Supporting Information

Synthesis of Main Chain Sulfur-Containing Aliphatic Polycarbonates by Organocatalytic Ring-Opening Polymerization of Macrocyclic Carbonates

Bingkun Yan, [a] Jiaqian Hou, [a] Chao Wei, *[a] Yan Xiao, [a] Meidong Lang*[a] and Farong Huang [a]

[a] Key Laboratory of Specially Functional Polymeric Materials and Related Technology of Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai, 200237, China.

* E-mail: mdlang@ecust.edu.cn, weichao107@163.com

Experiment

Materials

The synthesis of MS refers to the previous work.[1] 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)(pKa = 24.3), 1,5,7-triazabicyclo[4.4.0] dec-5-ene (TBD)(pKa = 26.0), 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD)(pKa = 25.5), dodecyl benzene sulphonic acid (DBSA)(pKa = −2.5), Diphenyl phosphate (DPP) (pKa = 2) were purchased from Sigma-Aldrich. The synthesis of thiourea (TU) (pKa =13.2) refers to the work of the predecessor.[2] Polyethylene glycol monomethyl ether (mPEG, M_n = 2000) and Polyethylene glycol (PEG, M_n = 2000) was dried via azeotropic distillation in anhydrous toluene. Dichloromethane (CH_2Cl_2), benzyl alcohol (BnOH) and other organic reagents are all both anhydrous reagents purchased from Aladdin Chemical Reagents Company and used without further purification.

Analytical Techniques.

Relative number-average molecular weight (M_n) and dispersity index ($Đ_M$) of all polymers were measured by Gel Permeation Chromatography (GPC) with a Waters 1515 equipped with *N,N*-dimethylformamide (DMF) as the eluent at a flow rate of 1.0 mL min^{-1} at 50 °C and polymethyl methacrylate (PMMA) as the standard. ^{1}H NMR , ^{13}C NMR, DOSY NMR and quantitative ^{13}C NMR experiments were performed on a Bruker Avance 400 and 600 MHz spectrometer at room temperature using deuterated reagents ($CDCl_3$, CD_2Cl_2) as solvent, and the data were analyzed with MestReNova software. Thermo-gravimetric analysis (TGA) was performed under nitrogen atmosphere on STA409PC apparatus with a heating rate of 10 °C min^{-1}. The glass transition temperature (Tg) of polymers were obtained using TA Instruments DSC Q2000 Differential Scanning Calorimeter at a heating and cooling rate of 10 °C min^{-1} under nitrogen atmosphere. Matrix-Assisted Laser Desorption/Ionization Time of Flight Mass Spectrometry (MALDI-ToF-MS) was performed on an AB/SCiex 4800 plus equipped with an nitrogen laser emitting at 337 nm and 2,5-dihydroxybenzoic acid (DHB) was used as matrices. The spectrum result was recorded in the linear mode. Baseline corrections and data analysis were performed using MassLynx version 4.1 and Polymerix Software, Sierra Analytics, Version 2.0.0.

Ring-opening polymerizations of MS using organic catalysis.

A general polymerization procedure is given as following: BnOH (40.0 µL, 0.02 mmol), MS (118.0mg, 0.4 mmol), TBD (2.8 mg, 0.02 mmol) and CH_2Cl_2 (0.625 mL) were added into a 3 mL vial containing a stir bar at room temperature. The experiment was carried out in a Schlenk Line. After a desired time depending on the experiment settings, the reaction was quenched by drops of small amounts of acetic acid (~20 µL). 30µL of solution was taken and dried for ^{1}H NMR characterization to determine the conversion and for GPC to determine the molecular weight and polydispersity ($Đ_M$), respectively. Monomer conversion was determined by comparing the area integral of the triplet at 4.39 ppm corresponding to -$CH_2SC\underline{H}_2$- (8*H*) of monomer with that of the triplet at 4.30 ppm corresponding to -$CH_2SC\underline{H}_2$- (8*H*) of polymer. The molecular weight (M_n) and DP were obtained by comparing the peak integral ratio at 4.30 ppm or 2.84 ppm of the repeat units of polymers and 5.17 ppm of the initiator BnOH (3.65 ppm of the initiator mPEG-OH or HO-PEG-OH). In addition, the reaction solution was then precipitated in anhydrous diethyl ether and dried in vacuum. Transparent viscous products, named as PS (BnOH-PS), were obtained with a yield about 80 %. The PS with different degree of polymerization (DP) and macroinitiator were carried out according to the same procedure.

Polymerization kinetics experiment.

A general polymerization kinetic procedure is given as following: MS (113.0 mg, 0.38 mmol), BnOH (38.4 µL, 0.019 mmol) and TBD (2.7 mg, 0.019 mmol) were added into a reaction NMR tube, with the designed degree of polymerization (DP) of 20. Then, 0.6 mL CD_2Cl_2 was added to initiate the polymerization and the NMR tube was transferred to the Bruker Avance 600 MHz at room temperature to analyze chemical shifts of the protons at a determined time intervals. The ^{1}H NMR spectra were obtained and used to calculate the conversion of MS through comparing the area integral of monomer (4.39 ppm) to that of polymer (4.30 ppm).

TBD catalytic mechanism study.

1:1 Mixtures of TBD with Benzyl Alcohol (initiator): 5.0 mg (0.036 mmol) TBD, 3.9 mg (0.036 mmol) BnOH and 0.6 mL CD_2Cl_2 were respectively added into a NMR tube and analyzed by ^{1}H NMR after 3 h of the reaction.

1:1 Mixtures of TBD with monomer: 5.0 mg (0.036 mmol) TBD, 10.7mg (0.036 mmol) MS and 0.6 mL CD_2Cl_2 were added into a NMR tube and analyzed by ^{1}H NMR after 3 h of the reaction.

MTBD catalytic mechanism study.

1:1 Mixtures of MTBD with Benzyl Alcohol (initiator): 5.0 mg (0.033 mmol) MTBD, 3.5 mg (0.033 mmol) BnOH and 0.6 mL CD_2Cl_2 were respectively added into a NMR tube and analyzed by ^{1}H NMR after 3 h of the reaction.

1:1 Mixtures of MTBD with monomer: 5.0 mg (0.033 mmol) MTBD, 9.7mg (0.033 mmol) MS and 0.6 mL CD_2Cl_2 were added into a NMR tube and analyzed by ^{1}H NMR after 3 h of the reaction.

Chain extension experiment

BnOH (80.0 μL, 0.04 mmol), MS (118.0mg, 0.4 mmol), TBD (2.8 mg, 0.02 mmol) and CH_2Cl_2 (0.625 mL) were added into a 3 mL vial containing a stir bar at room temperature. After reaction 2 h, ~30 μL of the solution was taken from the reaction for GPC and ^{1}H NMR testing. Then BnOH (80.0 μL, 0.02 mmol), MS (118.0mg, 0.4 mmol), and CH_2Cl_2 (0.625 mL) were added into the reaction under an argon atmosphere. After continuing to react for 3 h, ~30 μL of the solution was taken from the reaction for GPC and ^{1}H NMR testing. Same as the previous steps, the same procedure was conducted once more. BnOH (80.0 µL, 0.02 mmol), MS (118.0mg, 0.4 mmol), and CH_2Cl_2 (0.625 mL) were added into the reaction under an argon atmosphere. After continuing to react for 3 h, ~30 µL of the solution was taken from the reaction for GPC and ^{1}H NMR testing.

The copolymerization of MS with TBD.

A general polymerization procedure is given as following: MS (118.0 mg, 0.4 mmol), TMC (40.8 mg, 0.4 mmol), BnOH (40.0 µL, 0.02 mmol), TBD (5.6 mg, 0.04 mmol), and CH_2Cl_2 (1.25 mL) were added into a 3 mL vial containing a stir bar. The reaction mixture was stirred at room temperature. After 3 h, the reaction was terminated with acetic acid (~10 µL) and precipitated in anhydrous ether (~15 mL) to form transparent viscous products. The obtained products without any treatment were characterized with NMR and GPC instrument. The copolymerization of MS and TMC with TBD in different degree of polymerization (DP) were carried out according to the same procedure.

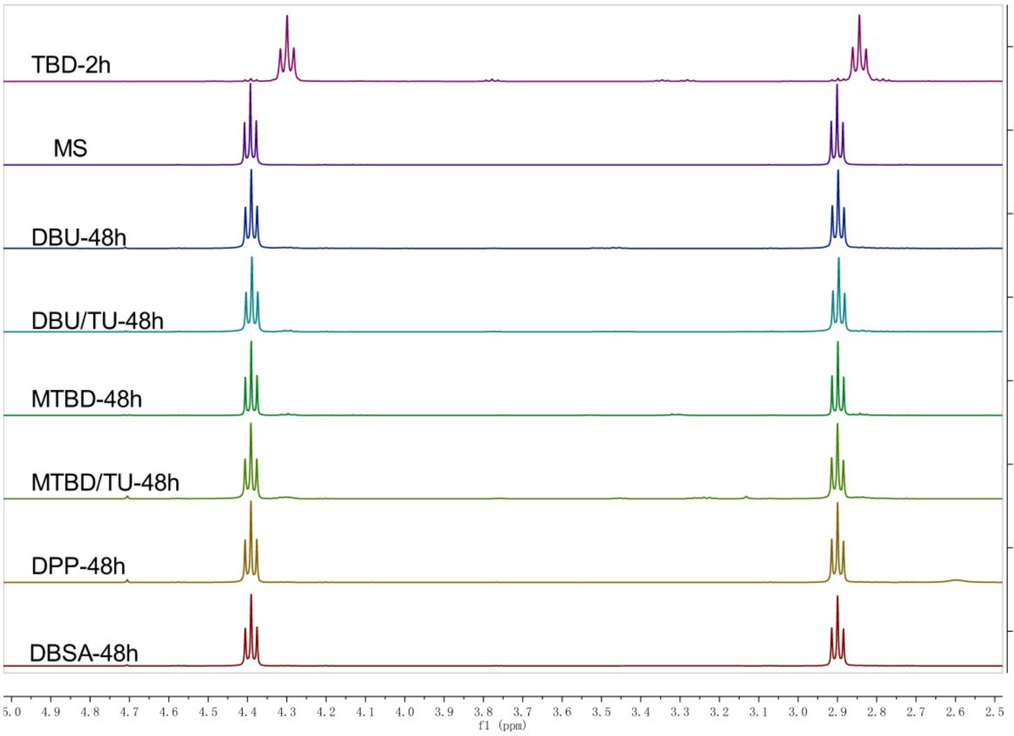

Fig. S1 The ^{1}H NMR spectra of ROP using different organocatalysts.

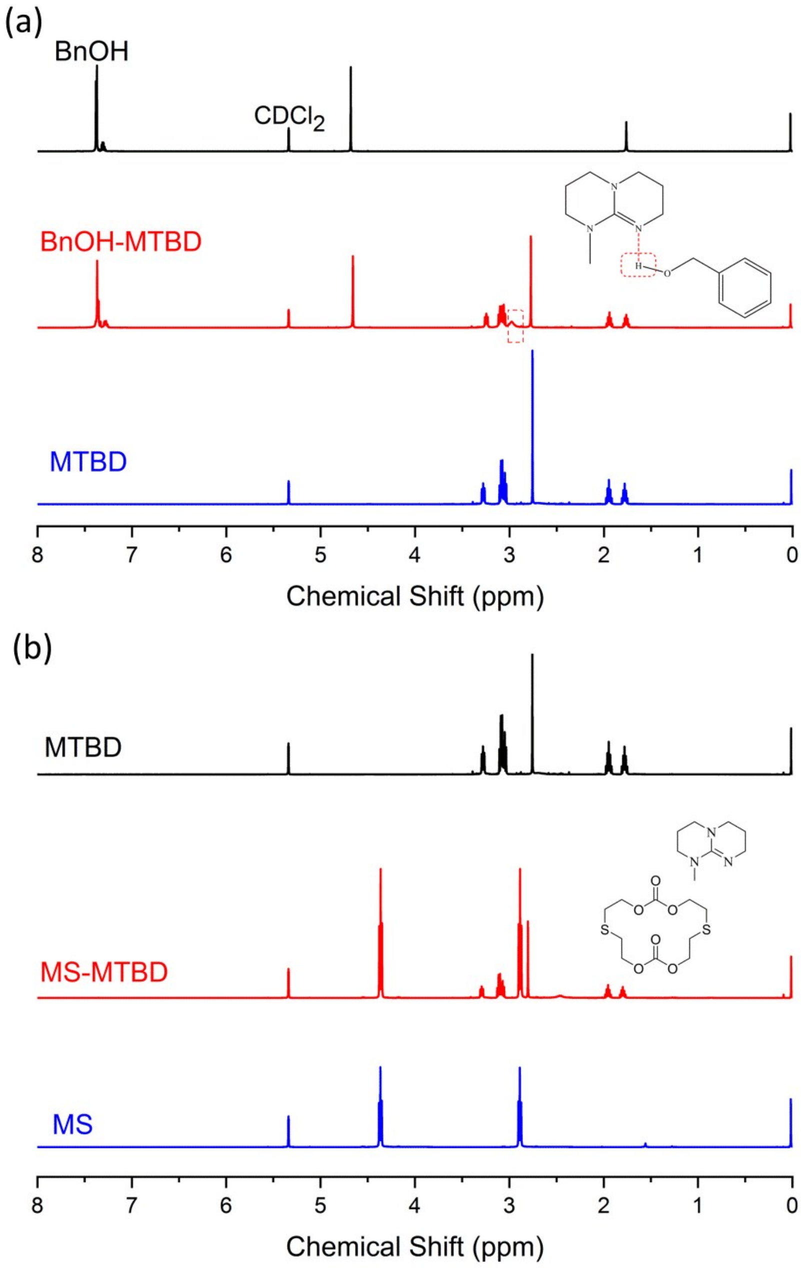

Fig. S2 (a) ^{1}H NMR spectra (Dichloromethane-d_2 25 ^{o}C) of MTBD, BnOH, and the mixture of MTBD and BnOH, the chemical shift of active hydrogen changed, which indicated that MTBD indeed activated initiator. (B) ^{1}H NMR spectra of (Dichloromethane-d_2 25 ^{o}C) MTBD, MS, and the mixture of MTBD and MS, the chemical shift not changed, which indicated that MTBD indeed cannot activated monomer.

Table S1 Result of ROP using thiourea catalysts.

Entry[a]	cat. (C)	[M]:[I]:[C][b]	[M]	solvent	time/h	conv. (%)[c]
1	DBU/TU	20:1:1/1	0.64	CH_2Cl_2	48	0
2	DBU/TU	20:1:1/3	0.64	CH_2Cl_2	48	0
3	DBU/TU	20:1:1/5	0.64	CH_2Cl_2	48	0
4	MTBD/TU	20:1:1/1	0.64	CH_2Cl_2	48	0
5	MTBD/TU	20:1:1/3	0.64	CH_2Cl_2	48	0
6	MTBD/TU	20:1:1/5	0.64	CH_2Cl_2	48	0

[a] All reactions were conducted with benzyl alcohol as the initiator at the specified initial monomer concentration in room temperature [b] [Monomer]:[initiator]:[catalyst], monomer to initiator (catalyst) ratio. [c] As determined by ^{1}H NMR spectroscopy.

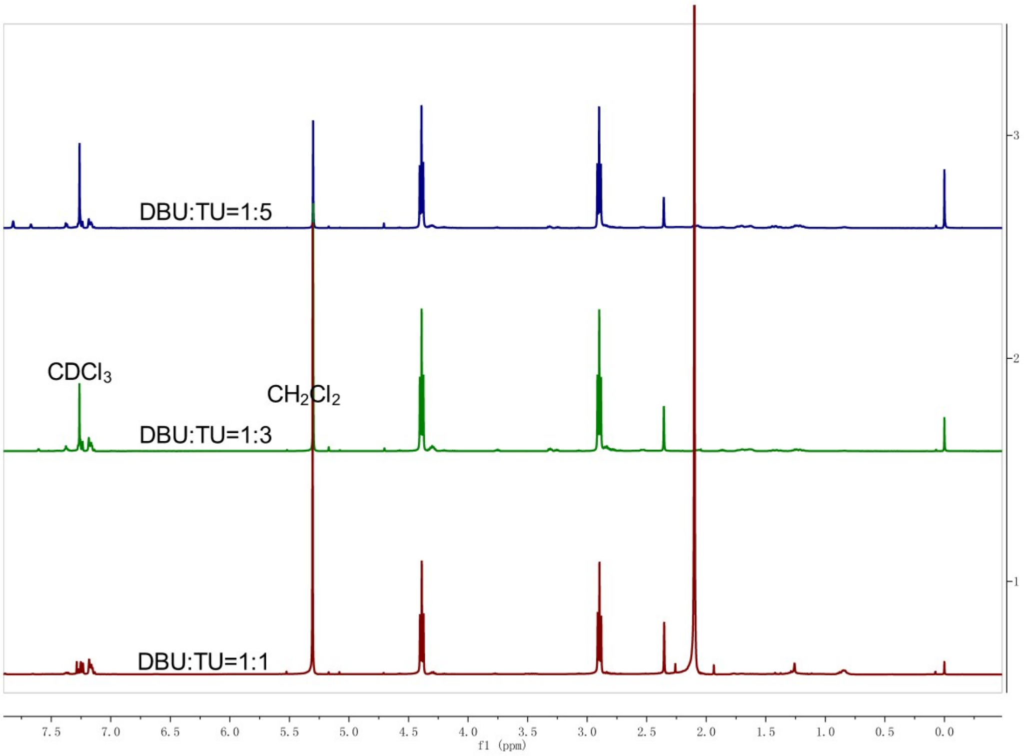

Fig. S3 The ^{1}H NMR spectra of ROP using different ratios DBU/TU.

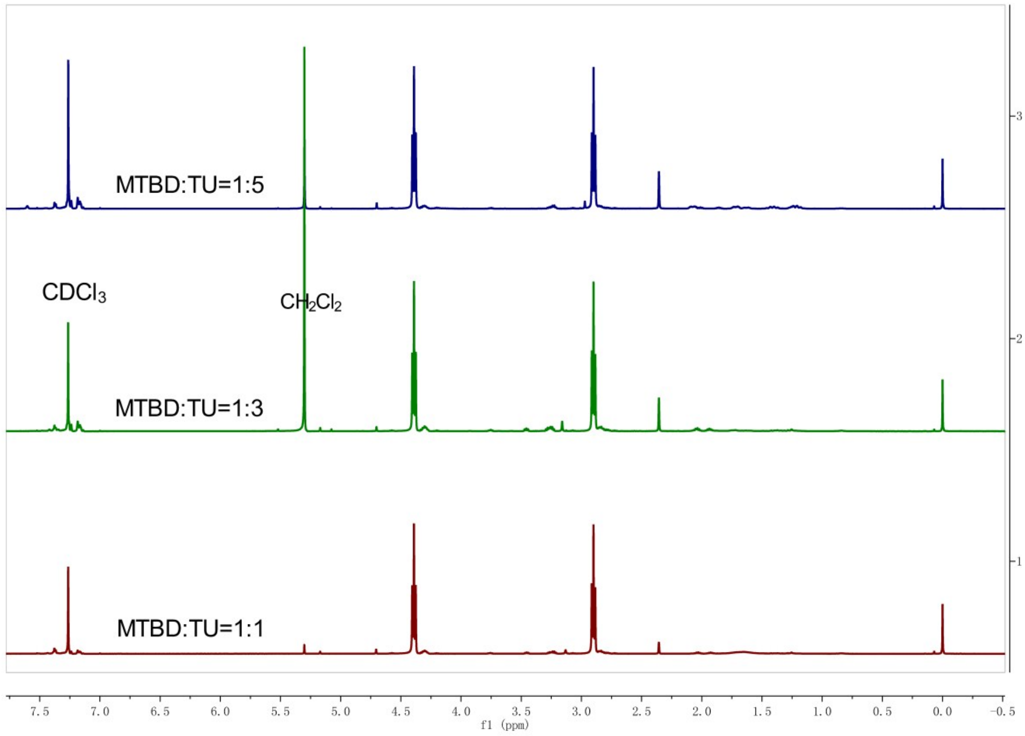

Fig. S4 The ^{1}H NMR spectra of ROP using different ratios MTBD/TU.

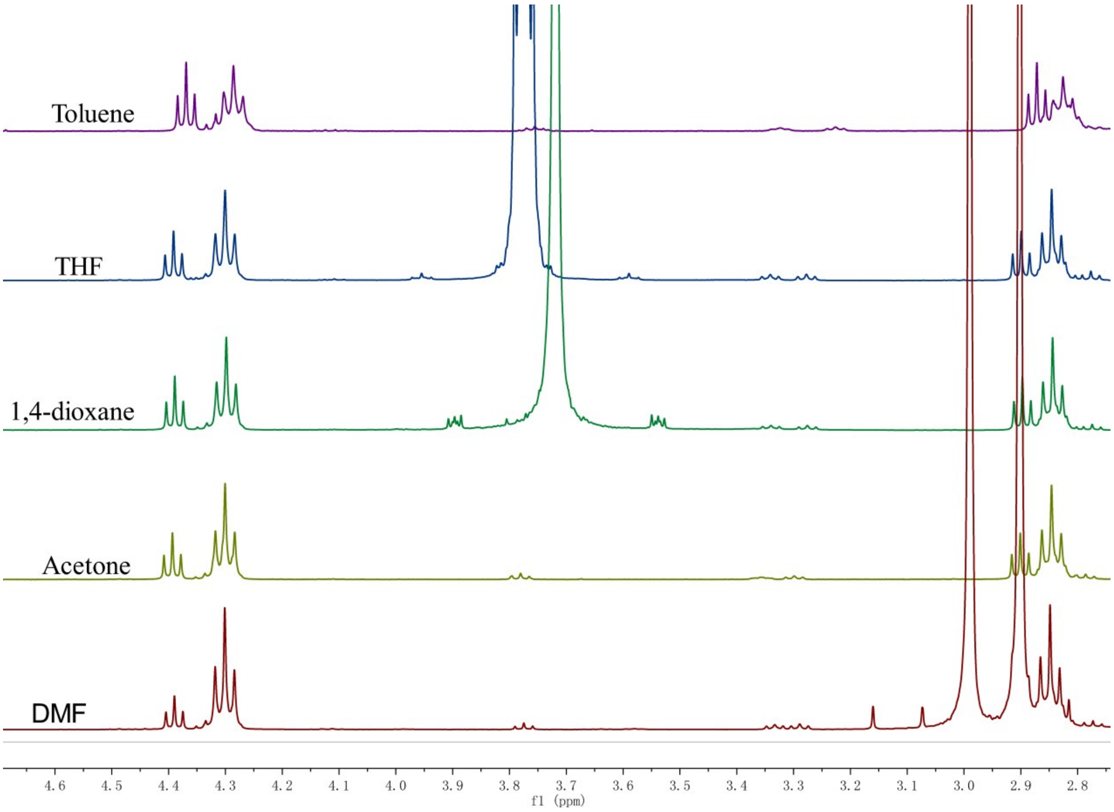

Fig. S5 The ^{1}H NMR spectra of ROP in different solutions using TBD as organocatalysts.

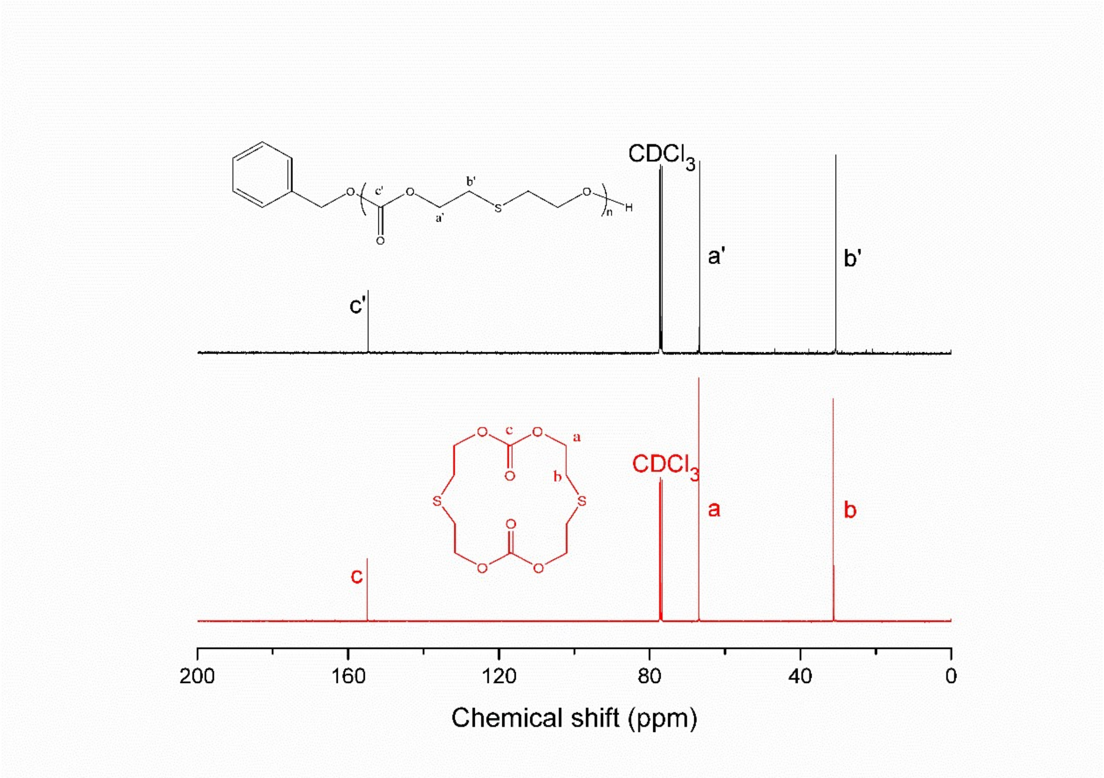

Fig. S6 The ^{13}C NMR spectra of MS and BnOH-PS.

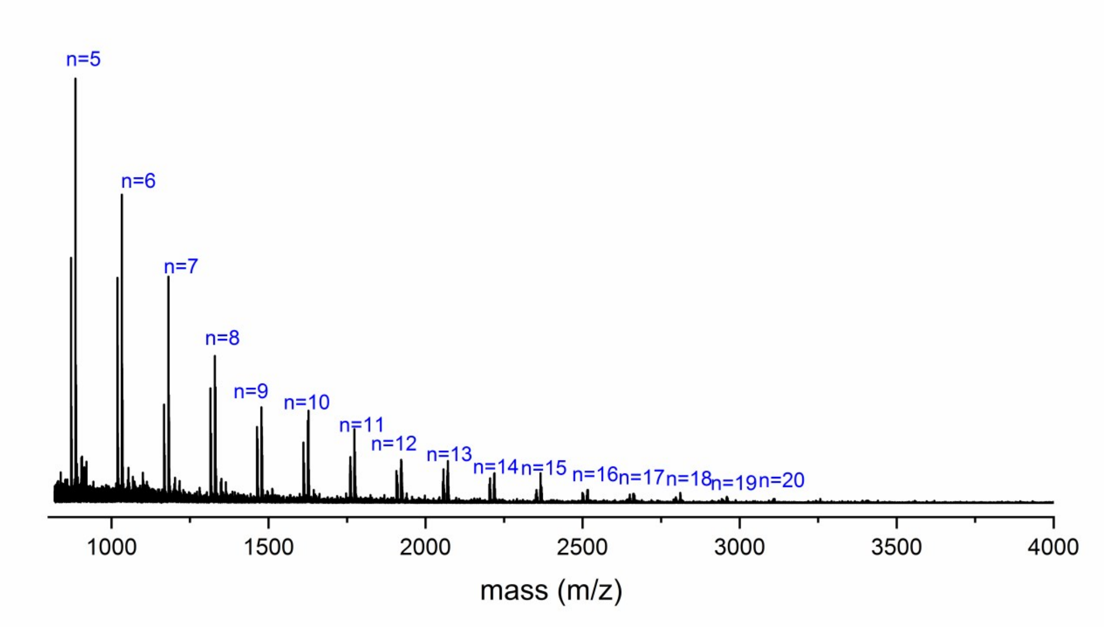

Fig. S7 The complete MALDI-ToF-MS of the BnOH-PS.

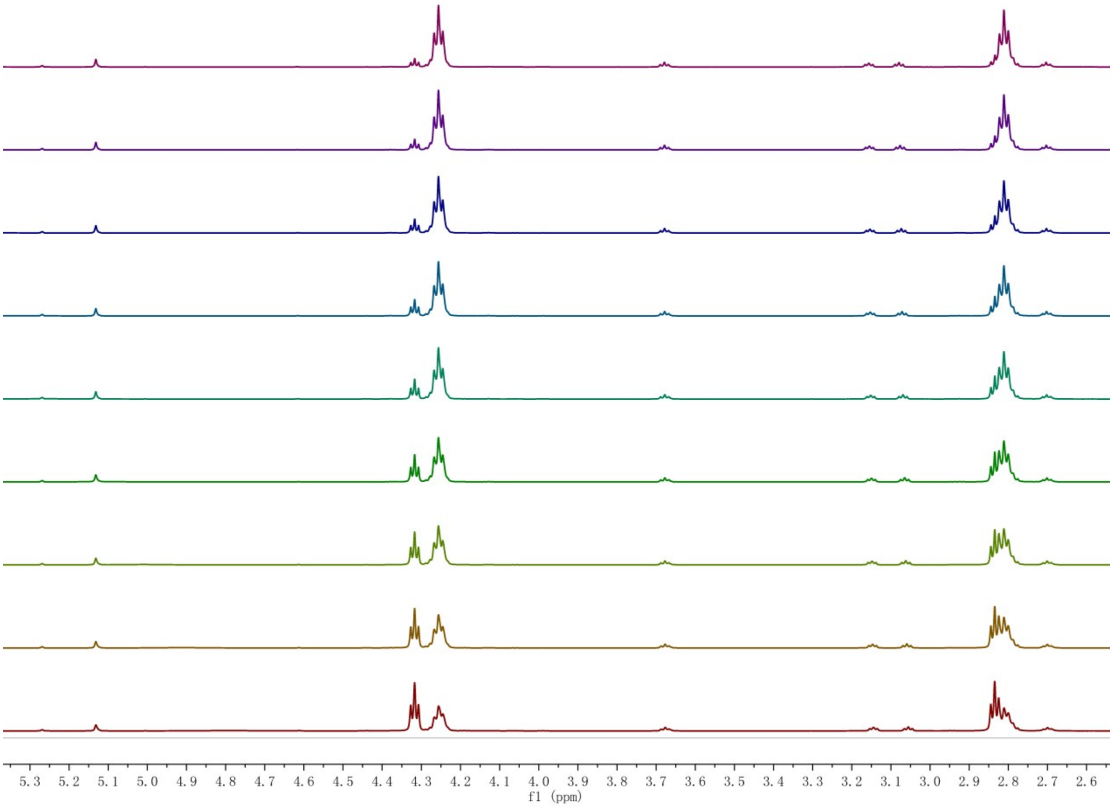

Fig. S8 The ^{1}H NMR spectra detection of TBD catalytic MS in ROP kinetics (BnOH-PS10).

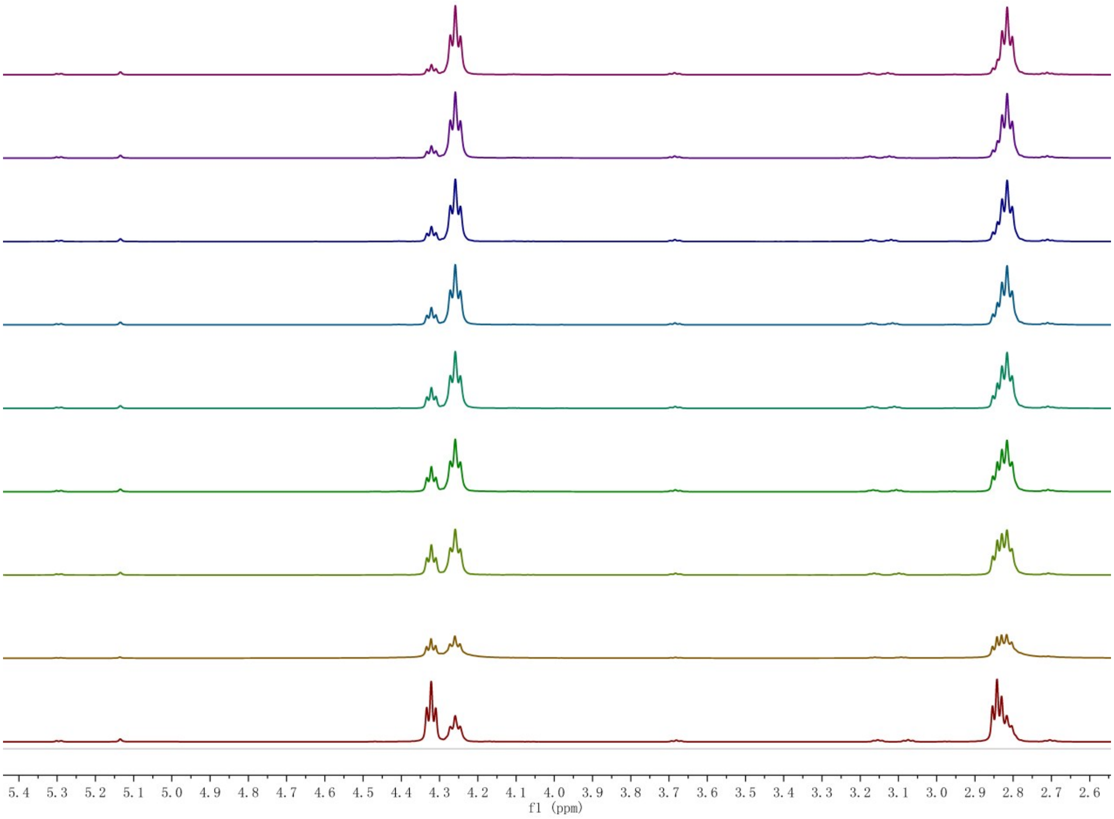

Fig. S9 The ^{1}H NMR spectra detection of TBD catalytic MS in ROP kinetics (BnOH-

PS20).

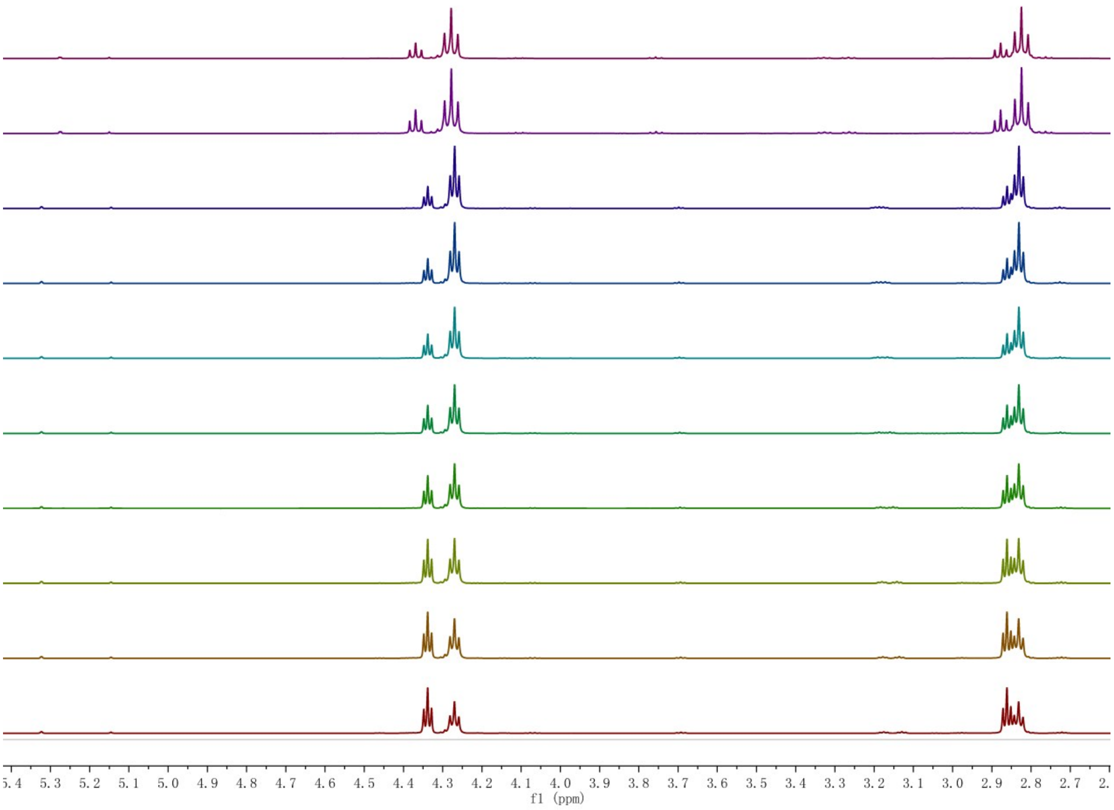

Fig. S10 The ^{1}H NMR spectra detection of TBD catalytic MS in ROP kinetics (BnOH-PS50).

Table S2 Results of ROP through adding monomers step by step.

Entry^a	[M]^b	time/h	conv. (%)^c	$M_n{}^d$ (KDa)	$M_{n\,\mathrm{NMR}}{}^c$ (KDa)	$M_{n\,\mathrm{GPC}}{}^e$ (KDa)	$Đ_M{}^e$
1	10eq.MS	2	98	3.1	3.0	6.6	1.28
2	Entry1+10eq.MS	3	96	6.1	5.8	8.7	1.23
3	Entry2+10eq.MS	3	93	9.1	8.4	9.8	1.22

^{a} All reactions were reacted using BnOH as initiator TBD as catalyst at R.T. with the specified initial monomer concentration $[M]_0$ =0.64 M. ^{b} Add 10 equivalent MS at regular intervals. ^{c} Molecular weight (kDa) determined by ^{1}H NMR spectroscopy. ^{d} Molecular weight (kDa) calculated by the feed ratios. ^{e} Determined in DMF by PMMA calibrated GPC.

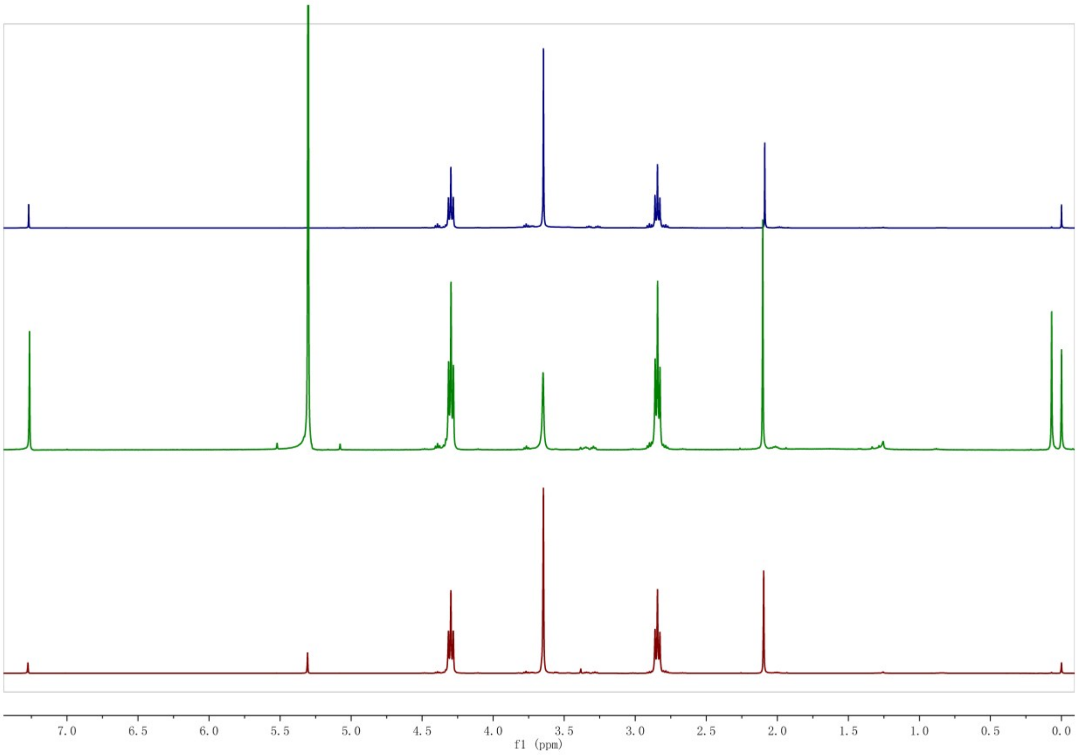

Fig. S11 The ^{1}H NMR spectra of mPEG-*b*-PS20 (down), mPEG-*b*-PS50 (middle), PEG-*b*-PS20 (up).

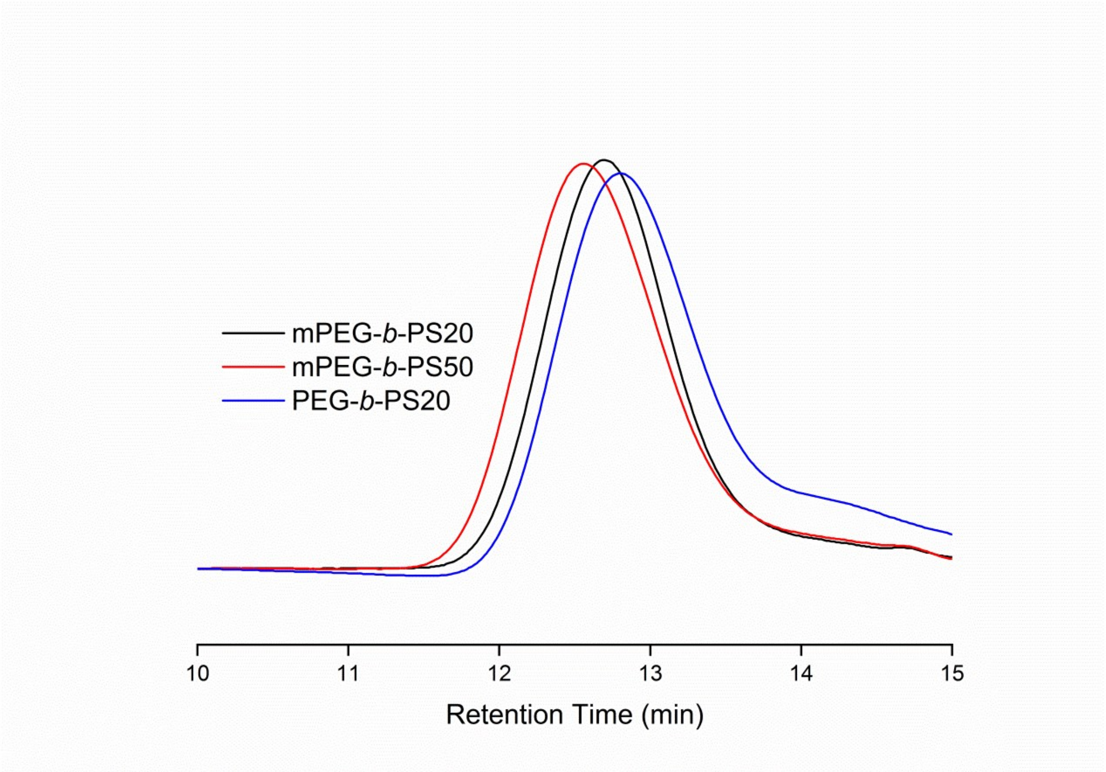

Fig. S12 The GPC crave of thioether polymer using PEG or mPEG as initiator.

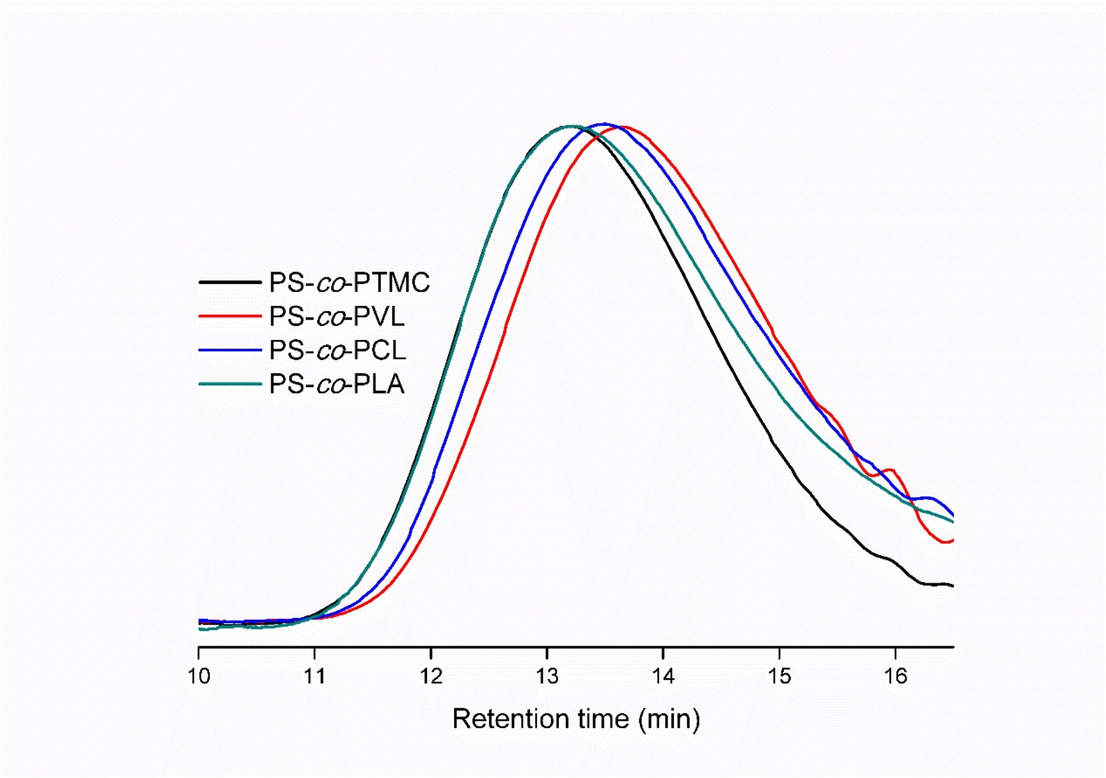

Fig. S13 The GPC curve of main chain thioether polymers.

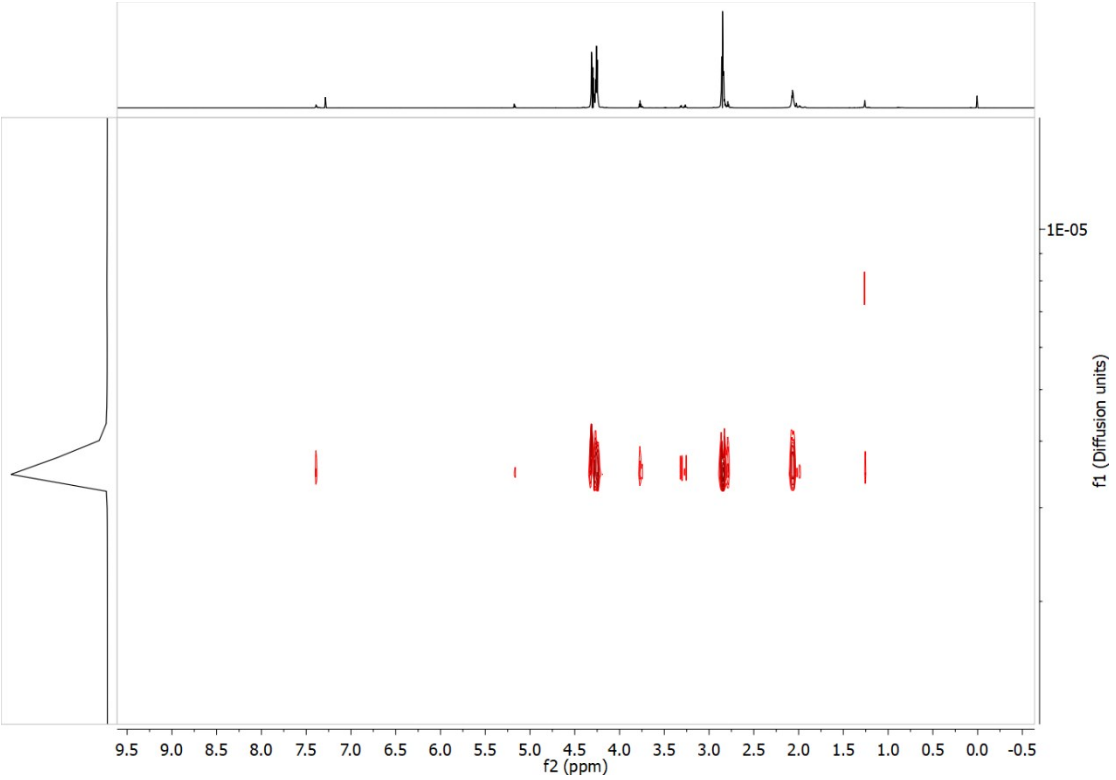

Fig. S14 Typical DOSY NMR spectra of PS-*co*-PTMC ($CDCl_3$).

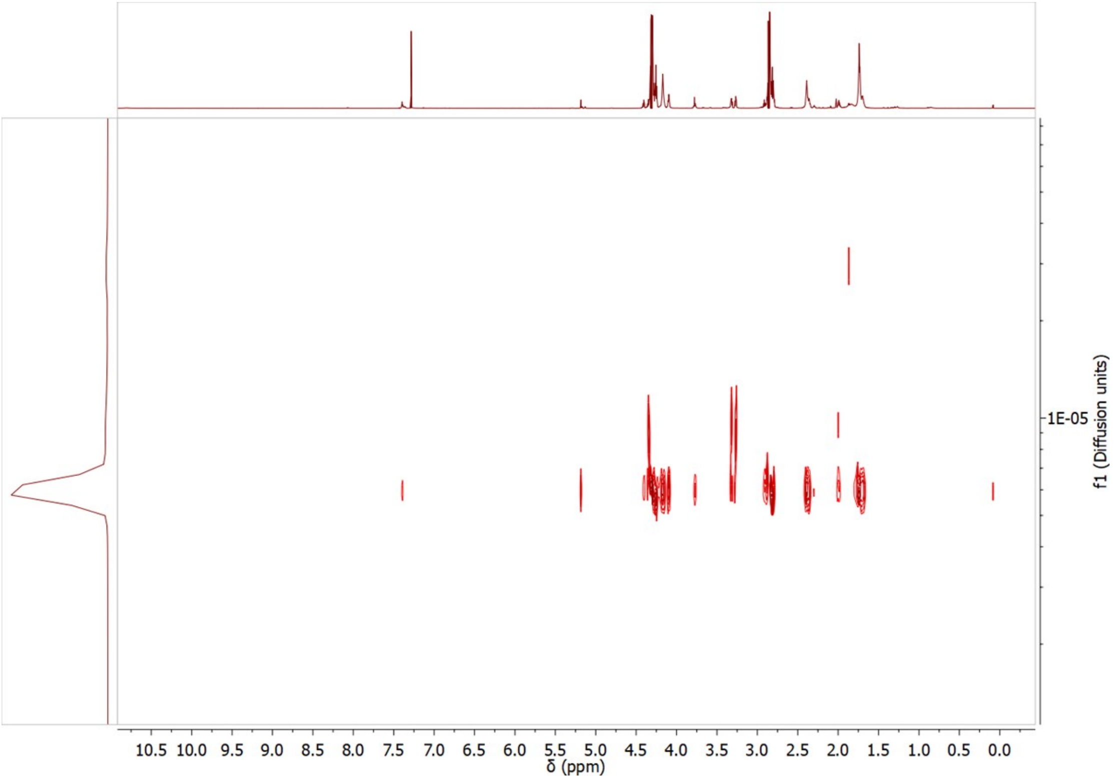

Fig. S15 Typical DOSY NMR spectra of PS-*co*-PVL ($CDCl_3$).

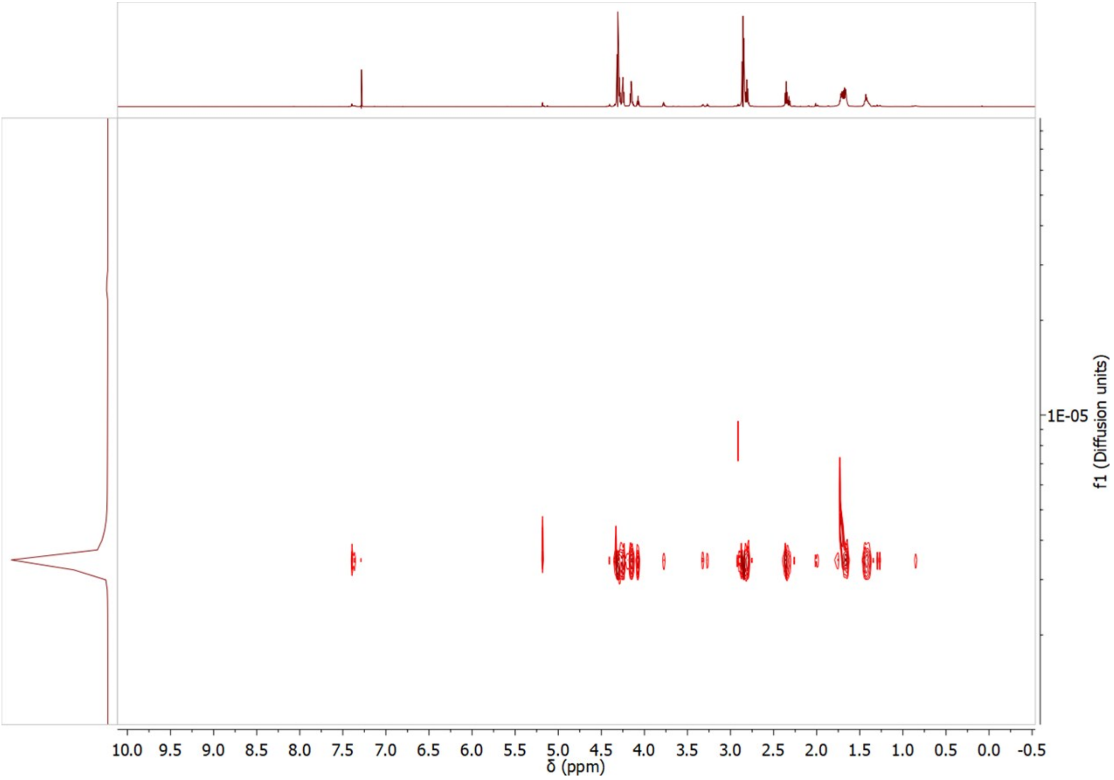

Fig. S16 Typical DOSY NMR spectra of PS-*co*-PCL ($CDCl_3$).

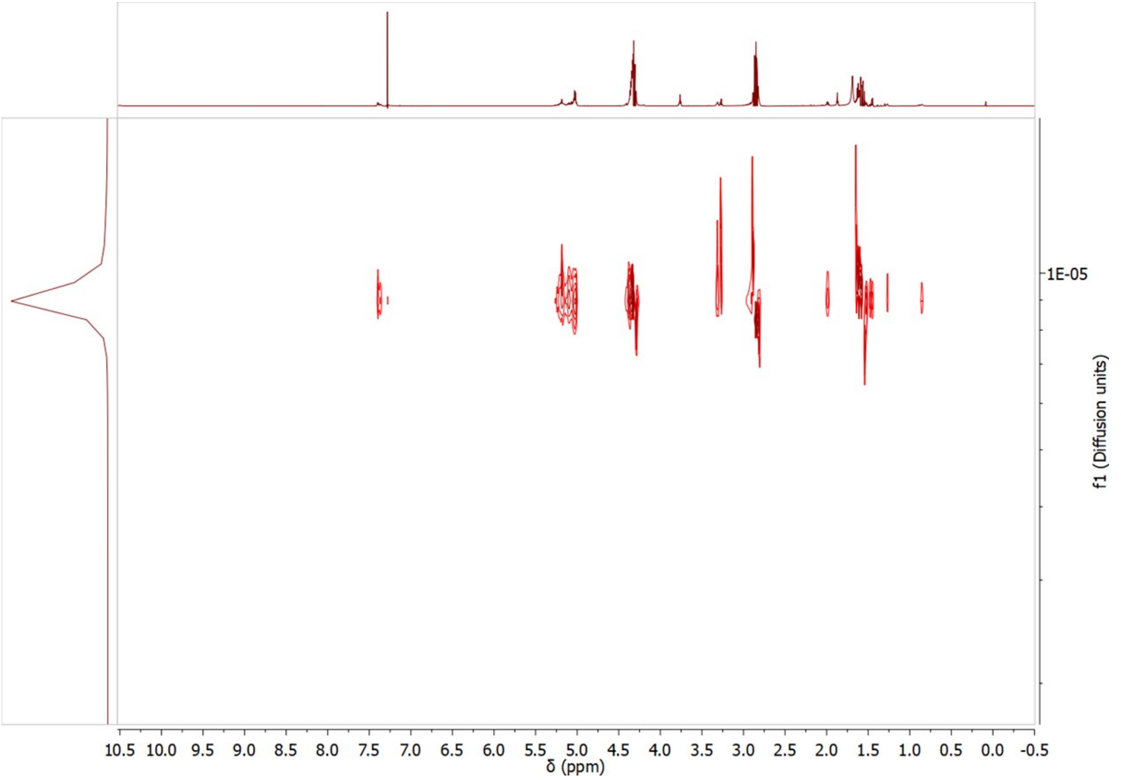

Fig. S17 Typical DOSY NMR spectra of PS-*co*-PLA ($CDCl_3$).

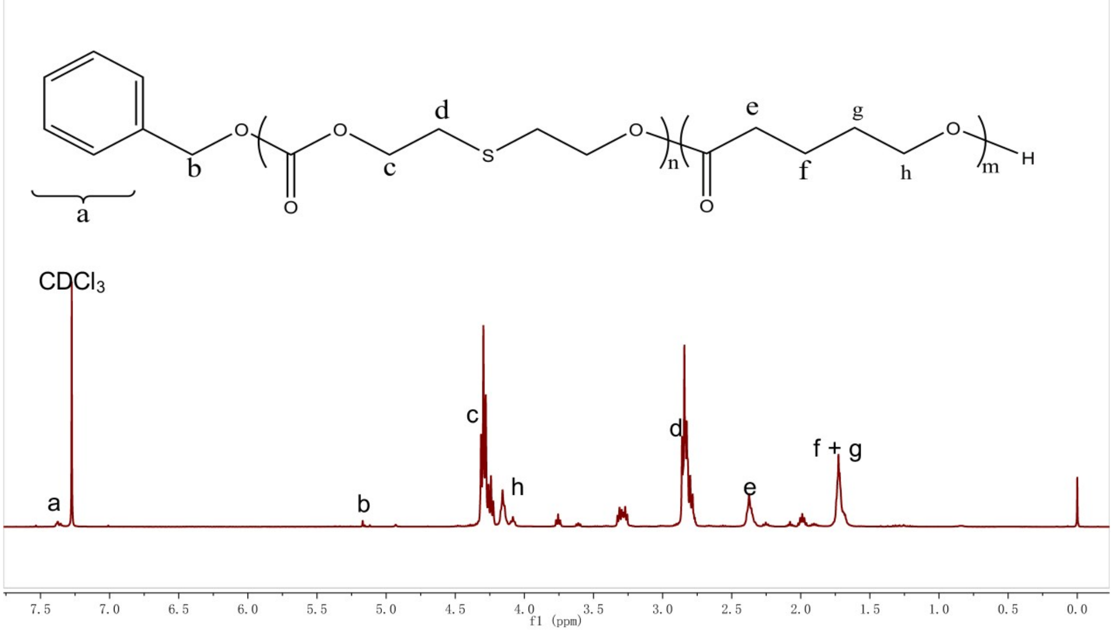

Fig. S18 The ^{1}H NMR spectra of PS-*co*-PVL.

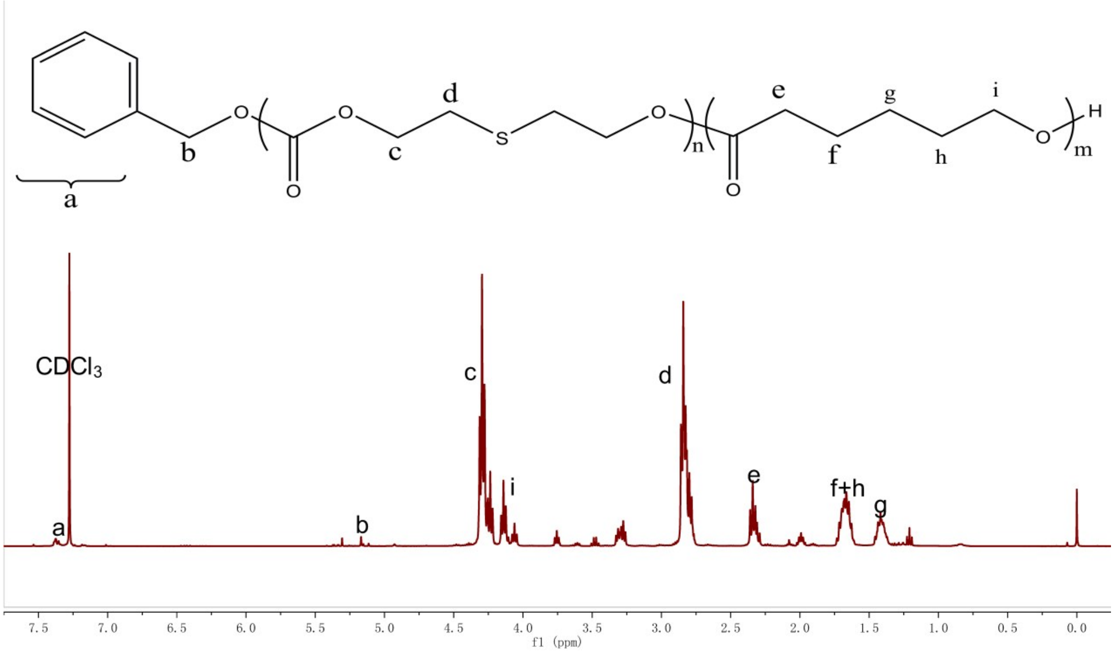

Fig. S19 The ^{1}H NMR spectra of PS-*co*-PCL.

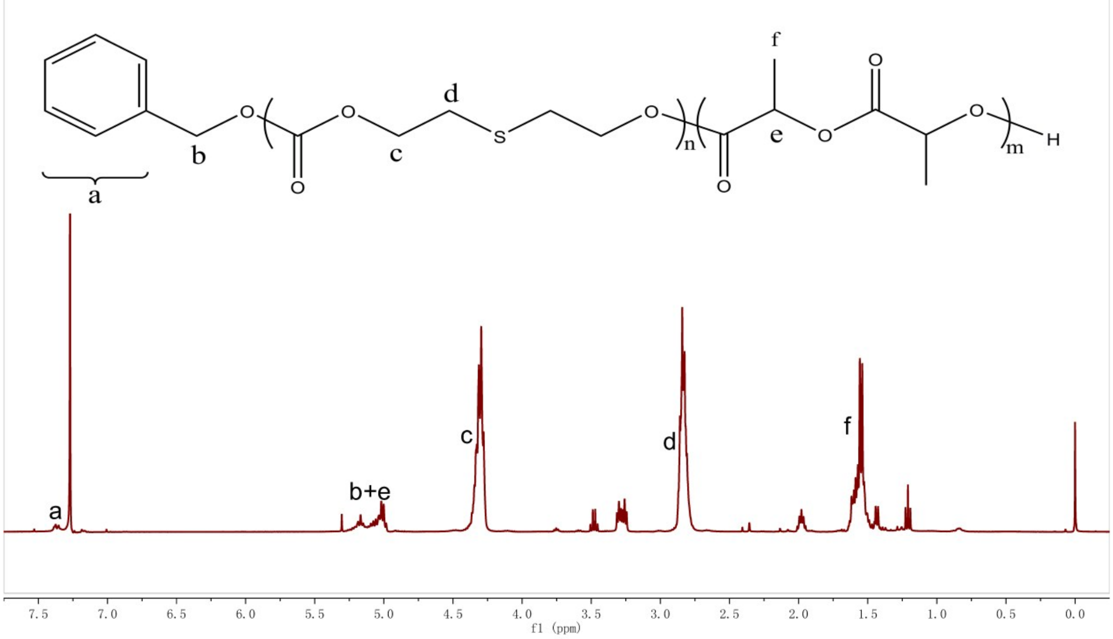

Fig. S20 The ^{1}H NMR spectra of PS-*co*-PLA.

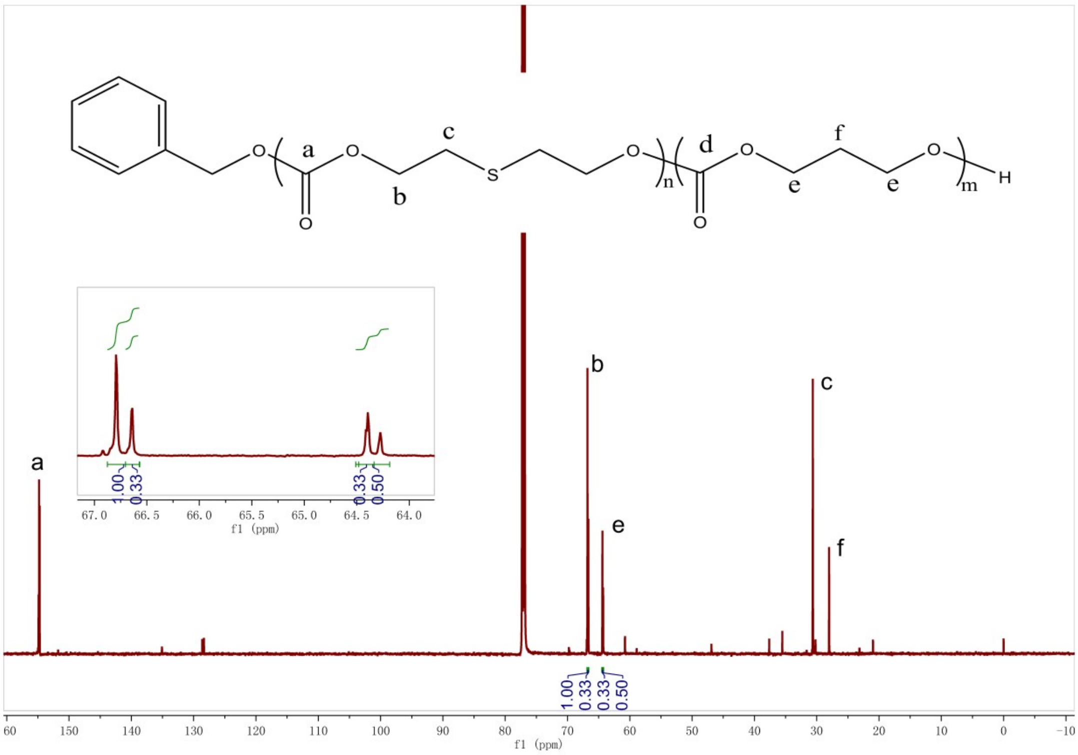

Fig. S21 The quantitative ^{13}C NMR spectra of PS-*co*-PTMC (table 3, entry 2), the proportion of random copolymerization is about 44%.

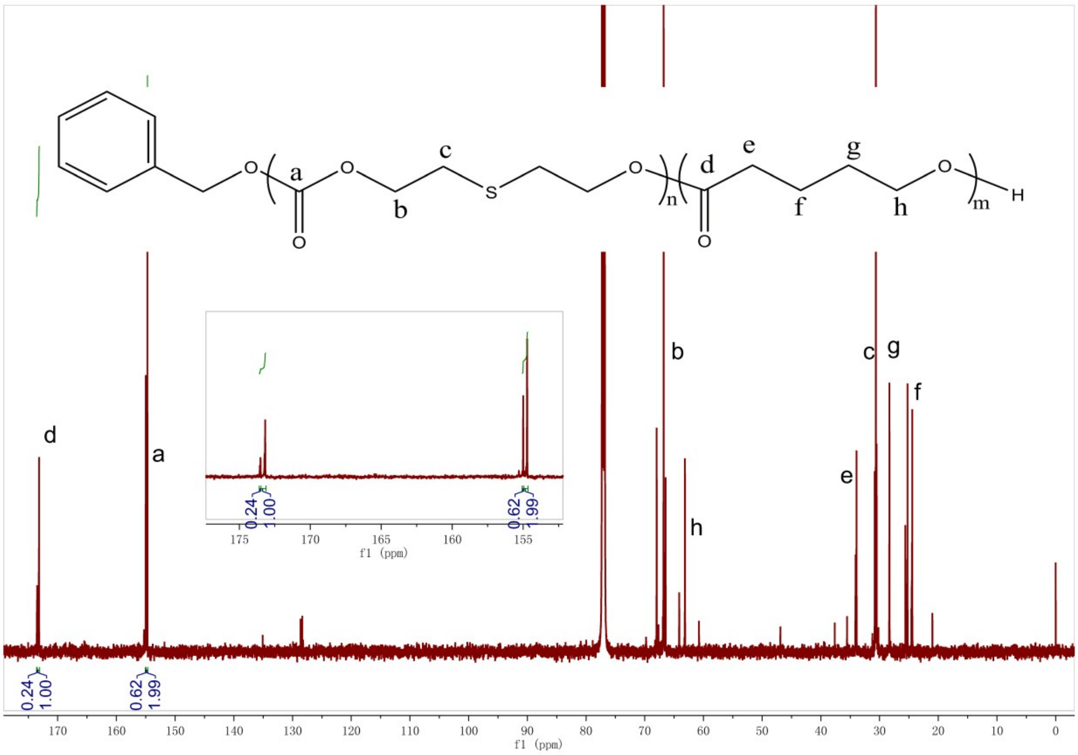

Fig. S22 The quantitative ^{13}C NMR spectra of PS-*co*-PVL (table 3, entry 3), the proportion of random copolymerization is about 29%.

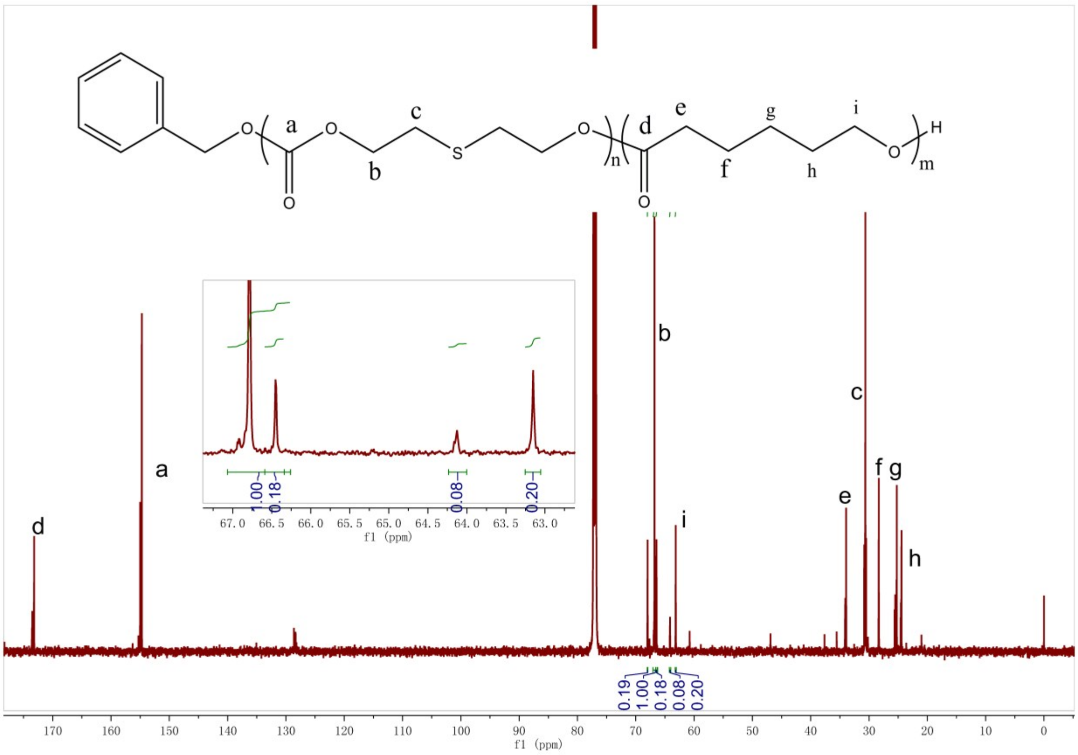

Fig. S23 The quantitative ^{13}C NMR spectra of PS-*co*-PCL (table 3, entry 4), the proportion of random copolymerization is about 20%.

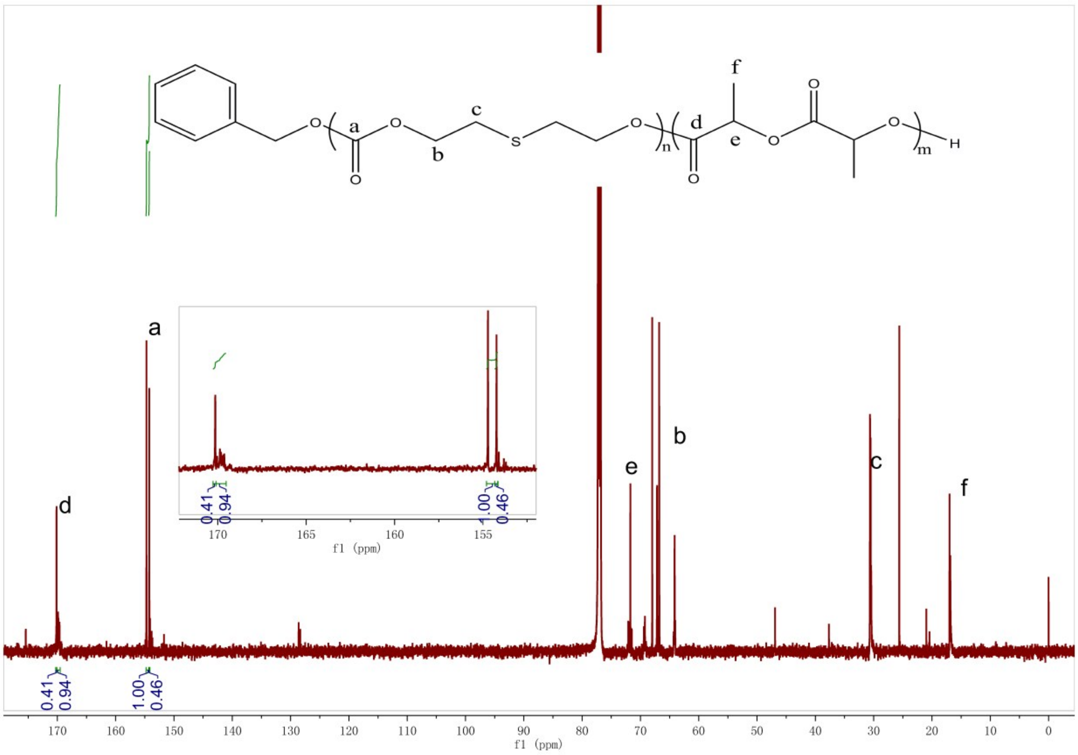

Fig. S24 The quantitative ^{13}C NMR spectra of PS-*co*-PLA (table 3, entry 5), the proportion of random copolymerization is about 45%.

References

1 B. Yan, Y. Zhang, C. Wei and Y. Xu, *Polym. Chem.*, 2018, **9**, 904-911.

2 R. C. Pratt, B. G. G. Lohmeijer, D. A. Long, P. N. P. Lundberg, A. P. Dove, H. B. Li, C. G. Wade, R. M. Waymouth and J. L. Hedrick, *Macromolecules*, 2006, **39**, 7863-7871.