Supporting Information

for

Alternating and Regioregular Copolymers with High Refractive Index from COS and Biomass-derived Epoxides

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Tables:

Table S1. Copolymerization of EGE with COS[a].

entry	cocatalyst	T(h)	Solv.	Conv. (%)[b]	TOF (h^{-1})[b]	Copolymer Selectivity (%)[b]	M_n (kg/mol)[c]	M_w/M_n[c]
1	[PPN]Cl	2.0	-	>99	500	94	7.3	1.15
2	[PPN]Cl	2.0	toluene	>99	500	90	9.6	1.21

[a] The copolymerization were performed in a 10 mL autoclave at 40°C in bulk and 25°C in solution (1.0 mL of solvent), [EGE]/[Cr]/ [cocatalyst]=1000/1/1, [chlorohydrin-1]/[EGE] =1/50, [EGE]/H_2O = 50/1, EGE 10.0 mmol; [b] Determined by ^1H NMR spectroscopy. TOF = Turnover frequency of EGE to polymers, (mol EGE consumed)/(mol Cr h). [c] Determined by gel permeation chromatography in THF, calibrated with polystyrene standards.

Table S2. GGE/COS copolymerization with different GGE /catalyst molar ratio and different solvents [a]

entry	Temp.(°C)	Conv.[b] (%)	TOF (h^{-1})[b]	Copolymer Selectivity[b] (%)	M_n (KDa)[c]	M_w/M_n[c]
1[d]	25	>99	125	96	12.6	1.29
2[e]	25	>99	250	96	17.3	1.28
3	25	>99	500	97	20.6	1.21
4[f]	25	95	475	92	13.2	1.32
5[g]	25	>99	500	98	22.3	1.38
6[h]	25	24	120	66	1.0	1.06
7	20	>99	500	97	18.1	1.33
8	40	>99	500	97	20.0	1.39
9	60	>99	500	95	20.4	1.37

[a] The reaction was performed at 25 °C with 1 mL DCM in a 10 mL autoclave for 2 h. (GGE 10 mmol, [chlorohydrin-**2**]/[GGE] =1/100, GGE/SalenCrCl/[PPN]Cl=1000/1/1) [b] Determined by ^1H NMR spectroscopy. TOF=Turnover frequency of bio-based epoxide to products, (Mol GGE consumed)/(mol Cr h). [c] Determined by gel permeation chromatography in tetrahydrofuran (THF), calibrated with polystyrene standards. [d] GGE/catalyst = 250/1. [e] GGE/catalyst = 500/1. [f] Solvent: 1mL THF. [G] Solvent: 1mL toluene. [h] GGE/H_2O=50/1.

Figures:

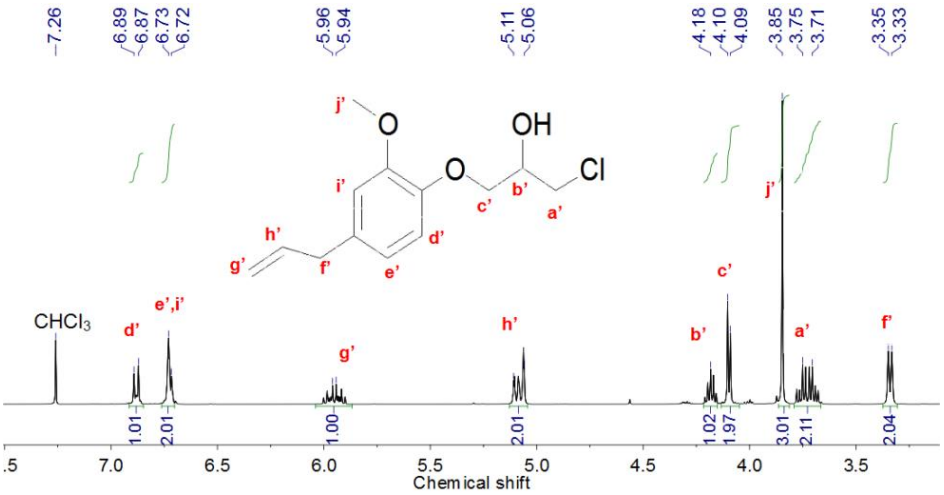


Fig. S1 ^{1}H NMR spectrum of chlorohydrin-**1**.

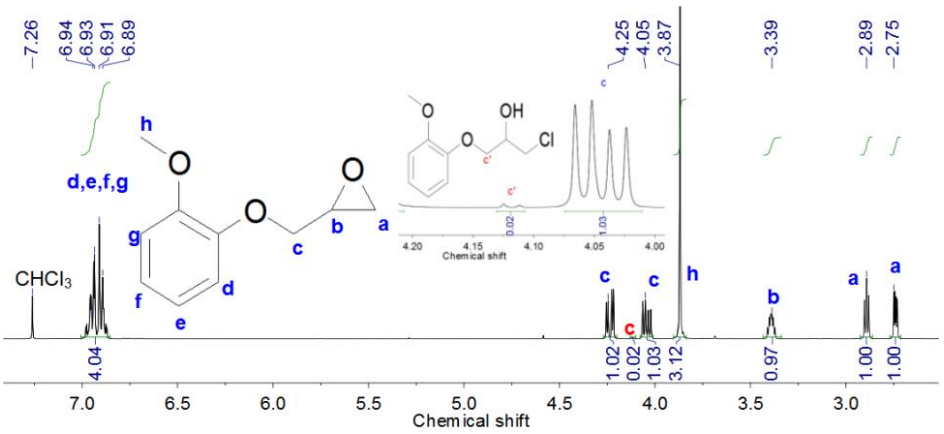


Fig. S2 ^{1}H NMR spectrum of GGE with 1.0 mol% chlorohydrin-**2**.

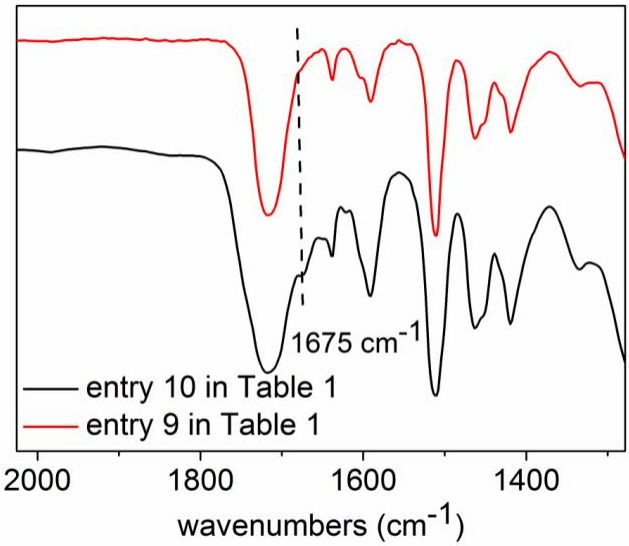


Fig.S3 FT-IR spectra of the copolymers of entries 9, 10 in Table 1.

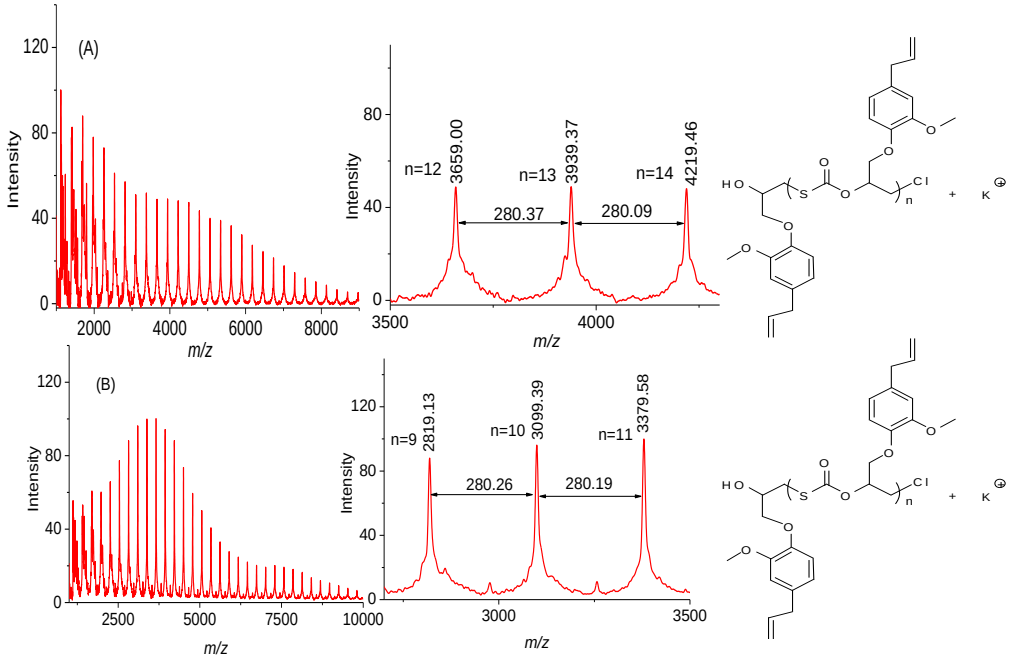


Fig. S4 MALDI-TOF mass spectra of the purified COS/EGE copolymers: (A) entry 1 in Table S1 ;(B) entry 2 in Table S1.

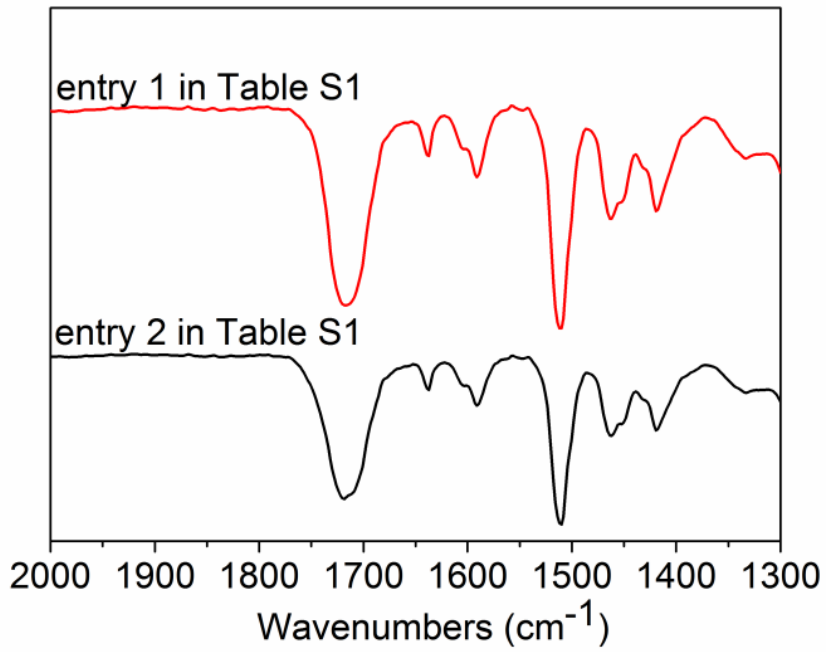


Fig. S5 FT-IR spectra of the copolymers of entries 1, 2 in Table S1.

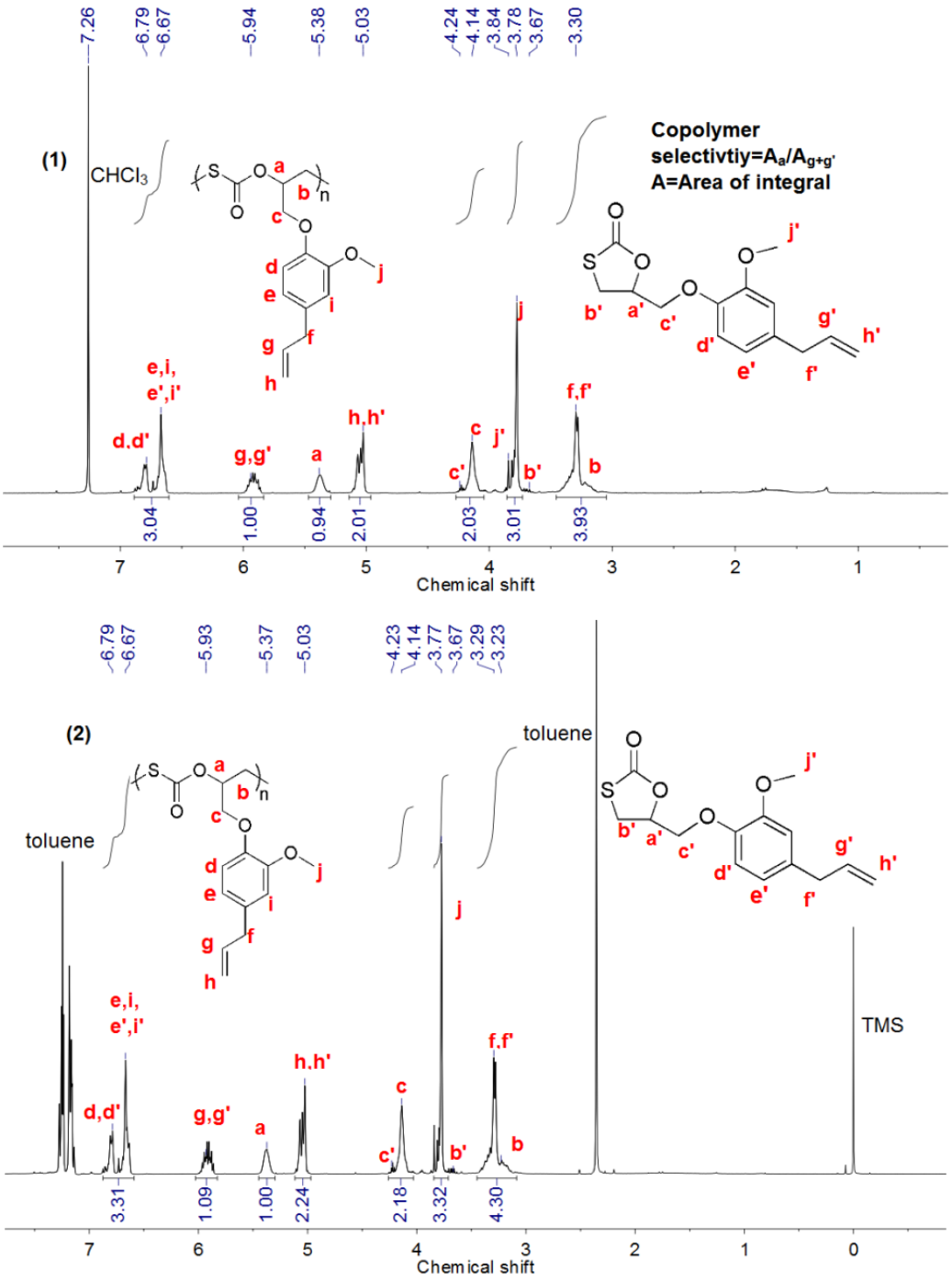
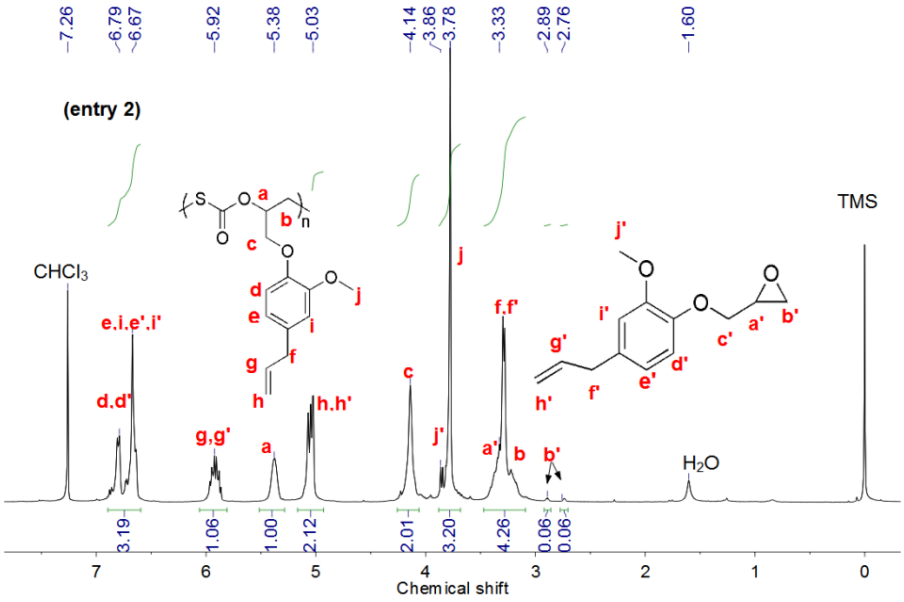
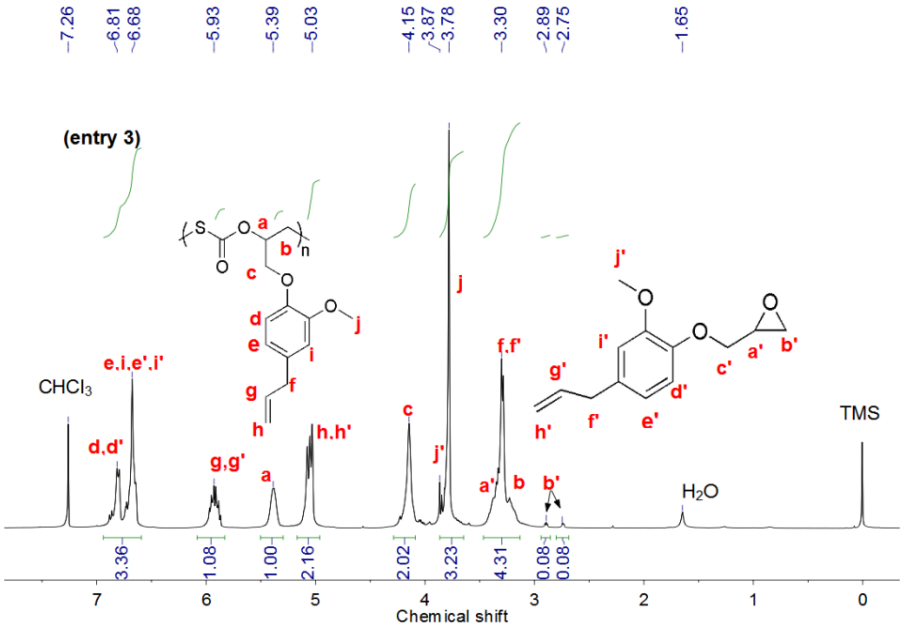
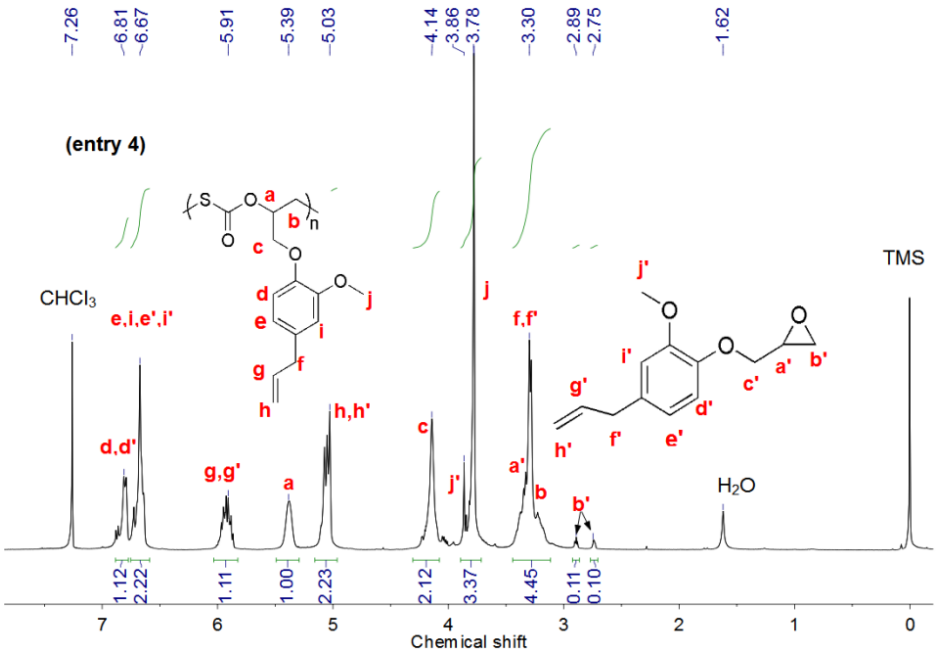


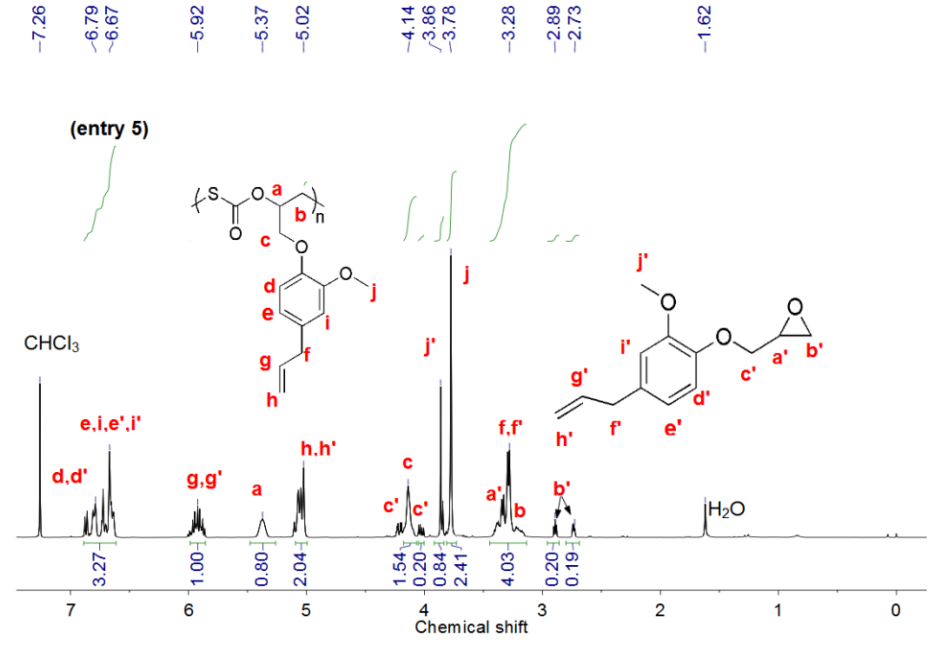
Fig. S6 (1)^{1}H NMR spectrum of the crude product of entry 1, Table S1; (2)^{1}H NMR spectrum of the crude product of entry 2, Table S1.

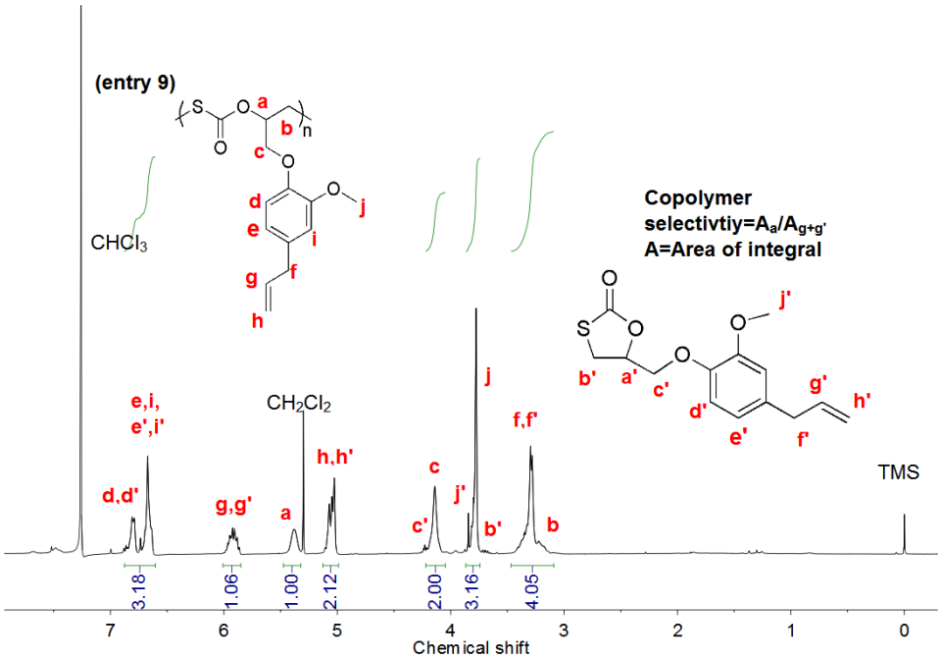
Selected ^{1}H NMR spectra of entries 2-5,9,10,13-17 in Table 1:

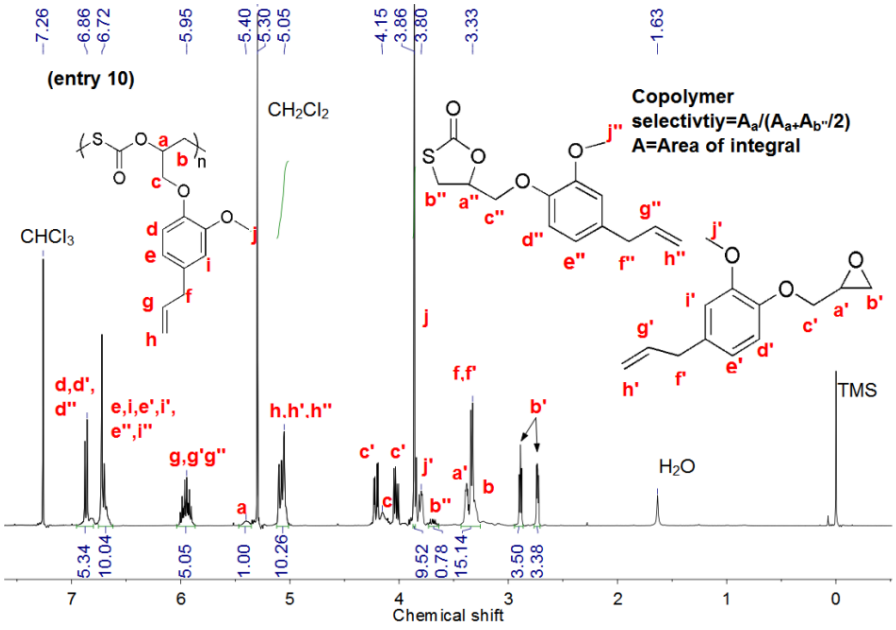


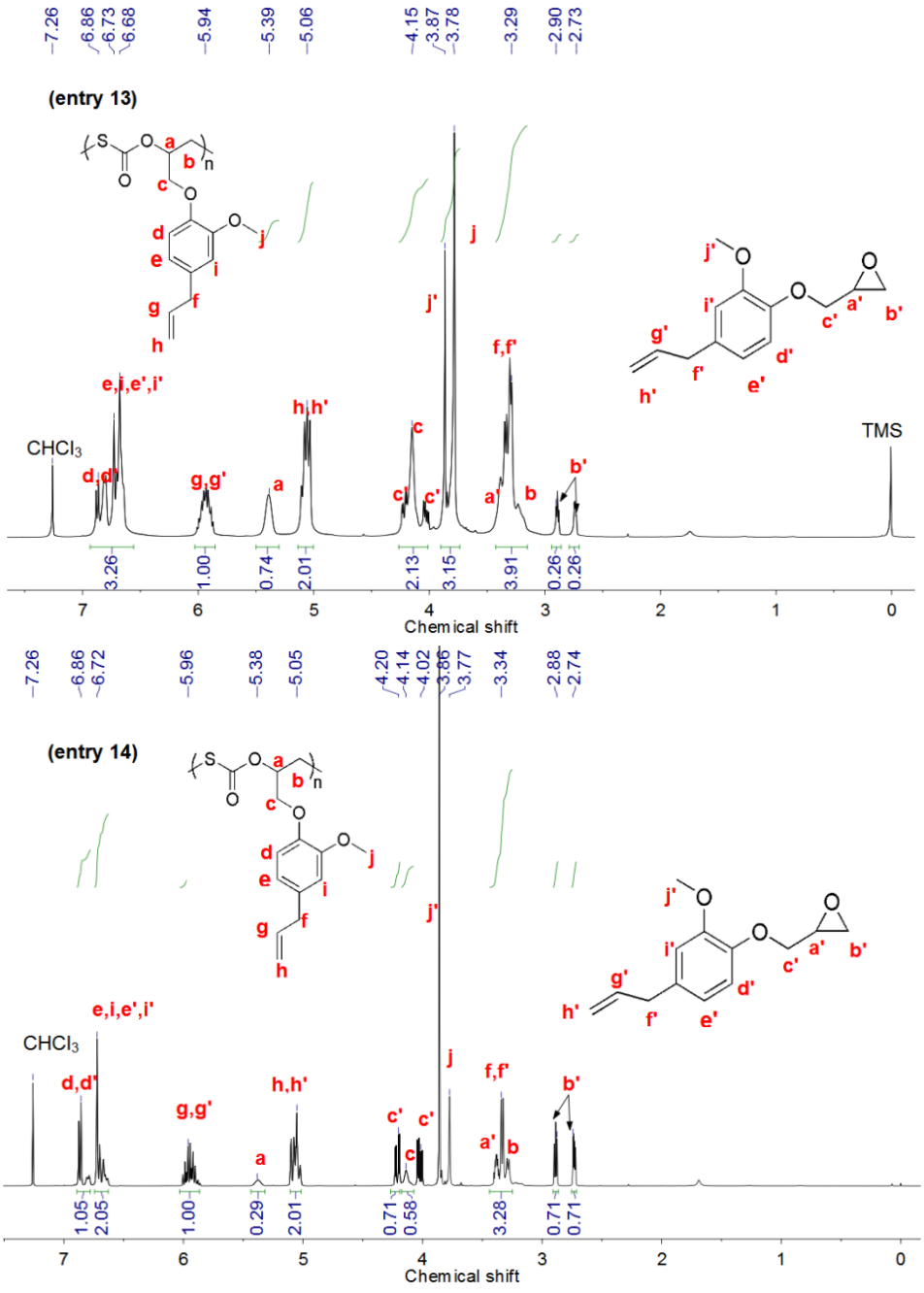


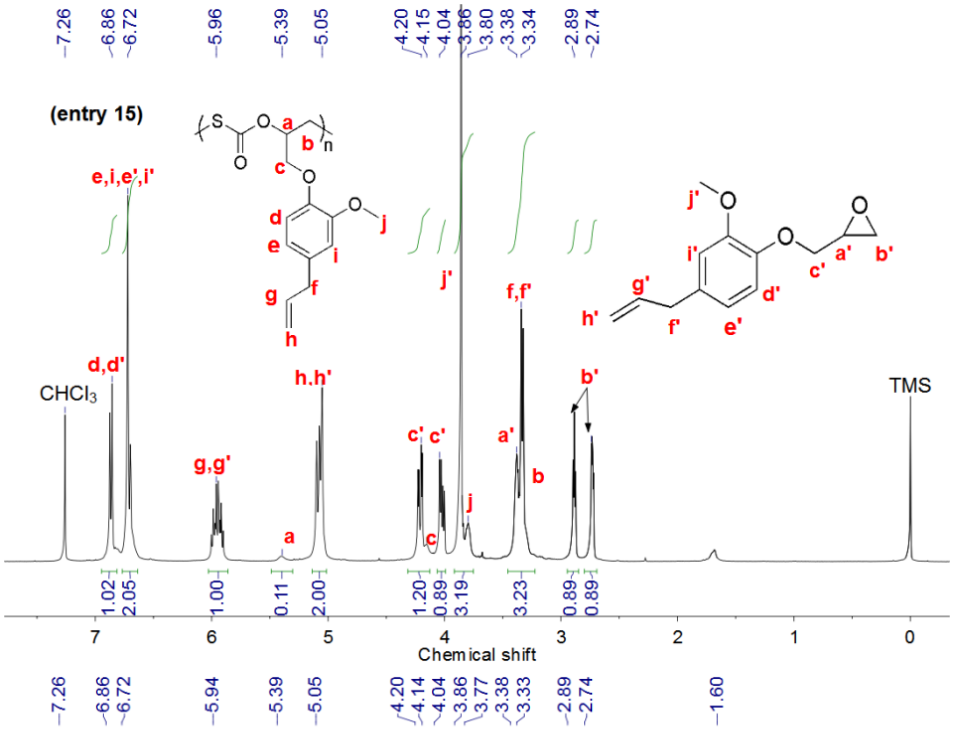

7.26
6.81
6.67
5.91
5.39
5.03
4.14
3.86
3.78
3.30
2.89
2.75
1.62
(entry 4)
CHCl3
TMS
H2O
Chemical shift

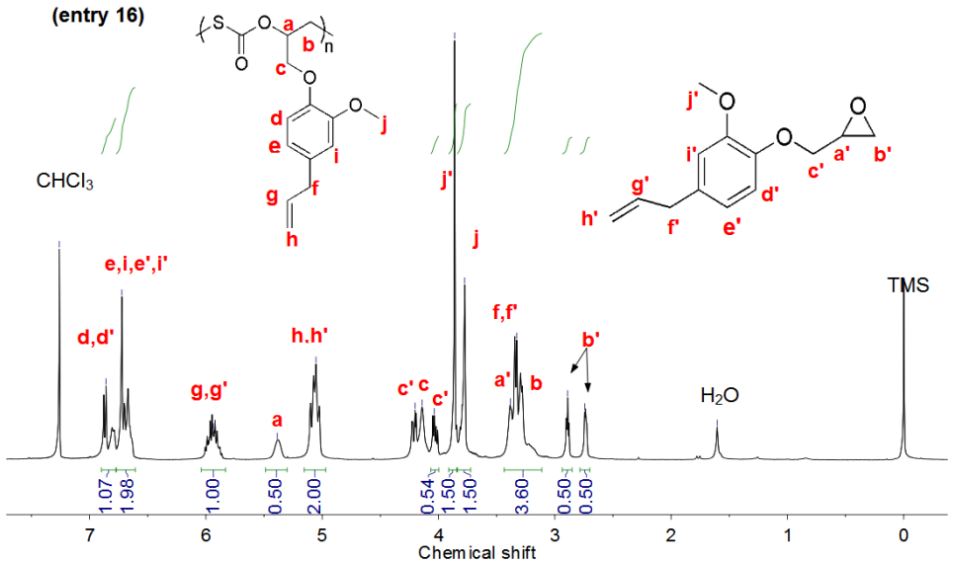

7.26
6.79
6.67
5.92
5.37
5.02
4.14
3.86
3.78
3.28
2.89
2.73
1.62
(entry 5)
CHCl3
H2O
Chemical shift


(entry 9)
CHCl3
CH2Cl2
TMS
Copolymer
selectivtiy=Aa/Ag+g'
A=Area of integral
3.18
1.06
1.00
2.12
2.00
3.16
4.05
Chemical shift


(entry 10)
CHCl3
CH2Cl2
H2O
TMS
Copolymer
selectivtiy=Aa/(Aa+Ab''/2)
A=Area of integral
5.34
10.04
5.05
1.00
10.26
9.52
0.78
15.14
3.50
3.38
Chemical shift


7.26
6.86
6.73
6.68
5.94
5.39
5.06
4.15
3.87
3.78
3.29
2.90
2.73
(entry 13)
CHCl3
TMS
Chemical shift
7.26
6.86
6.72
5.96
5.38
5.05
4.20
4.14
4.02
3.86
3.77
3.34
2.88
2.74
(entry 14)
CHCl3
Chemical shift


(entry 15)
7.26
6.86
6.72
5.96
5.39
5.05
4.20
4.15
4.04
3.86
3.80
3.38
3.34
2.89
2.74
e,i,e',i'
d,d'
CHCl3
g,g'
h.h'
c' c'
a'
b
j'
f,f'
b'
TMS
1.02
2.05
1.00
0.11
2.00
1.20
0.89
3.19
3.23
0.89
0.89
Chemical shift


(entry 16)
7.26
6.86
6.72
5.94
5.39
5.05
4.20
4.14
4.04
3.86
3.77
3.38
3.33
2.89
2.74
1.60
CHCl3
e,i,e',i'
d,d'
g,g'
h.h'
c' c
c'
a
j'
j
f,f'
a'
b
b'
H2O
TMS
1.07
1.98
1.00
0.50
2.00
0.54
1.50
1.50
3.60
0.50
0.50
Chemical shift

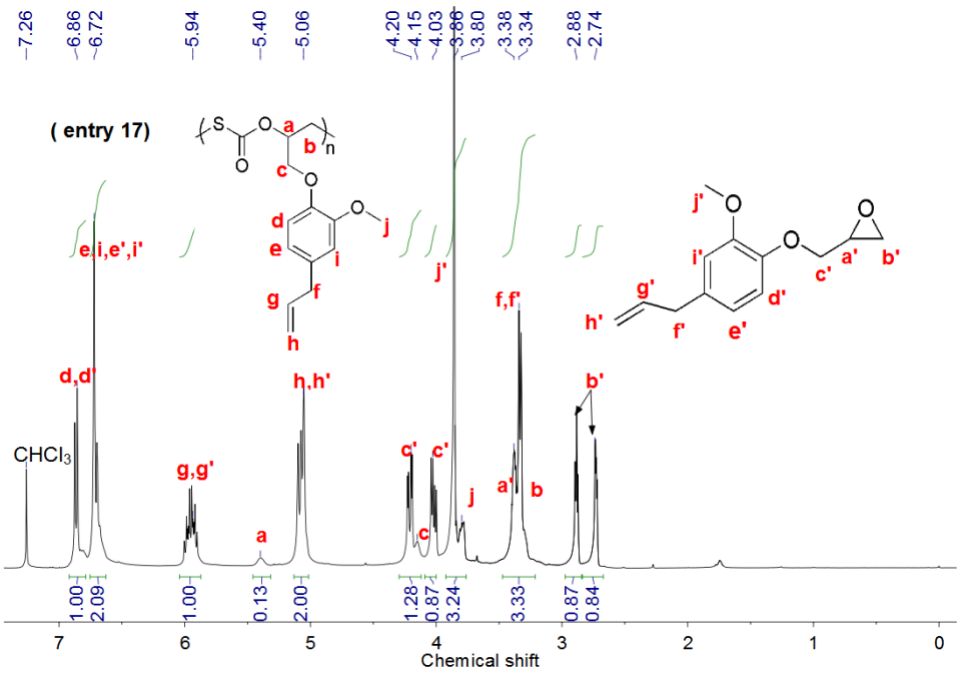


Fig. S7 ^{1}H NMR spectra of the crude products of the entries 2-5,9,10,13-17 in Table 1

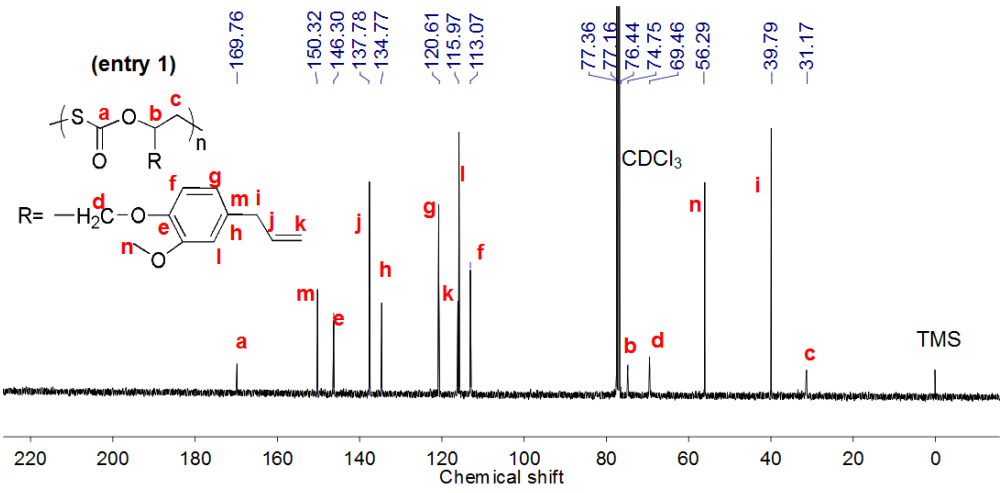
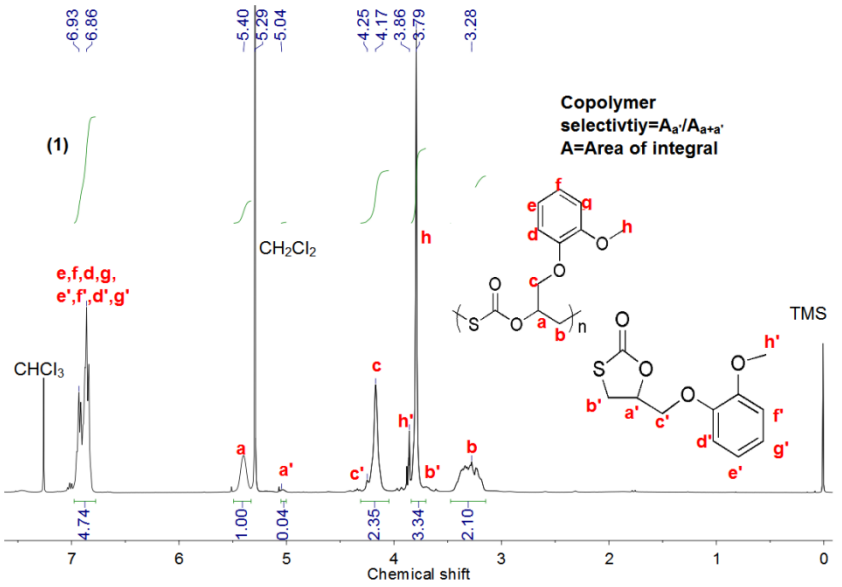
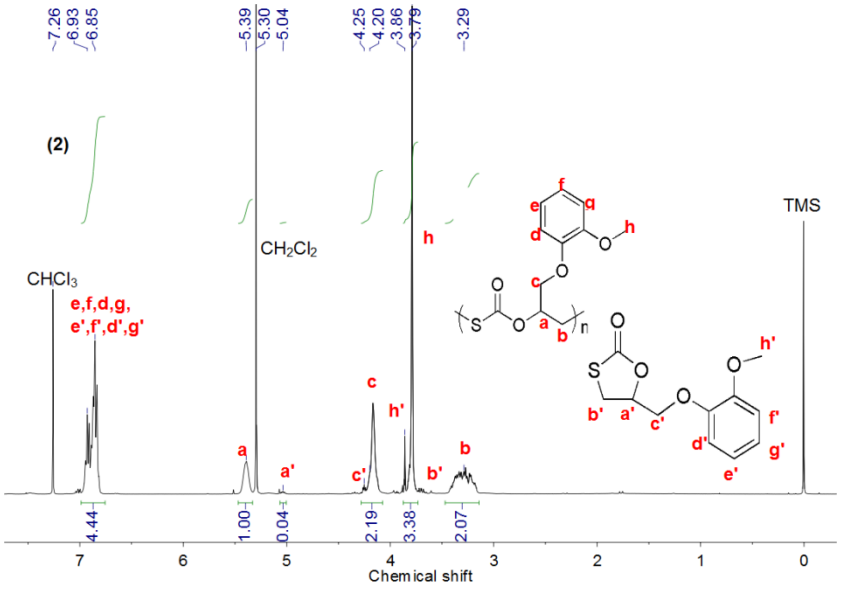
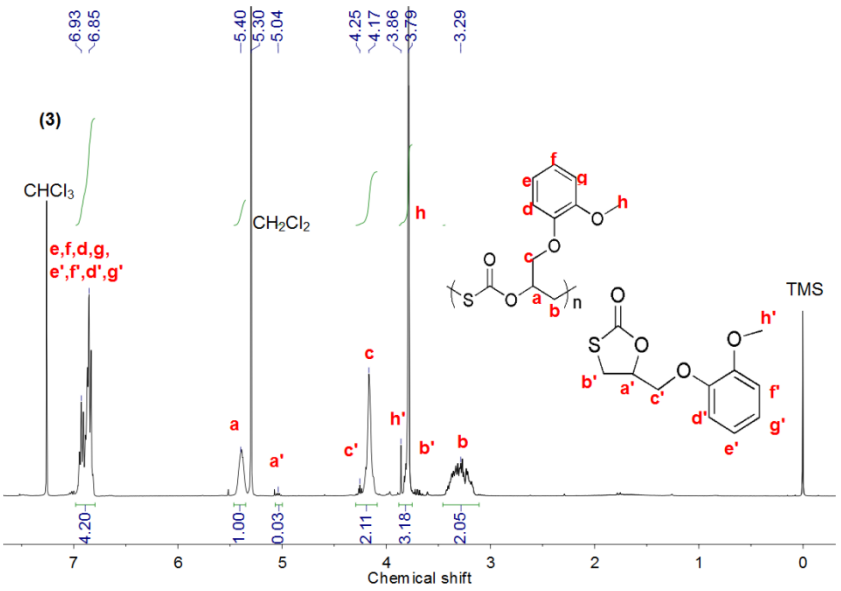


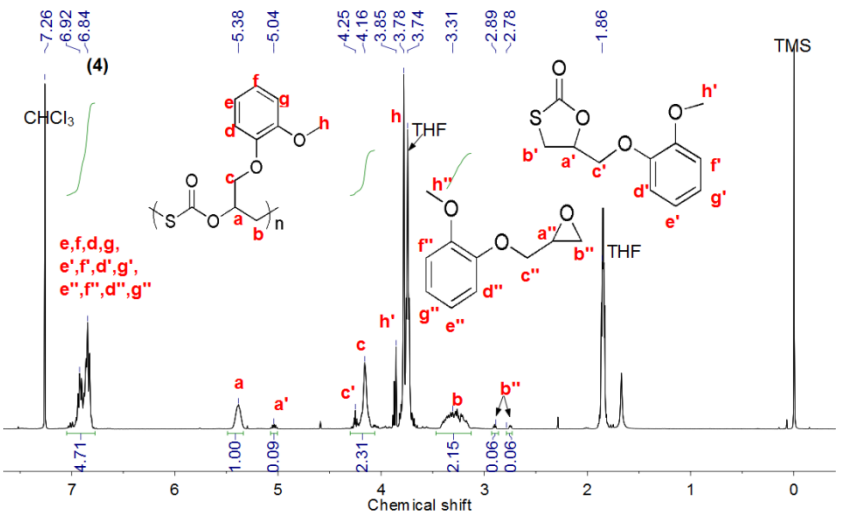
Fig. S8 ^{13}C NMR spectrum of the crude product of entry 1 in Table 1

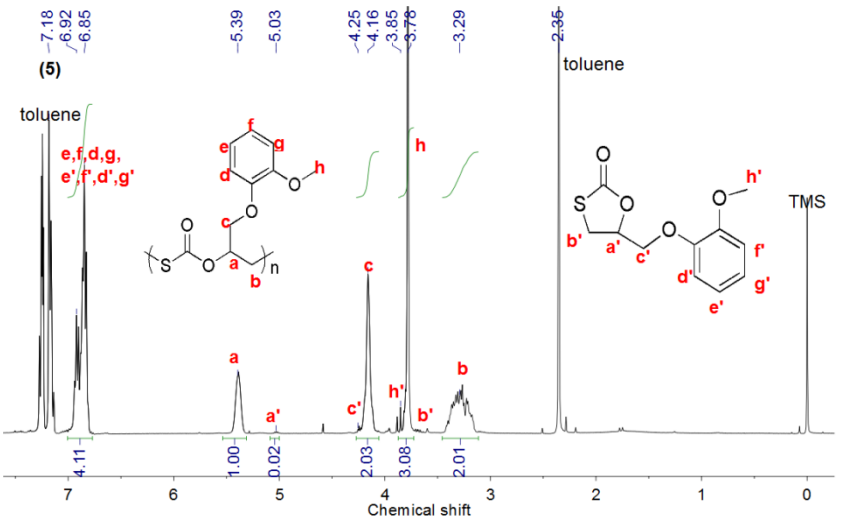
^{1}H NMR spectra of crude polymers in Table S2:

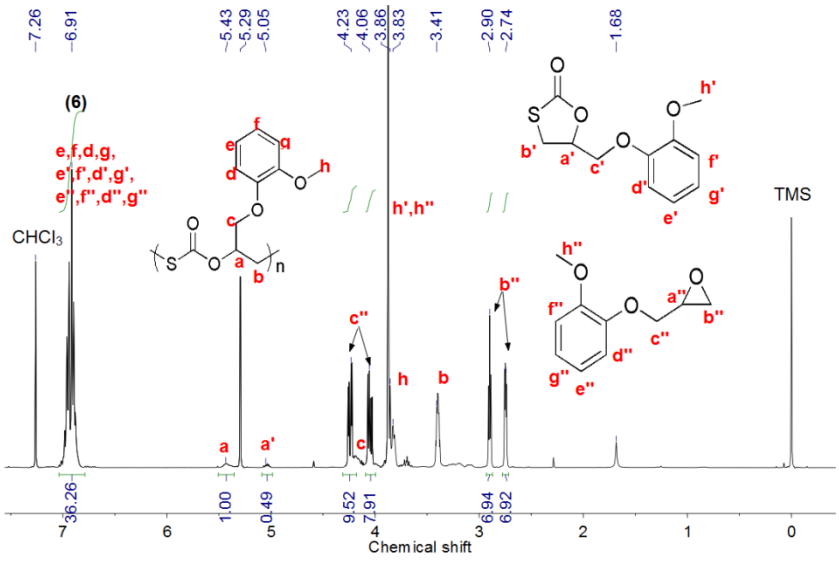


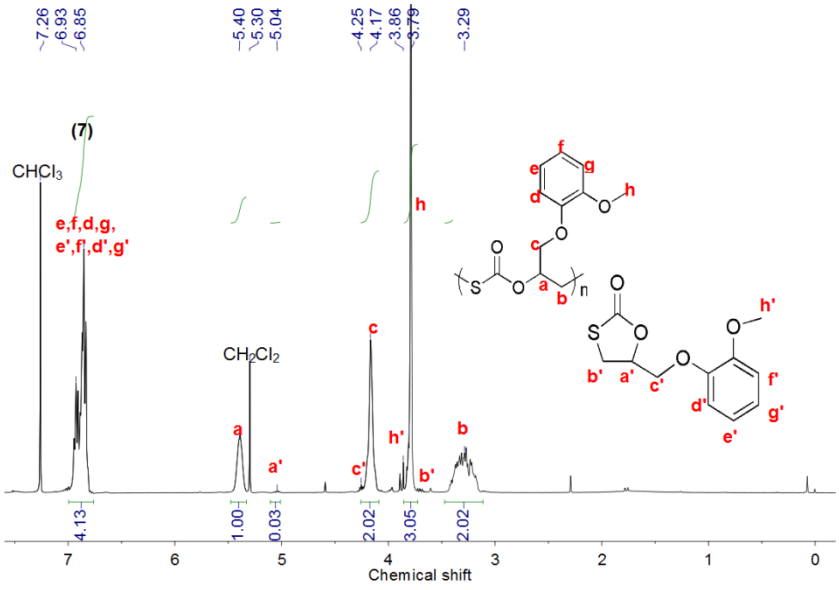


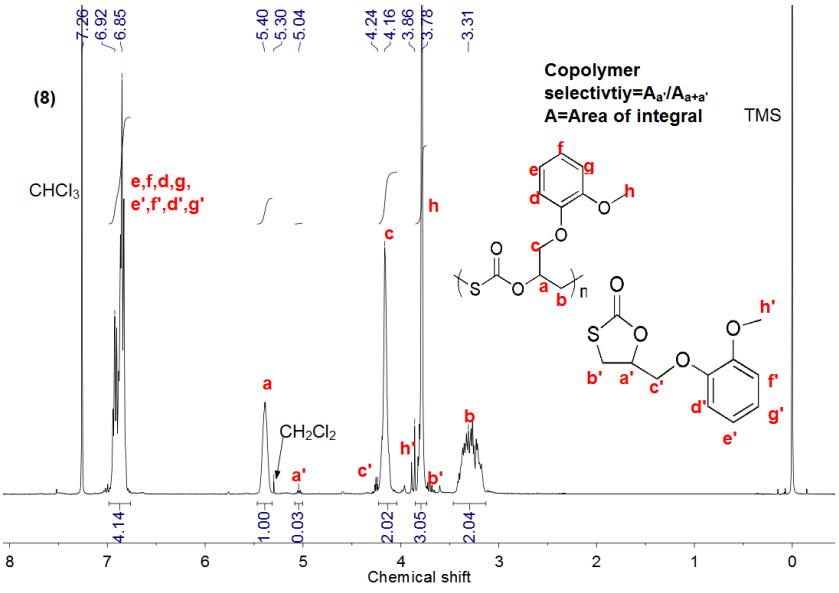

(3)
6.93
6.85
5.40
5.30
5.04
4.25
4.17
3.86
3.79
3.29
CHCl3
CH2Cl2
e,f,d,g,
e',f',d',g'
TMS
Chemical shift


(4)
7.26
6.92
6.84
5.38
5.04
4.25
4.16
3.85
3.78
3.74
3.31
2.89
2.78
1.86
CHCl3
THF
THF
TMS
e,f,d,g,
e',f',d',g',
e'',f'',d'',g''
Chemical shift


(5)
7.18
6.92
6.85
5.39
5.03
4.25
4.16
3.85
3.78
3.29
2.36
toluene
toluene
TMS
e,f,d,g,
e',f',d',g'
Chemical shift


(6)
e,f,d,g,
e',f',d',g',
e'',f'',d'',g''
CHCl3
TMS
h',h''
Chemical shift


(7)
CHCl3
e,f,d,g,
e',f',d',g'
CH2Cl2
Chemical shift


(8)
CHCl3
e,f,d,g,
e',f',d',g'
CH2Cl2
Copolymer
selectivtiy=Aa'/Aa+a'
A=Area of integral
TMS
Chemical shift

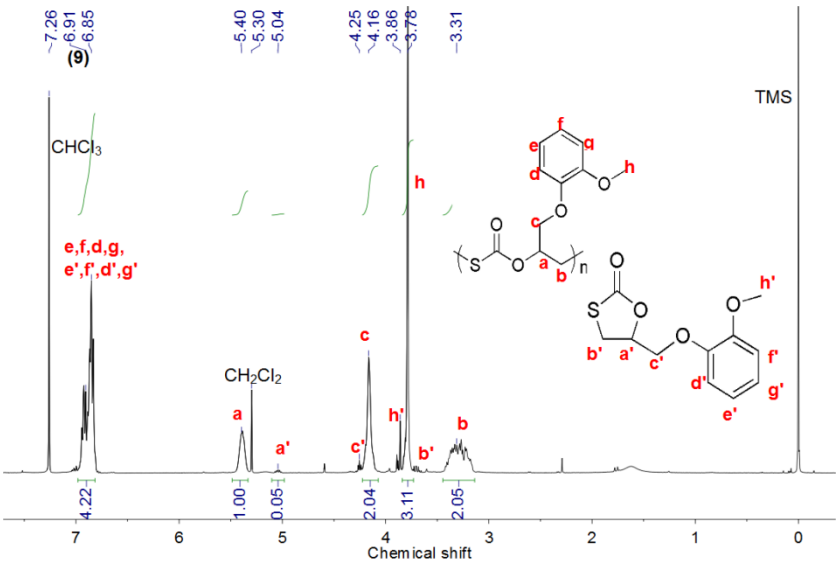
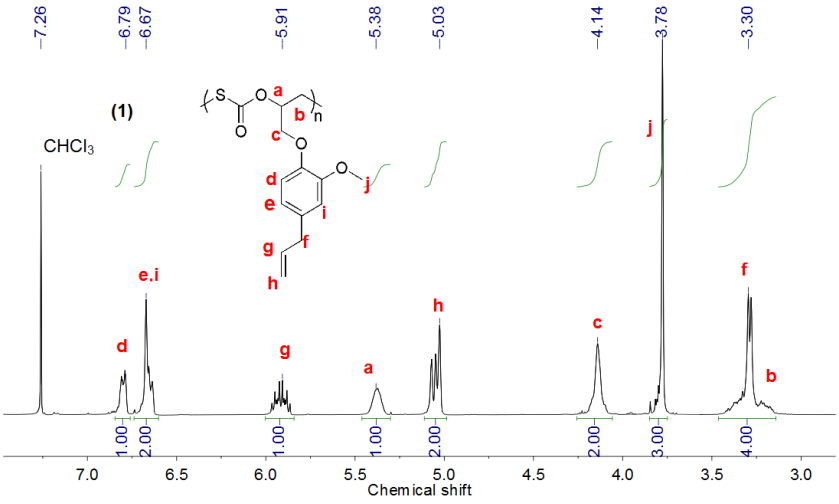
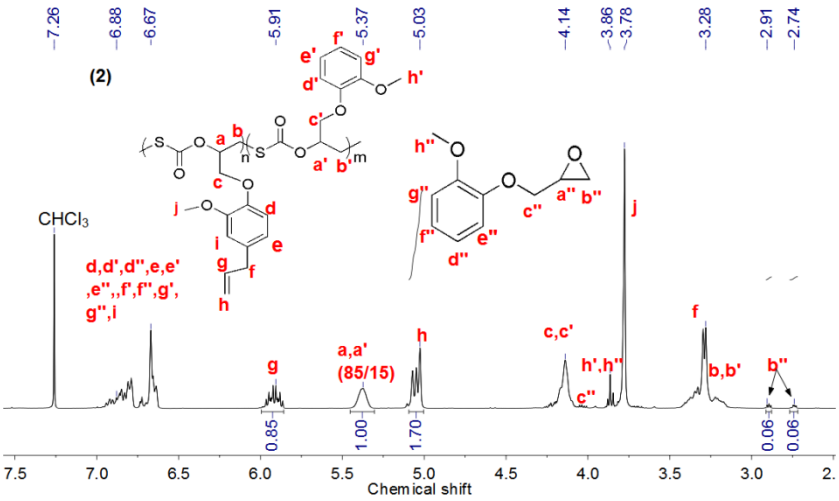


Fig. S9 ^{1}H NMR spectra of the crude product of entries 1-9, Table S2.

^{1}H NMR spectra of crude polymers in Table 2:





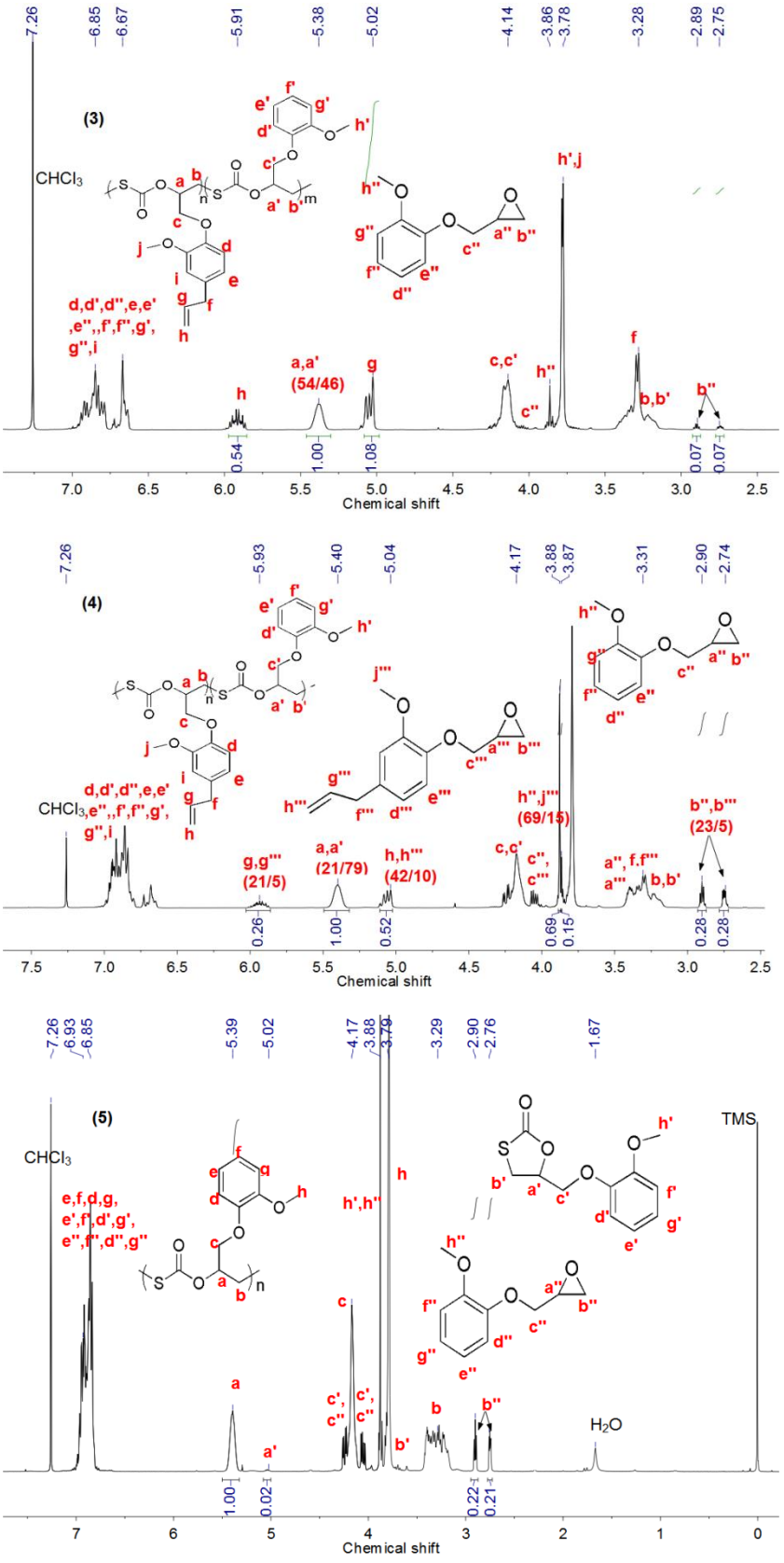


Fig. S10 ^{1}H NMR spectra of the crude product (entries 1-5, Table 2)

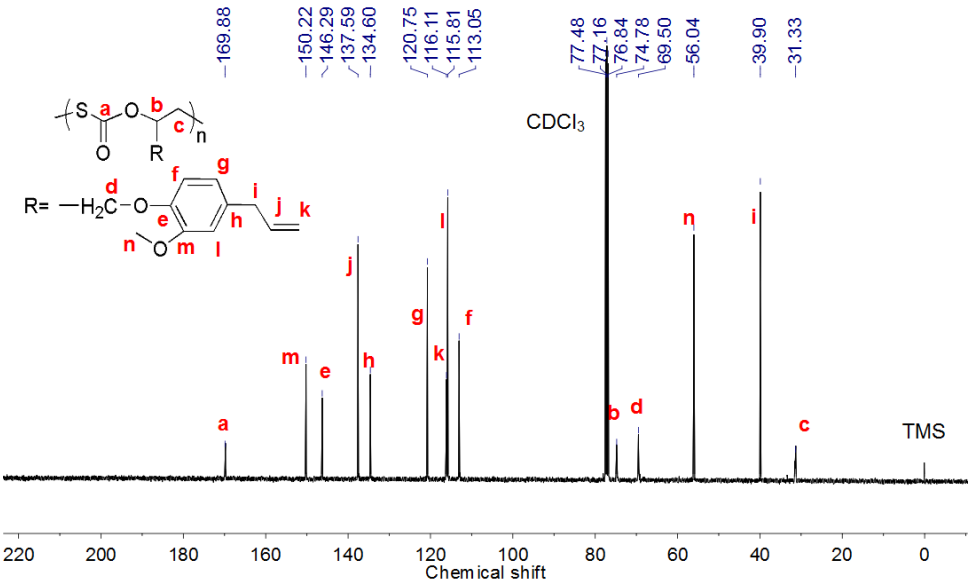
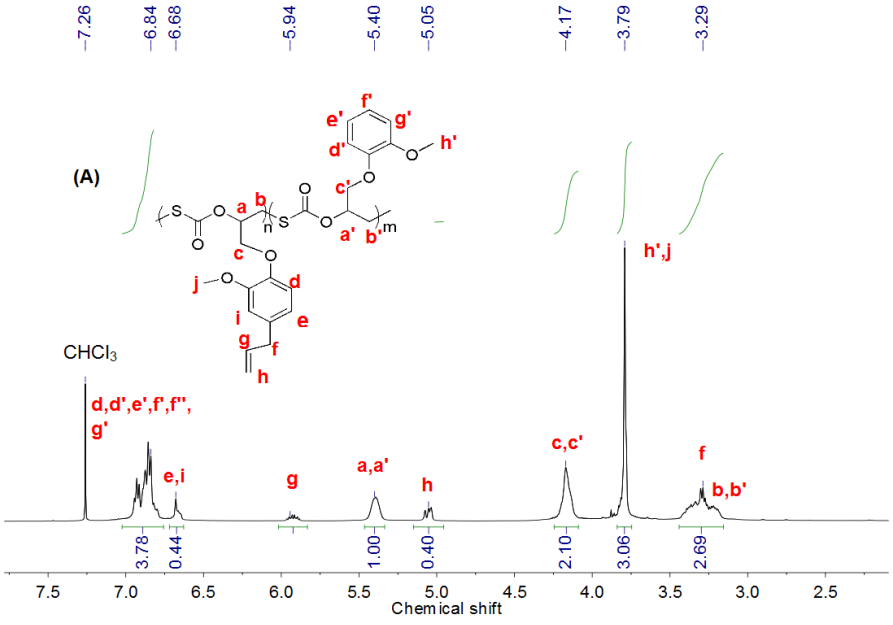


Fig. S11 ^{13}C NMR spectrum of the crude product (entry 1, Table 2).



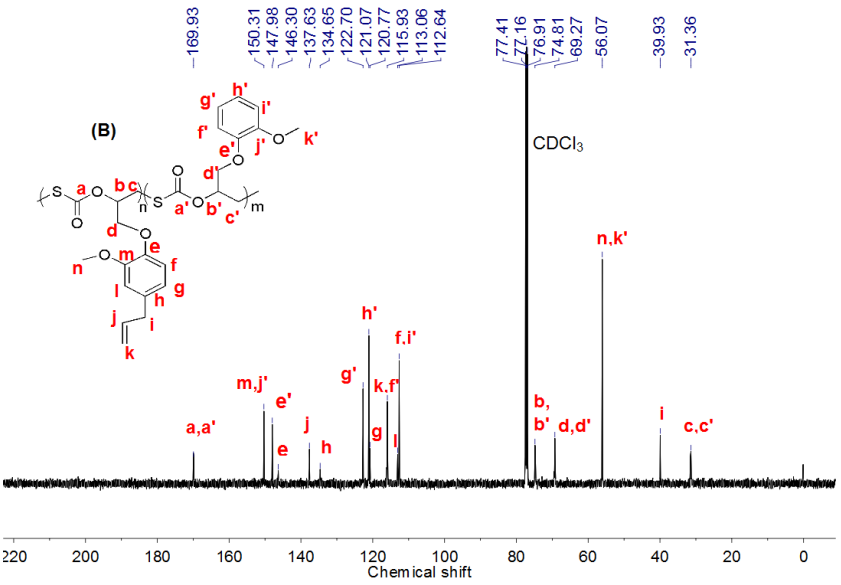


Fig. S12 (A) ^{1}H NMR and (B) ^{13}C NMR spectra of the purified product (entry 4, Table 2).

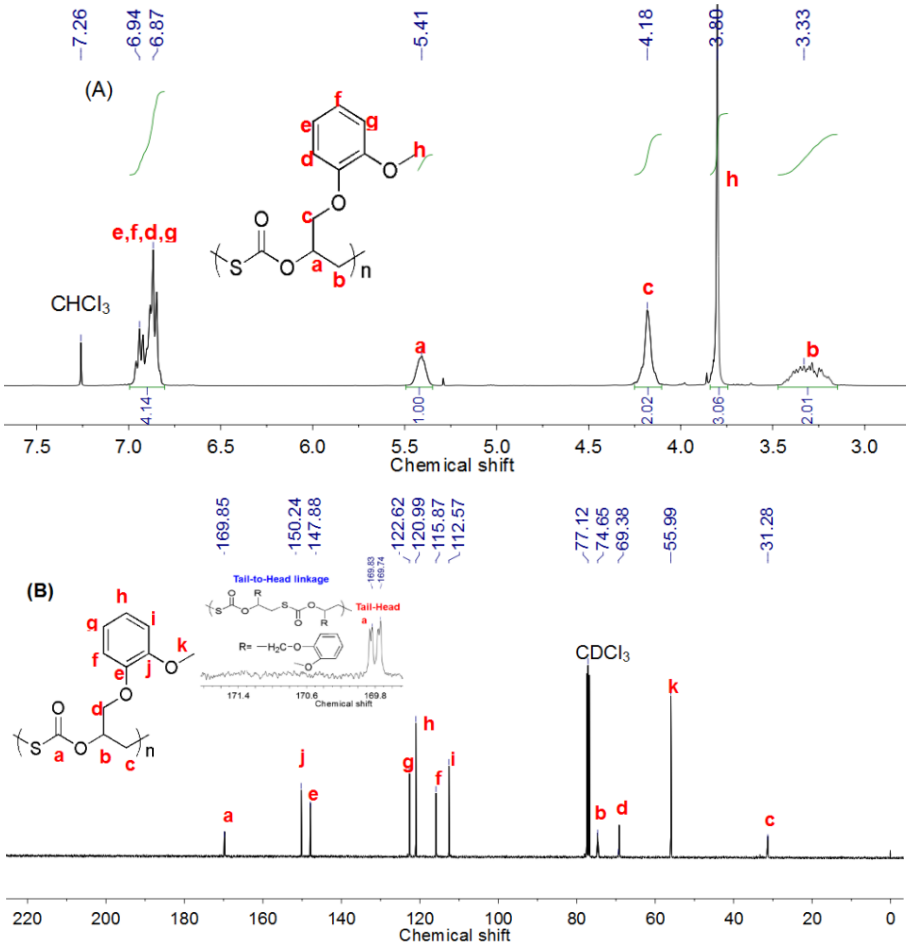


Fig. S13 (A) ^{1}H NMR and (B) ^{13}C NMR spectra of the purified product (entry 5, Table 2).

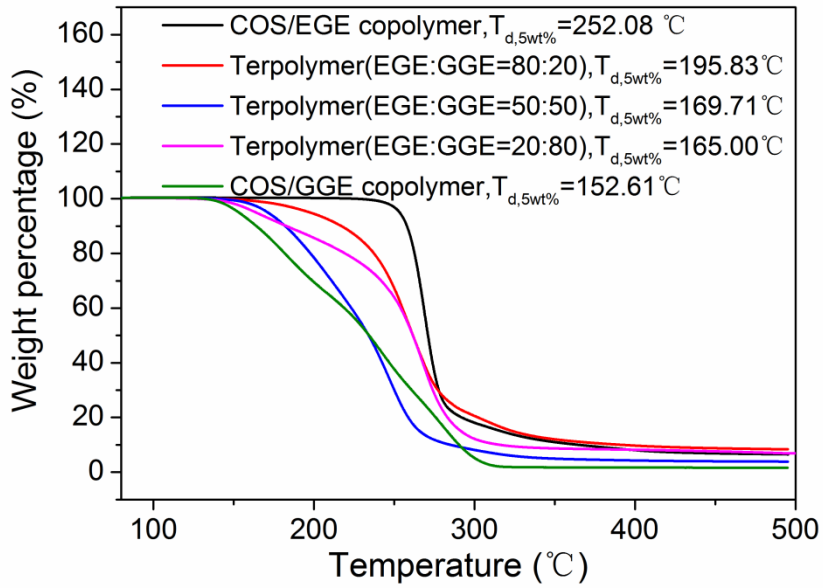


Fig. S14 TheTGA curves of the polymers in Table 2.

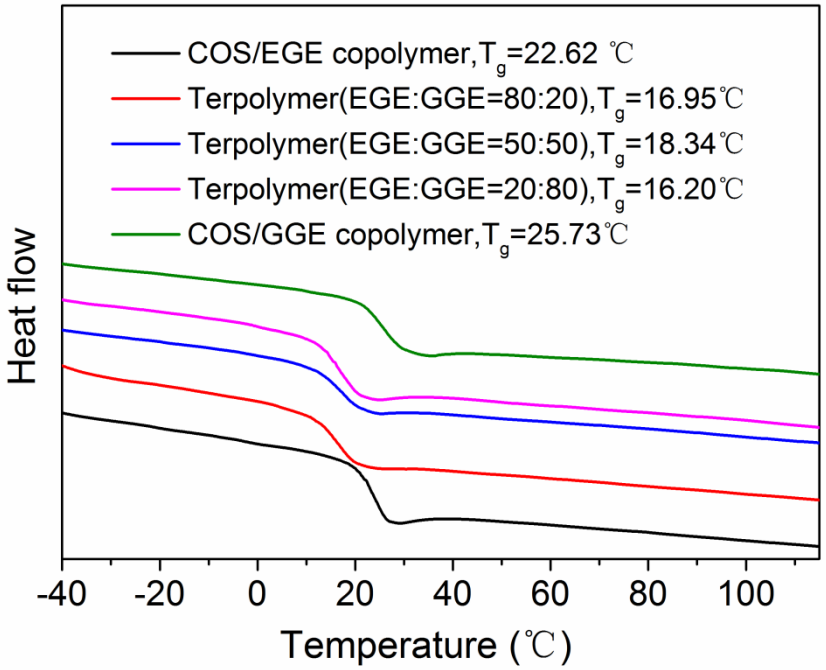


Fig. S15 The DSC curves of the polymers in Table 2.