (M_w/M_n) of PPS[b]
1	124.0	1.32	25.6	2.0
2	110.0	1.22	20.1	1.35
3	96.0	1.57	15.4	1.27
4	26.0	1.47	19.7	1.31
5	20.6	1.93	20.3	1.54

[a] Reactions were performed in TCB (0.5 mL) using neat PPMTC (118 mg, 1 mmol) and DBU in a 10 ml autoclave for 4 h. The repeating units-to-base molar ratio ([PPMTC]:[DBU]) was 50:1. [b] Determined by GPC.

Table S2. Repurposing PPMTC to PPS with DBU at 100 ℃[a]
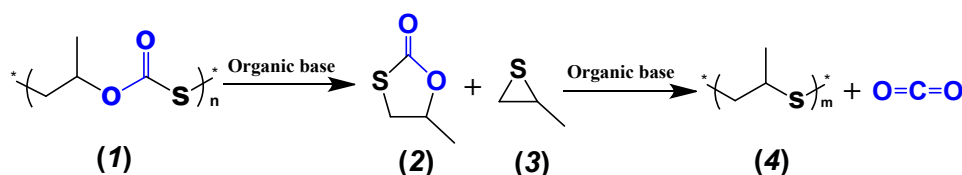
Entry	Reaction time (min)	(**1**):(**2**):(**3**):(**4**)[b]	M_n (kg/mol)[c]	$Đ$ (M_w/M_n)[c]
1	0	100:0:0:0	110.0	1.2
2	1	81:16:3:0	97.2	1.4
3	2	70:24:6:0	5.8	1.2
4	3	20:59:21:0	-	-
5	5	13:52:25:10	14.3	1.3
6	7	0:13:11:76	18.4	1.3
7	9	0:3:5:92	20.0	1.3
8	12	0:0:3:97	20.1	1.4
9	15	0:0:0:100	20.2	1.4

[a] Reactions were performed in TCB (0.5 mL) using neat PPMTC (118 mg, 1 mmol) and DBU in a 10

ml autoclave at 100 ℃. The repeating units-to-base molar ratio ([PPMTC]:[DBU]) was 50:1. [b] Determined by ^{1}H NMR spectroscopy. [c] Determined by GPC.

Table S3. Repurposing PPMTC to PPS using DBU at low temperatures[a]

Entry	Base	T (℃)	(**1**):(**2**):(**3**):(**4**)[b]	t (h)[c]
1[d]	DBU	-15	93:7:0:0	24
2[d]	DBU	0	95:5:0:0	6
3[d]	DBU	25	88:12:0:0	0.5

[a] Reactions were performed in CDCl$_3$ using neat PPMTC (118 mg, 1 mmol) and different organic bases in a 10 ml autoclave for 15 min. The repeating units-to-base molar ratio ([PPMTC]:[Base]) was 50:1. [b] Determined by ^{1}H NMR spectroscopy.

Proposed Mechanism of Repurposing PPMTC to PPS

Scheme S1. Proposed Mechanism of Repurposing PPMTC to PPS by DBU
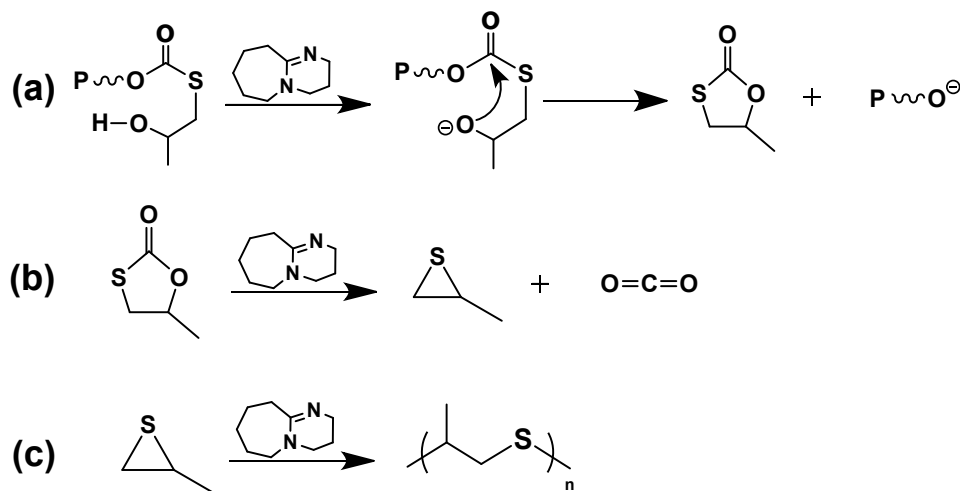
Typical NMR Spectra and Representative GPC Curve
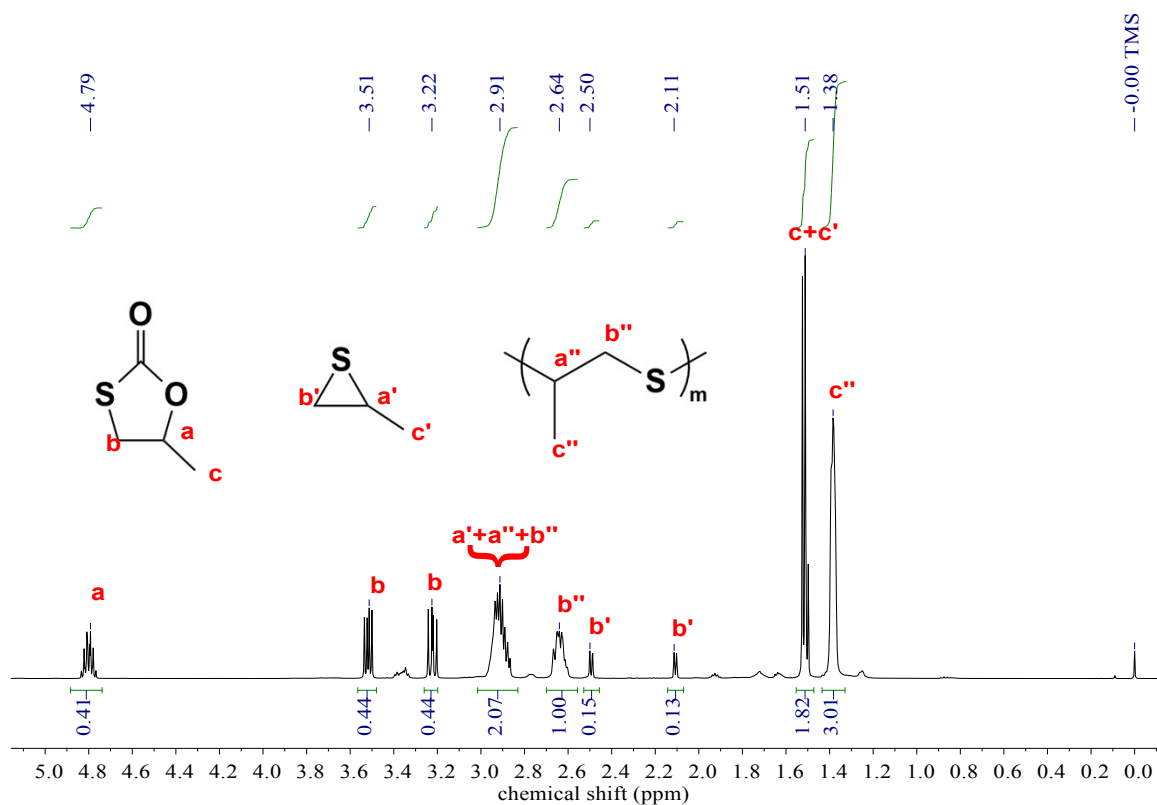
Figure S1. ^{1}H NMR spectra of the crude product in entry 2, Table 1.
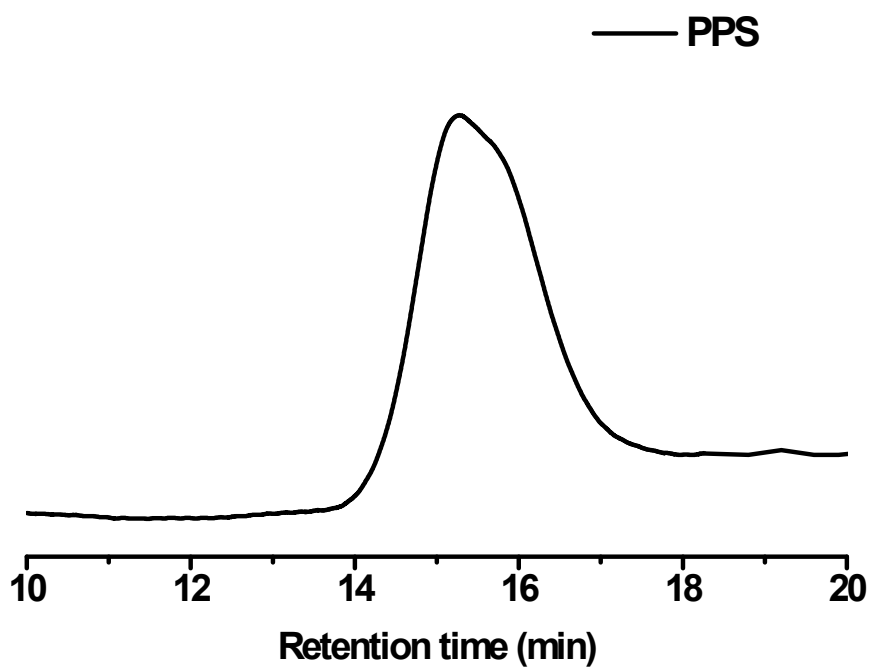
Figure S2. GPC curve of purified product of entry 3, Table 1.
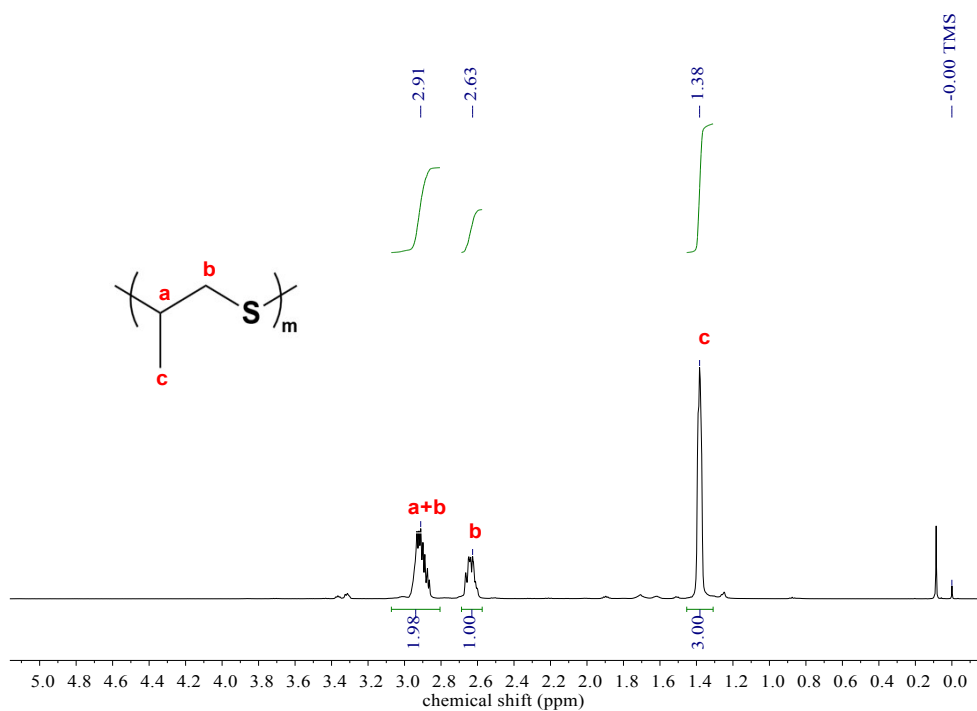
Figure S3. ^{1}H NMR spectra of the crude product in entry 7, Table 1.
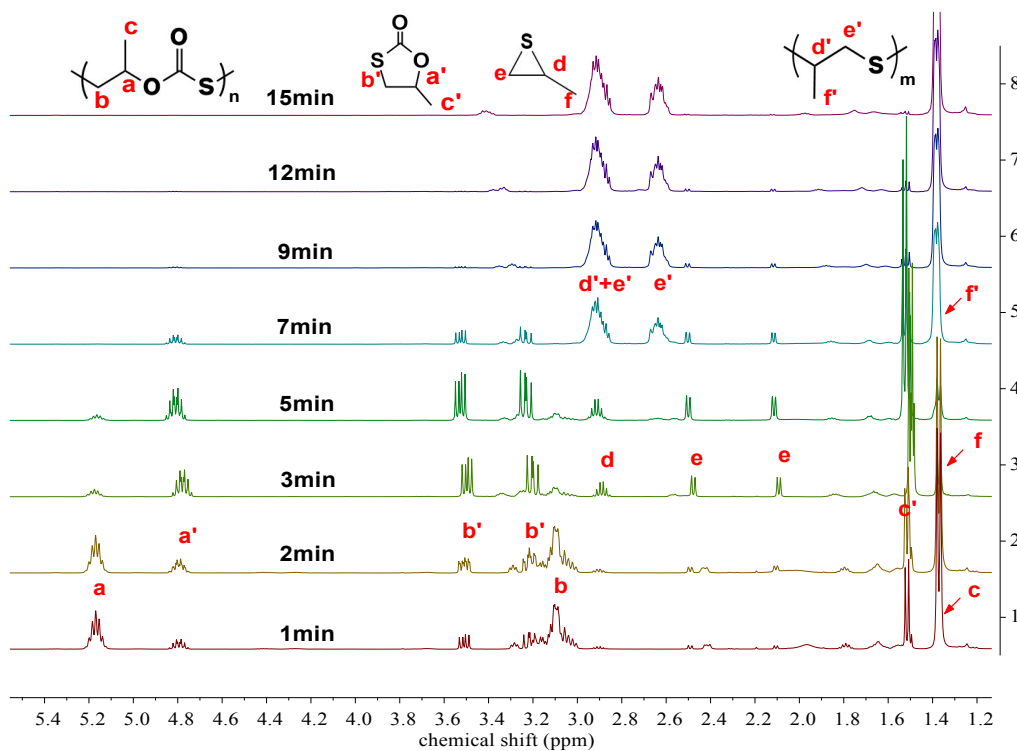
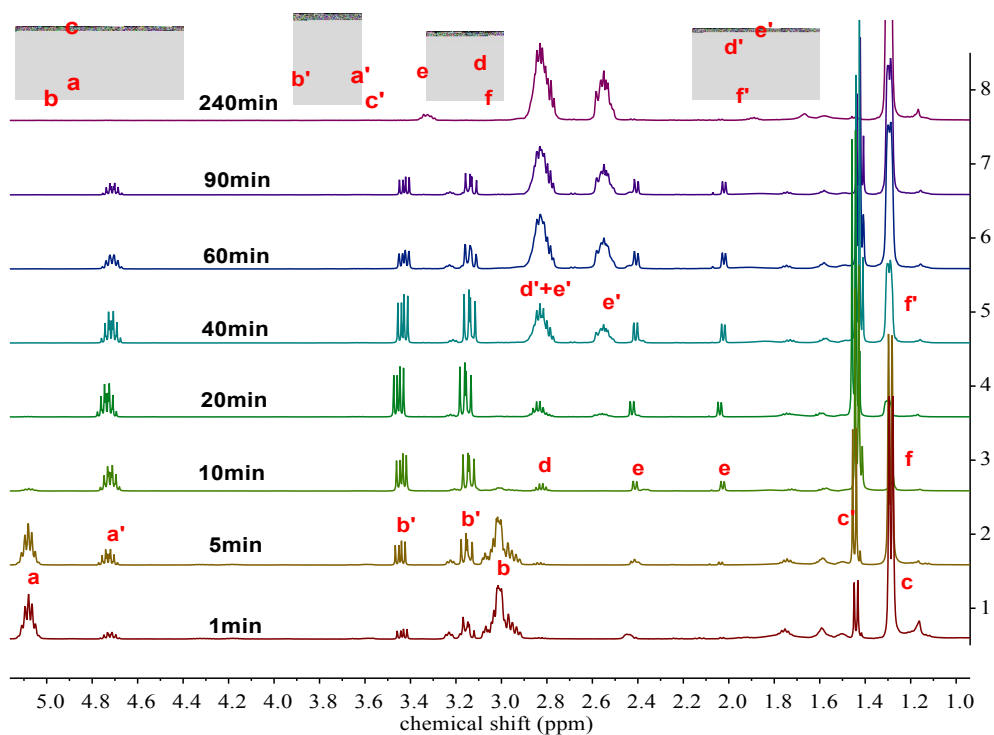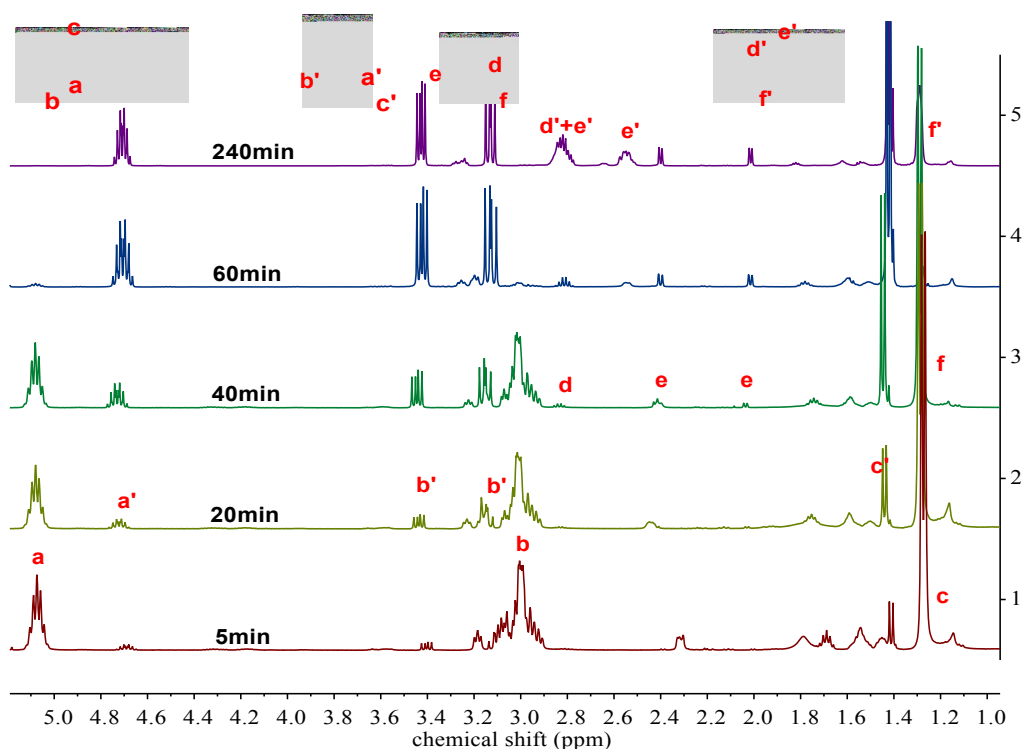**Figure S4.** ^{1}H NMR of the crude products varied with reaction time at 100 °C with PPMTC/DBU=50/1.
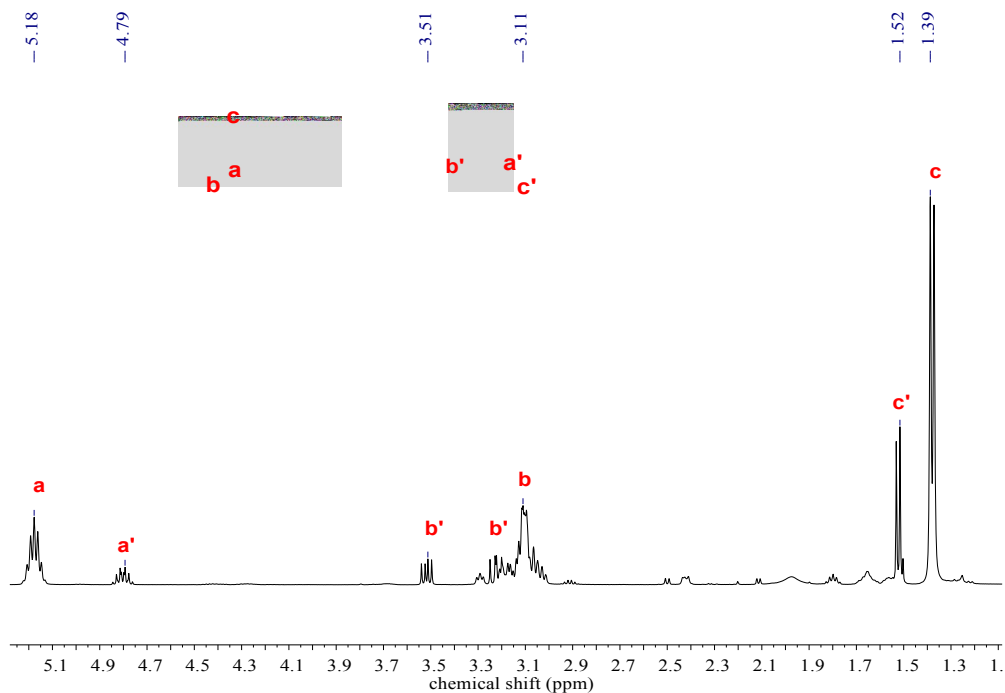
Figure S5. ^{1}H NMR of the crude products of repurposing carboxyl-terminated PPMTC to PPS with DBU at 60 ºC for 4 h.
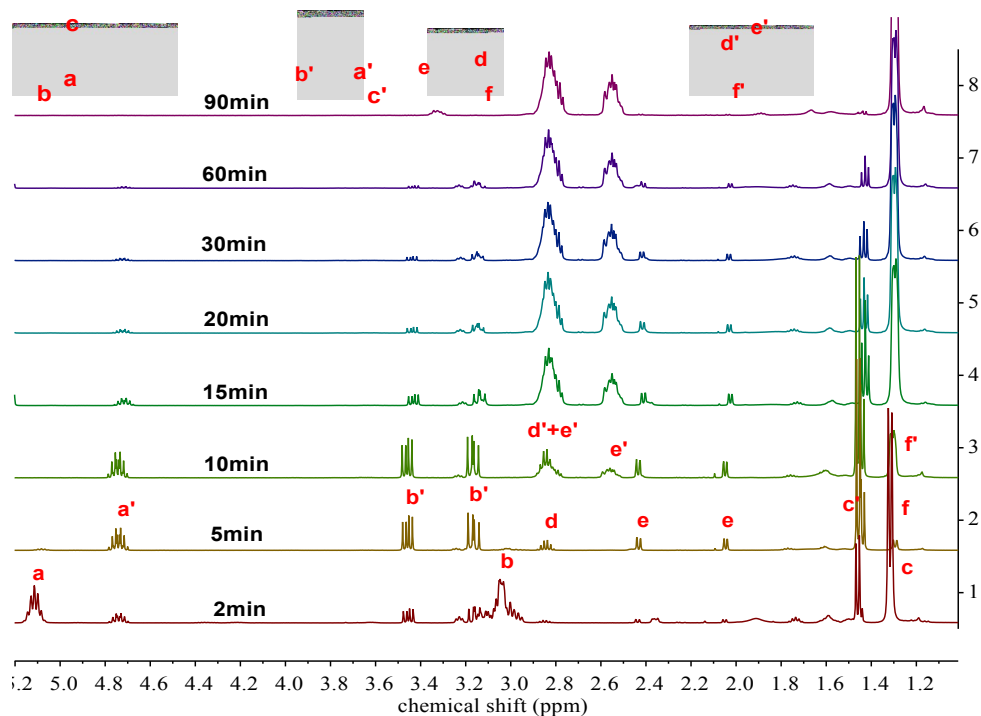
Figure S6. ^{1}H NMR of the crude products varied with reaction time at 80 ºC with PPMTC/DBU=50/1.

Figure S7. ^{1}H NMR of the crude products varied with reaction time at 60 °C with PPMTC/DBU=50/1.

Figure S8. ^{1}H NMR of the crude products varied with reaction time at 25 °C with PPMTC/DBU=50/1.
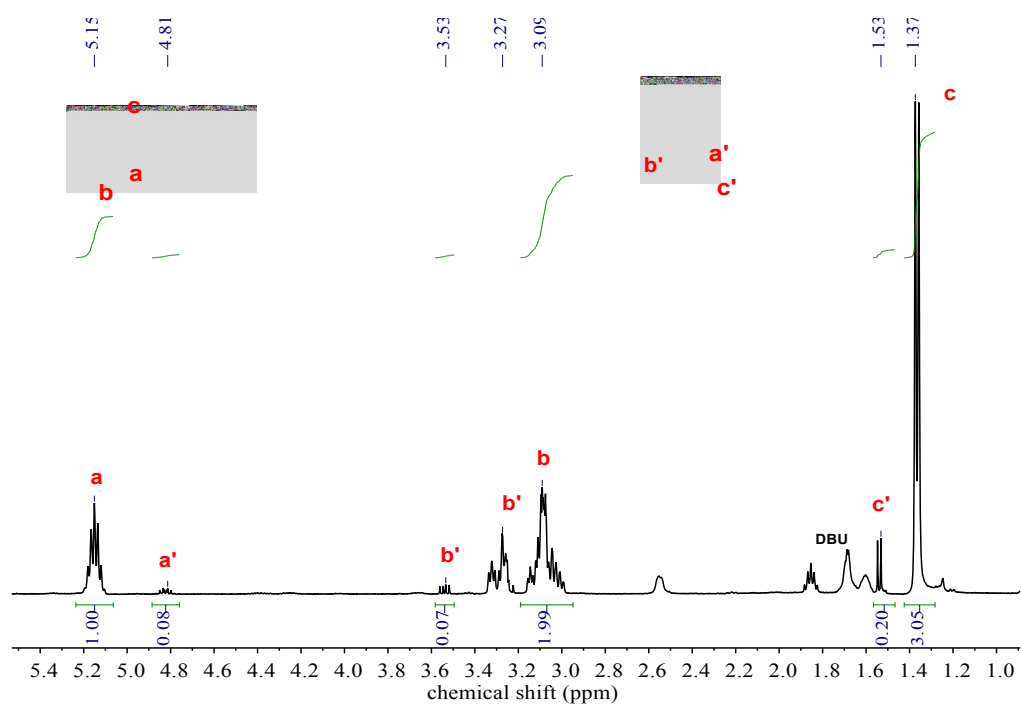
Figure S9. ¹H NMR spectra of the crude product in entry 1, Table S3.
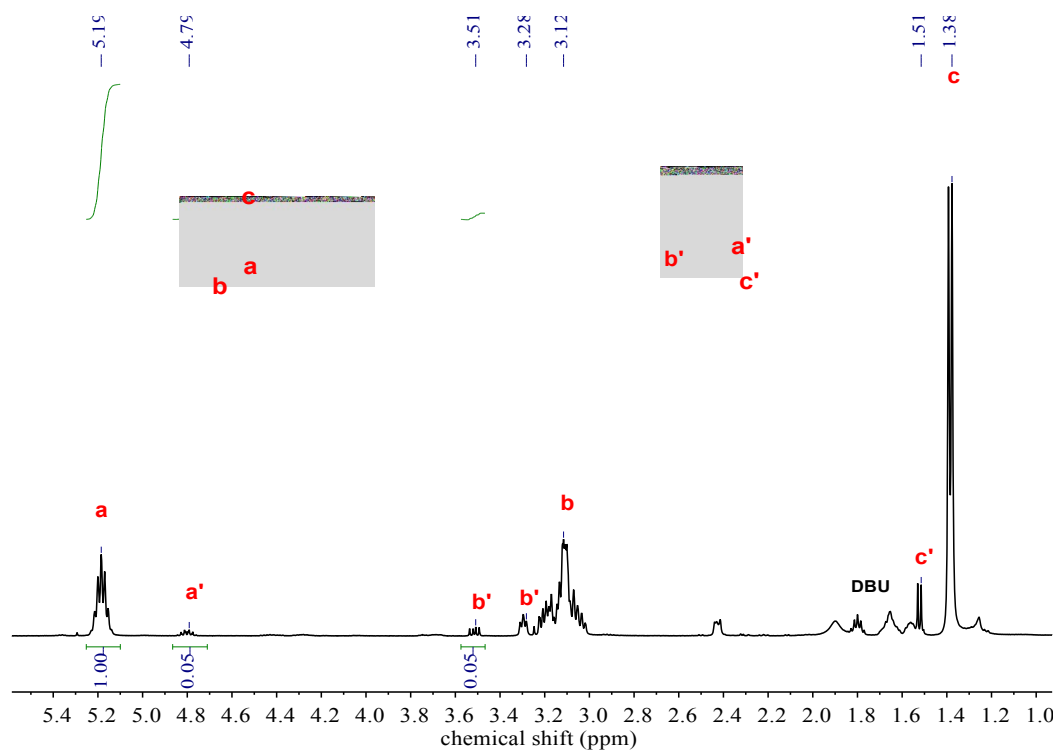
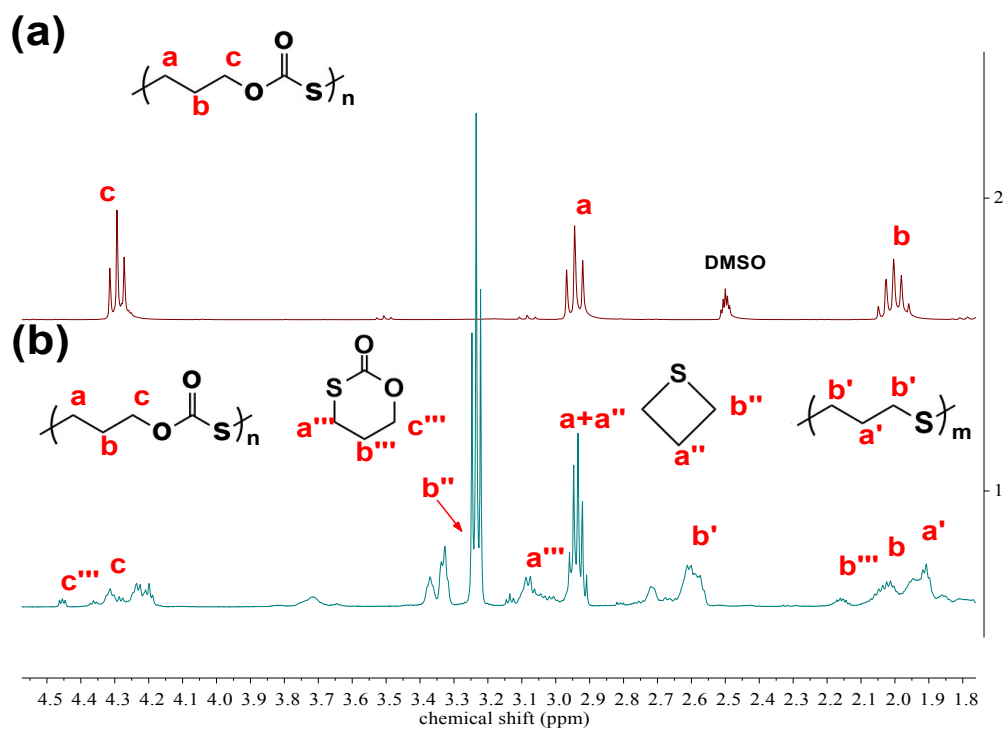**Figure S10.** ¹H NMR spectra of the crude product in entry 2, Table S3.
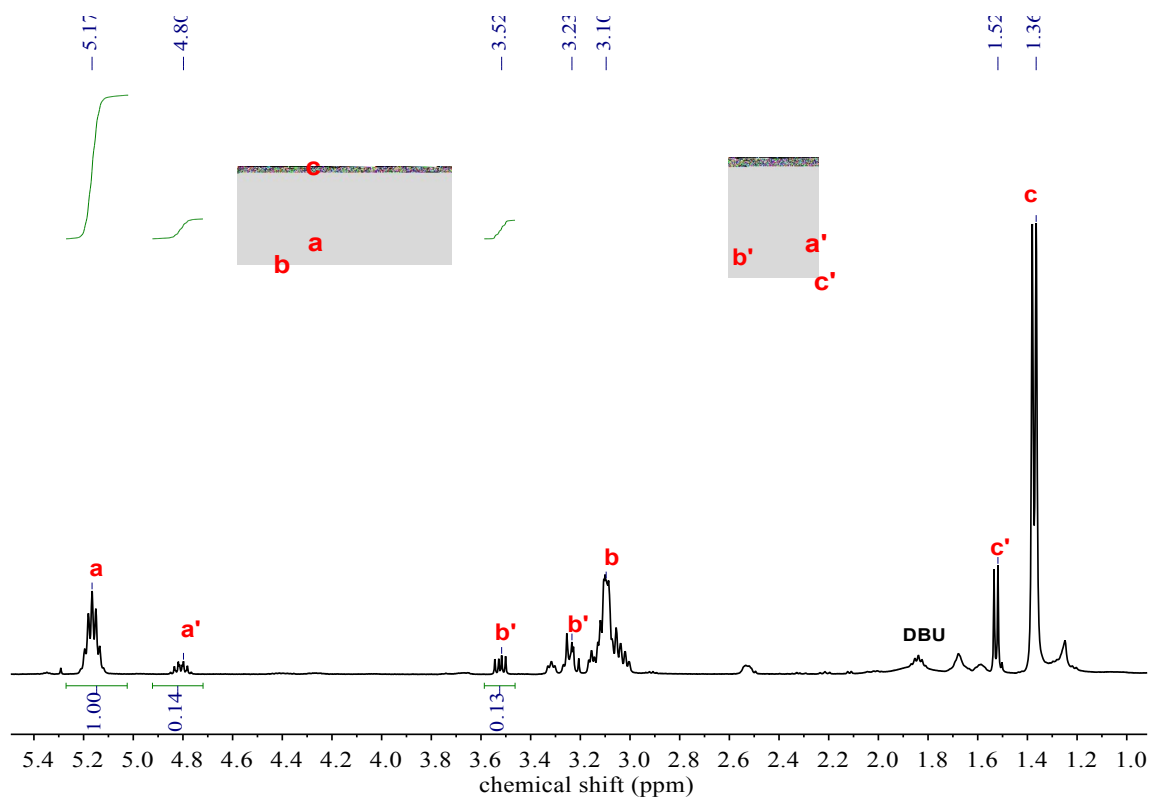
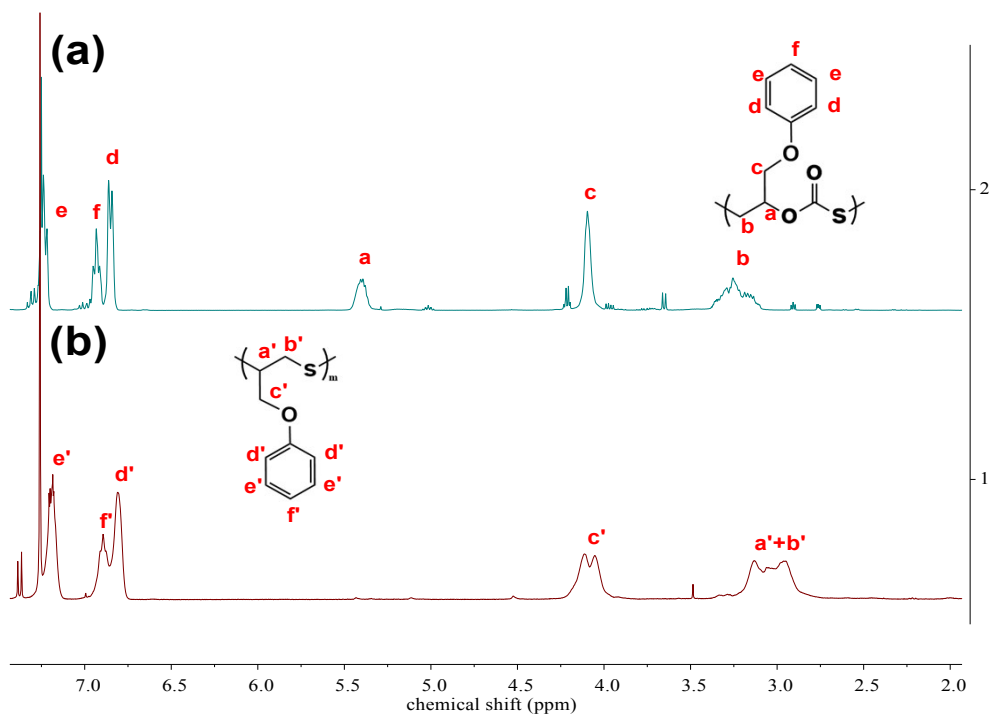**Figure S11.** ^{1}H NMR spectra of the crude product in entry 3, Table S3.

(b)

− 30.82

a
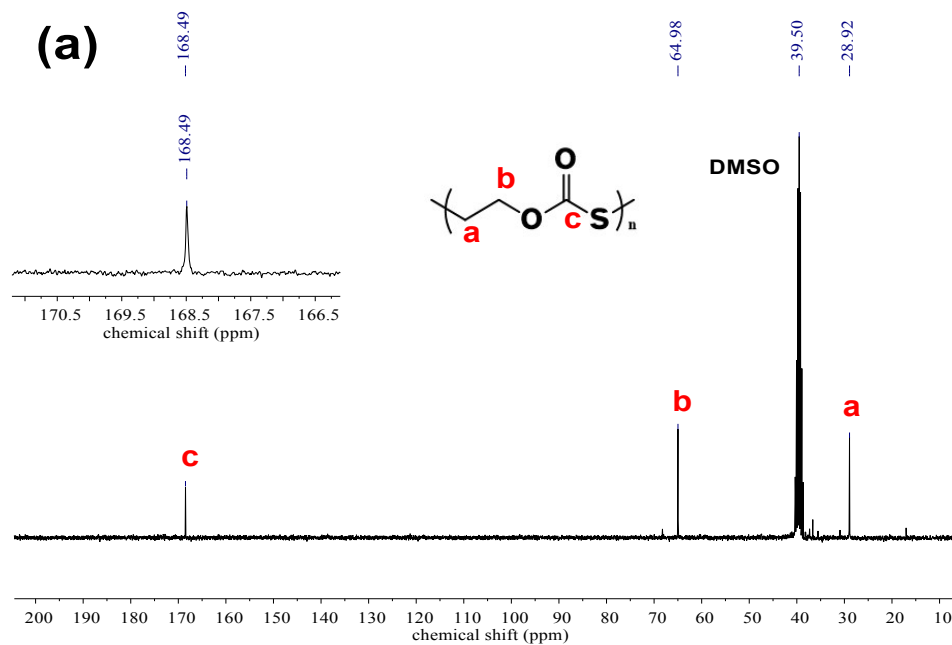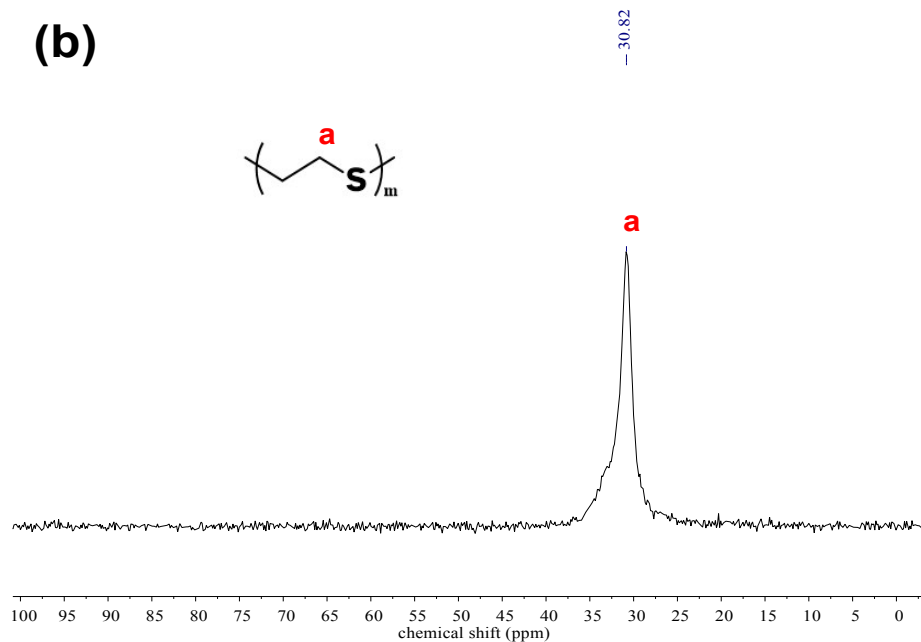
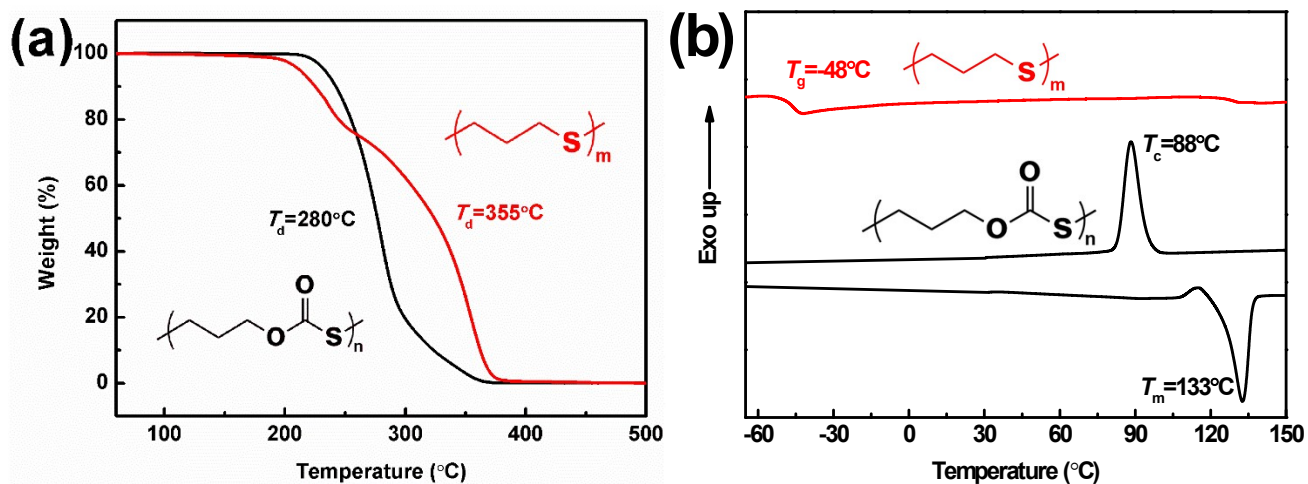**Figure S12.** (a) ^{13}C NMR in $(CD_3)_2SO$ of PEMTC. (b) solid state ^{13}C NMR of PES.

Figure S13. (a) ^{1}H NMR in $(CD_3)_2SO$ of purified poly(trimethylene monothiocarbonate). (b) ^{1}H NMR in CD_3Cl of the crude products in entry 2, Table 2.

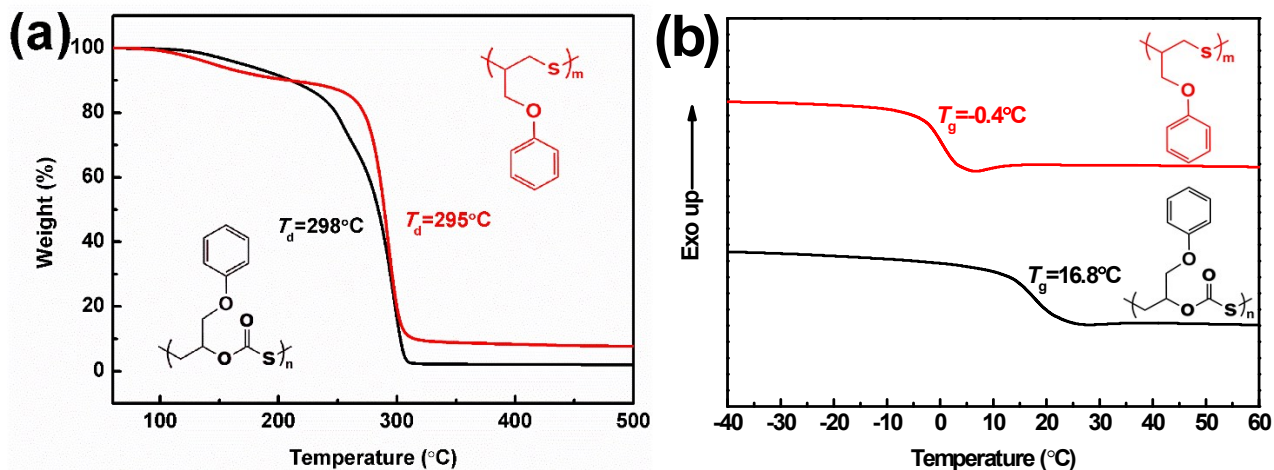**Figure S14.** ¹H NMR of (a) the purified poly(allyloxy benzene monothiocarbonate) and (b) the poly(allyloxy benzene sulfide).
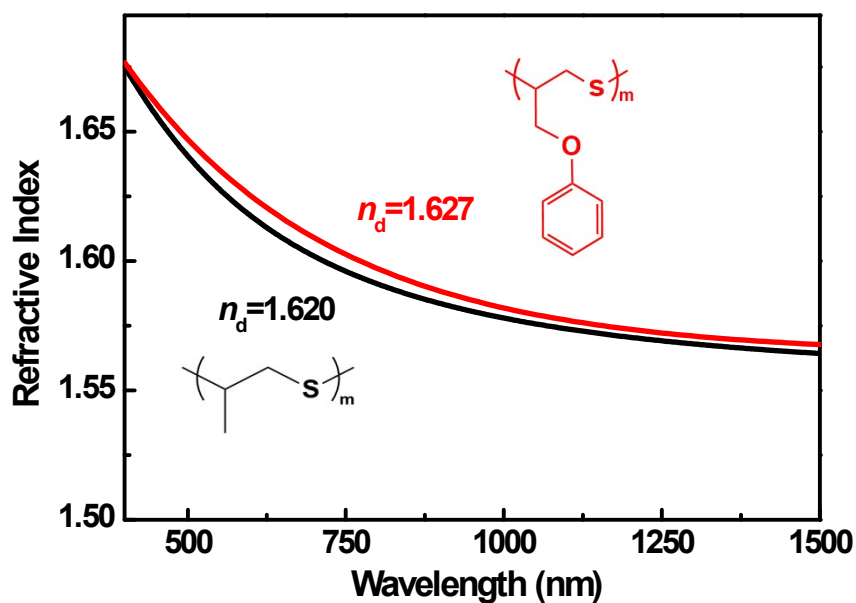
**Properties of PMTCs and Poly(thioether)s**

Figure S15. (a) TGA weight loss curves and (b) DSC curves of the poly(trimethylene monothiocarbonate) and poly(trimethylene sulfide).
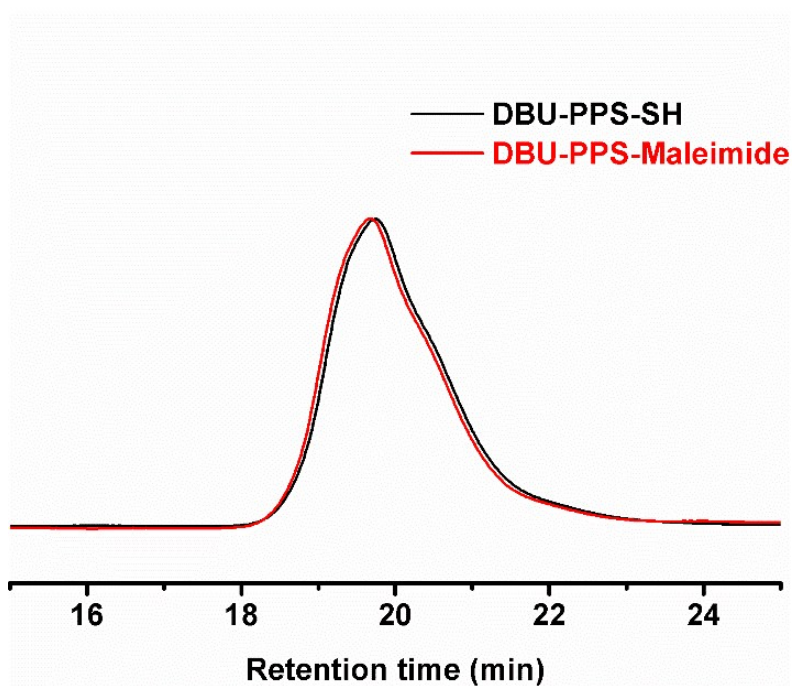
Figure S16. (a) TGA weight loss curves and (b) DSC heating curves of the poly(allyloxy benzene monothiocarbonate) and the poly(allyloxy benzene sulfide).
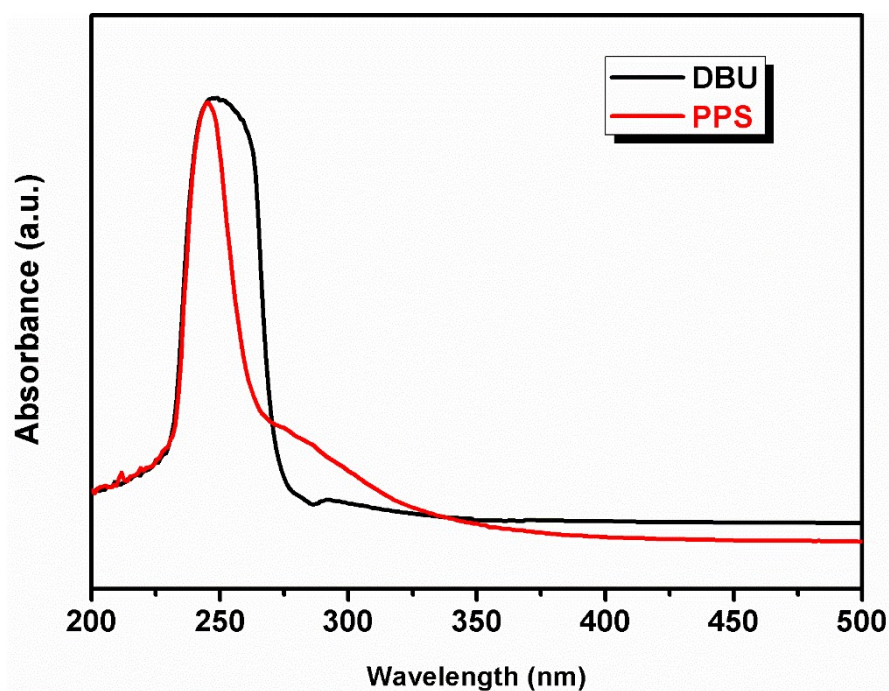

Figure S17. The refractive indices of PPS and poly(allyloxy benzene sulfide).
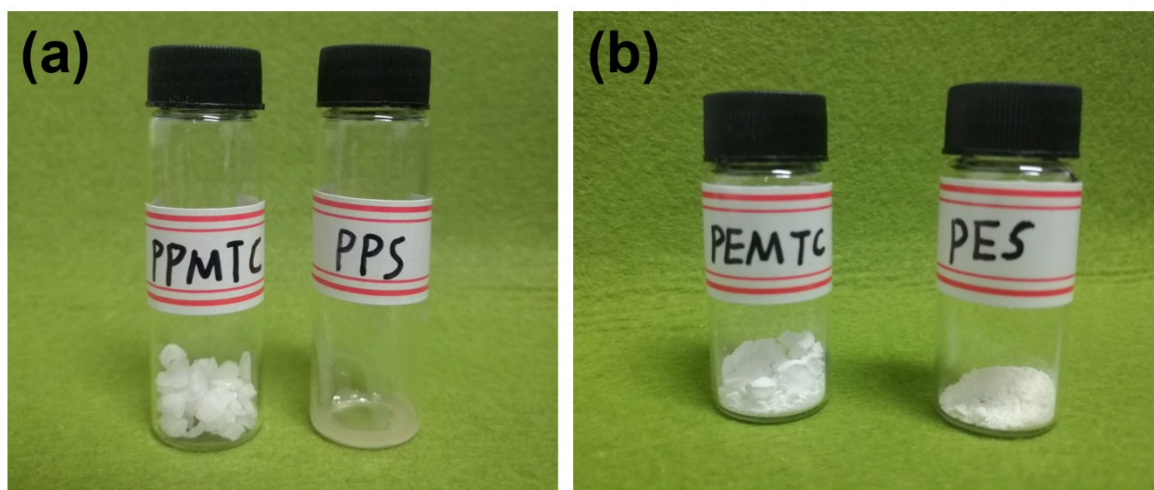
Figure S18. Images of the PPMTC, PPS, PEMTC and PES.

Figure S19. GPC curve of the products capped by maleimide.

Figure S20. UV spectra of the purified PPS.

References

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