Supporting Information for

Bio-Based Polyesters by Ring-Opening Copolymerization of Eugenyl Glycidy Ether and Cyclic Anhydrides Using Binuclear [OSSO]CrCl Complex

Binyuan Liu,*[a, b] Junwu Chen,[a] Ning Liu, [b] Huining Ding,[a] Xianmin Wu,[a] Bin Dai* [b] and Il Kim*[c]

[a] Hebei Key Laboratory of Functional Polymer, School of Chemical Engineering and Technology, Hebei University of Technology, Tianjin 300130, China

[b] School of Chemistry and Chemical Engineering, Key Laboratory for Green Processing of Chemical Engineering of Xinjiang Bingtuan, Shihezi University, Shihezi 832003, China

[c] BK21 PLUS Center for Advanced Chemical Technology, Department of Polymer Science and Engineering, Pusan National University, Busan 46241, Korea

*Correspondence authors： E-mail: byliu@hebut.edu.cn (B. Y. Liu) , dbinly@126.com (B. Dai) and ilkim@pusan.ac.kr (I. Kim)

Experimental section

Materials and methods

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All manipulations involving air- and/or water-sensitive compounds were carried out with the standard Schlenk and vacuum line techniques under argon atmosphere. Tetrabutylammonium bromide (TBAB), Toluene and THF were refluxed and distilled over Na-benzophenone under nitrogen. All epoxides, including epichlorohydrin (ECH), allyl glycidyl ether (AGE), cyclohexene oxide (CHO), propylene oxide (PO), phenyl glycidyl ether (PGE) were stirred over powered CaH_2 at room temperature over 48 h and vacuum-distilled before use. Triethylamine, dichloromethane were stirred over powered CaH_2 at room temperature over 48 h and distilled before use. Ethane-1,2-dithiol, $^{n}BuLi$, $CrCl_3(THF)_3$, eugenol, and benzoic acid were purchased from Sigma-Aldrich and used directly.

All ^{1}H NMR spectra were recorded on a Bruker-400 spectrometer at frequency of 400 MHz. All ^{13}C NMR spectra were recorded on a Bruker-400 spectrometer at frequency of 100 MHz. Chemical shifts are given in ppm relative to TMS.

Infrared (IR) spectra were obtained on a Bruker Vector 22 spectrometer at a resolution of 4 cm^{-1} (16 scans collected). The measured compounds and polymers were dissolved in CH_2Cl_2, then the solution was spin coating on KBr plates and dried. The molecular weight of polymer was determined by using gel permeation chromatography (GPC) on a Agilent 1260 Infinity instrument with a refractive index detector, calibrated with polystyrene standards. The columns used were MIXED-B 10 um 300 × 7.5 mm columns held at 35 ℃ using THF as eluents at a flow rate of 1.0 mL/min.

ESI-MS experiments were carried out using a Bruker Q-TOF mass spectrometer. The stock solutions of the chromium complexes and PPNCl were mixed in 1/10 volumes and diluted with CH_2Cl_2 to a concentration of 10^{-4} mol/L, stirred at 30 ℃ for 30 min, and stocked for 1 hours. After the polymerization is completed, samples are taken directly without post-treatment such as methanol washing and precipitation, and the solutions of polymer were made in acetonitrile to a concentration of 1×10^{-4} mol/L. The solutions of Complex 1(or H_2L^1) were made in acetonitrile to a concentration of 1×10^{-4} mol/L. Then, these solutions were diluted with the same volume of acetonitrile

before introducing into the source of the mass spectrometer. All the mass spectra were recorded using a Bruker Q-Tof mass spectrometer equipped with an orthogonal electrospray source (Z-spray) operated in positive ion mode. Mass spectra were acquired over the range of m/z 50-3000. For the ESI-MS of the polymer, the voltage between the needle and the electrospray chamber was set at 2.0 KV, for the ESI-MS of the ligand and the complex, the voltage between the needle and the electrospray chamber was set at 3.0 KV, and both of the source temperature were kept at 200 ℃. The solution was injected into the ESI-MS at a flow-rate of 2.0 mL/min.

Magnetisation measurements, at temperatures between 5 K and 300 K, were carried out using a PPMS-9 vibrating sample magnetometer at 1 Tesla. Elemental analyses were determined by a Flash EA 1112 automatic element analyzer. The valence state of elements were determined using XPS, the spectra were recorded with an ESCALAB 250Xi spectrometer.

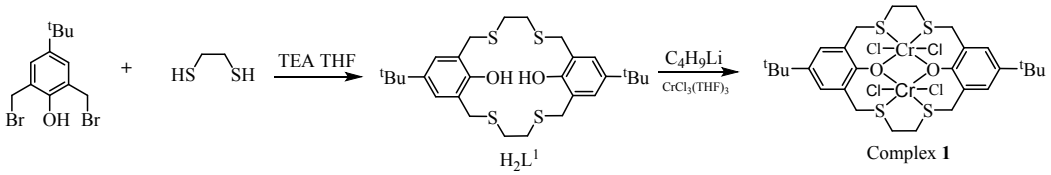
Synthetic Process (Scheme S1)

2, 6-Bis(bromomethyl)-4-*t*butylphenol.

2, 6-bis(bromomethyl)-4-*t*butylphenol was synthesized according to the report.[S1]

Ligand H_2L^1.[S2] To a solution of 2,6-bis(bromomethyl)-4-*t*butylphenol 6.7 g, 0.02 mol）in THF (100 mL) was added ethane-1,2-dithiol (1.88 g, 1.8 ml, 0.02 mol), and the reaction mixture was refluxed for 15 min. Following this, triethylamine (4.04 g, 0.04 mol) was added dropwise at 0 ℃. Stirring was continued for 30 min at room temperature. After the reaction was stirred for 24 h at 45 ℃, it was filtered and the filtrate was concentrated under reduced pressure, then the solution of resulting mixture in diethyl ether was washed with saturated NH_4Cl solution (3 × 150 cm^3), water (100 cm^3), dried ($MgSO_4$) and evaporated to dryness, the product was dissolved in a small portion ethyl acetate and precipitate in cold ethanol petroleum ether yielding after drying in vacuum 3.26 g (61%) of yellow solid. FT-IR, ν/cm^{-1}: 640(w), 741(s), 884(m), 1198(s), 1359(m), 1477(s), 2862(s), 2923(s), 2957(vs), 3321(b). UV-Vis: 235 nm, 288 nm. ^{1}H NMR (400MHz, $CDCl_3$): (δH, ppm): 1.20(s, 8H, -C(CH_3)$_3$), 2.59(s, 4H, -CH_2), 3.71(s, 4H, -CH_2), 6.64(s, 2H, Ar-OH), 7.03(s, 4H, Ar-H). ^{13}C NMR(101 MHz, $CDCl_3$) δ/ppm: 31.33, 31.57, 34.06, 123.63, 126.92, 143.16, 151.09.

Anal. Calcd for $C_{28}H_{40}O_2S_4$: C, 62.64; H, 7.51;S, 23.89. Found: C, 62.86; H, 7.49; S, 23.79. ESI-MS(m/z): $[H_2L^1+H]^+$: 537.19, Found 537.20.



Scheme S1 Synthesis of the H_2L^1 and Complex 1

Complex 1. [S2, S3]

The ligand H_2L^1 (1.89 g, 3.5 mmol) was dissolved in 20 mL dried THF. Then the solution temperature was reduced to -15 ℃ and ^{n}BuLi (3.2 mL（8 mmol, 2.5 mol/L) was added dropwise. The reaction mixture was stirred for 2 h at room temperature. Then it was added dropwise to $CrCl_3(THF)_3$ (2.9 g, 7.76 mmol) and stirred at 25 ℃ overnight. The solvent was removed in vacuum, and the resulting solid was dissolved in dichloromethane. The reaction mixture was filtered to remove LiCl, and the solvent removed in vacuum to afford dark green Complex 1. The yield was 1.8 g, 73%. Anal. Calcd for $C_{28}H_{38}Cr_2Cl_4O_2S_4$: C, 43.08; H, 4.91;S, 16.43. Found: C, 42.56; H, 4.90; S, 16.55. ESI-MS(m/z): [complex 1+Na]$^+$: 802.93, Found 803.15.

Complex 2. Complex **2** was synthesized according to the earlier literature.[S4]

Eugenyl Glycidy Ether (EGE).[S5] 32.58 g (198.42 mmol) of eugenol, 98 mL (1252.2 mmol) of ECH and 3.62 g (11.2 mmol) of TBAB were stirred in a 250 mL flask at 100 °C for one hour. The mixture was cooled down to 30 ℃ and then 112.5 mL of an aqueous solution of 20% NaOH and 3.62 g (11.2 mmol) of TBAB were added and maintained under stirring for 90 min. Once finished 50 mL of ethyl acetate was added to the mixture for dilution. The phases were separated and the organic layer was washed twice with water and dried with magnesium sulphate. The solvent and excess epichlorohydrin were eliminated in a rotary evaporator at 60 ℃. The mixture was purified by silica-gel chromatography using hexane/ethyl acetate 10/1, The product is a pale yellow liquid with 92% yield. ^{1}H NMR (400MHz, $CDCl_3$): (δH, ppm): 6.64-6.53 (d, 3H, Ar), 5.9-6.0 m (m, 1H, -CH=), 5.0-5.1 m (m, 2H, -CH=), 4.19 (dd, 1 H, epoxy ring), 3.98 (dd, 1 H, epoxy ring), 3.83 (S, 3H, CH_3), 3.39 (d, 2H, CH_2-Ar), 3.3

m (s, 1H, epoxy ring), 2.84 (dd,1 H, -CH_2-O-), 2.65 (dd,1 H, -CH_2-O-).

Modification of Poly(SA-*alt*-EGE) via *thiol–ene* reaction.[S6] Poly(EGE-*alt*-SA) (1.16 g), 9.5 mg dimethoxy-2-phenylacetophenone (0.03 mmol), THF (4.0 mL), was added to a 15 mL pre-dried Schlenk flask under argon and stirred until a homogenous solution was attained. After this, 3-Mercapto-1,2-propanediol (0.587 g, 5.44 mmol) was added to the solution by syringe, and the reaction mixture was stir in the dark for half an hour at room temperature and then put it in ultraviolet light for 3 h, then terminated by adding distilled water and the polymer was precipitated. The final polymer was dried in vacuum at 50 °C for 24 h.

EGE hydrolysis with benzoic acid catalysed by Complex 1/PPNCl.[S7] 59 mg (0.075 mmol) Complex 1 and 86 mg (0.15 mmol) PPNCl were added to a vial containing 1.5 mL EGE (7.5 mmol) and 0.915 g benzoic acid (7.5 mmol) dissolved in 1.0 mL toluene, the reaction was stirred for 48 h at 90 ℃. Upon completion the reaction mixture was poured into hexanes, and the supernatant was collected. The hexane was removed under vacuum, and the remaining products were examined by ^{1}H NMR.

References

S1. V. J. Hesler, B. W. Skelton, A. H. White, D. H. Brown and M. V. Baker, *J. Incl. Phenom. Macro.*, 2015, **82**, 53–69.

S2. J. Liu, Y. Y. Bao, Y. Liu, W. M. Ren and X. B. Lu, *Polym. Chem*., 2013, **4**, 1439-1444.

S3. D. J. Darensbourg, M. U Osit Karroonnirum, R. R. Poland, J. H. Reibenspies and B. Cetinkaya, *Macromolecules*, 2009, **42**, 6992-6998.

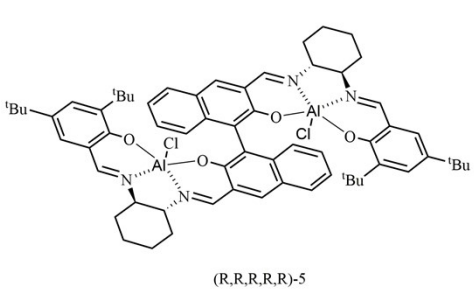
S4. G. S. Si, L. Zhang, B. Han, Z. Y. Duan, B. Q. Li, J. C. Dong, X. Q. Li, and B. Y. Liu, *Polym. Chem.,* 2015, **6**, 6372-6377.

S5. D. Guzmána, X. Ramis, X. Fernández-Francos, S. D. L. Flor and A. Serraa, *Eur. Polym. J.,* 2017, **93**, 530-544.

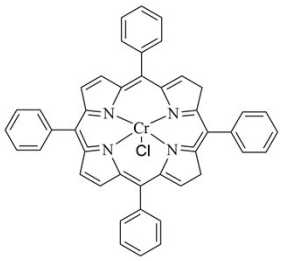
S6. J. Yue, X. Y. Li, G. J. Mo, R. Wang, Y. B. Huang and X. B. Jing, *Macromolecules*, 2010, **43**, 9645-9654.

S7. D. H. Nicole, Y. Li and H. C. Malcolm, *Macromolecules,* 2013, **46**, 692-698.

Table S1 Effect of complexes and epoxides on the SA and PA reactive sequence in the copolymerization.



(R,R,R,R)-5



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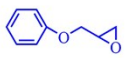
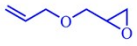
Epoxide monomers

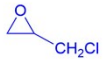


PGE



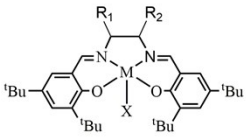
AGE

CHO

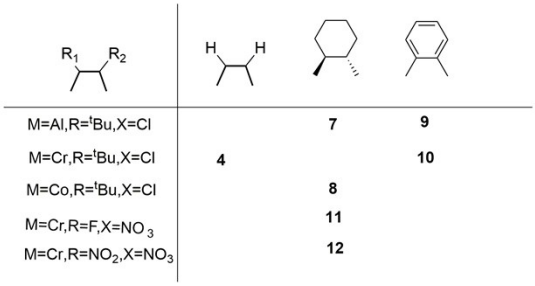


ECH

PO



4,7-12



Entry	CA	Epoxide	Complex	Temp (°C)	Time (h)	Yield [a] (%)	TOF [b] (h^{-1})	Ref.
1	SA	PGE	**5**	50	10.0	39	39	S8
2	PA	PGE	**5**	25	5.0	45	90	S8
3	SA	CHO	**6**	100	5.0	81	41	S9
4	PA	CHO	**6**	100	5.0	100	50	S9
5	SA	CHO	**7**	110	5.0	30	15	S10
6	PA	CHO	**7**	110	5.0	50	25	S10
7	SA	CHO	**8**	110	5.0	57	29	S10
8	PA	CHO	**8**	110	5.0	100	50	S10
9	SA	CHO	**9**	110	5.0	99	50	S10
10	PA	CHO	**9**	110	5.0	73	37	S10
11	SA	CHO	**10**	100	5.0	43	22	S9
12	PA	CHO	**10**	100	5.0	100	50	S9
13	SA	ECH	**11**	30	5.0	83	66	S11
14	PA	ECH	**11**	30	2.5	80	128	S11
15	SA	PO	**12**	30	1.5	11	28	S11
16	PA	PO	**12**	30	1.5	9	24	S11

[a] Determined by ^{1}H NMR. [b] Turnover frequency (TOF) = mol of consumed epoxide/mol of catalyst per hour. Entries 1 and 2: PGE/CA/catalyst/PPNCl/toluene molar ratio = 1000/500/1/2/500, Epoxides: 50 mmol. Entries 3-12: CHO/CA/Cat/DMAP=250/250/1/1, toluene: 0.9 mL, Epoxides: 2.5 mmol. Entries 13-16: Epoxides/CA/Cat/$PPNO_3$= 200:100:1:1, bulk polymerization.

References

S8. J. Li, B. H. Ren, W. M. Ren, H. Z and X. B. Lu. *J. Am. Chem. Soc.,* 2019, **141**, 8937-8942.

S9. S. Huijser, E. Hosseininejad, R. Sablong, C. d. Jong, C. E. Koning and R. Duchateau, *Macromolecules*, 2011, **44**, 1132-1139.

S10. E. Hosseini, N. C. G. W. van Melis, C. E. Koning and R. Duchateau, *Macromolecules,* 2012, **45**, 1770-1776.

S11. A. M. DiCiccio, J. M. Longo, G. G. Rodríguez-Calero and G. W. Coates. *J. Am. Chem. Soc.* 2016, **138**, 7107-7113.

Table S2 Effect of reaction conditions on the copolymerization of EGE/SA[a]

Entry	SA/EGE	Temp (℃)	Time (h)	Yield [b] (%)	TOF (h^{-1})	M_n [c] (g/mol)	$Đ$ [c]
1	250/250	85	2.0	60.8	76	5600	1.86
2	250/250	90	2.0	87.1	109	7600	1.91
3	250/250	100	1.0	60.1	150	5900	1.95
4	250/250	100	2.0	~100	125	8000	2.06
5	250/250	110	1.0	95.1	238	8500	1.97
6	350/350	110	1.0	82.1	277	7100	1.88
7	500/500	110	1.0	60.9	305	5600	1.91
8	500/500	110	2.0	96.3	241	7900	1.93

[a] Dinuclear [OSSO]CrCl(Cr)/PPNCl=1/1, toluene: 1.0 mL, EGE: 1.65g (7.5 mmol) ; [b] According to isolated mass; [c] Determined by gel permeation chromatography in THF.

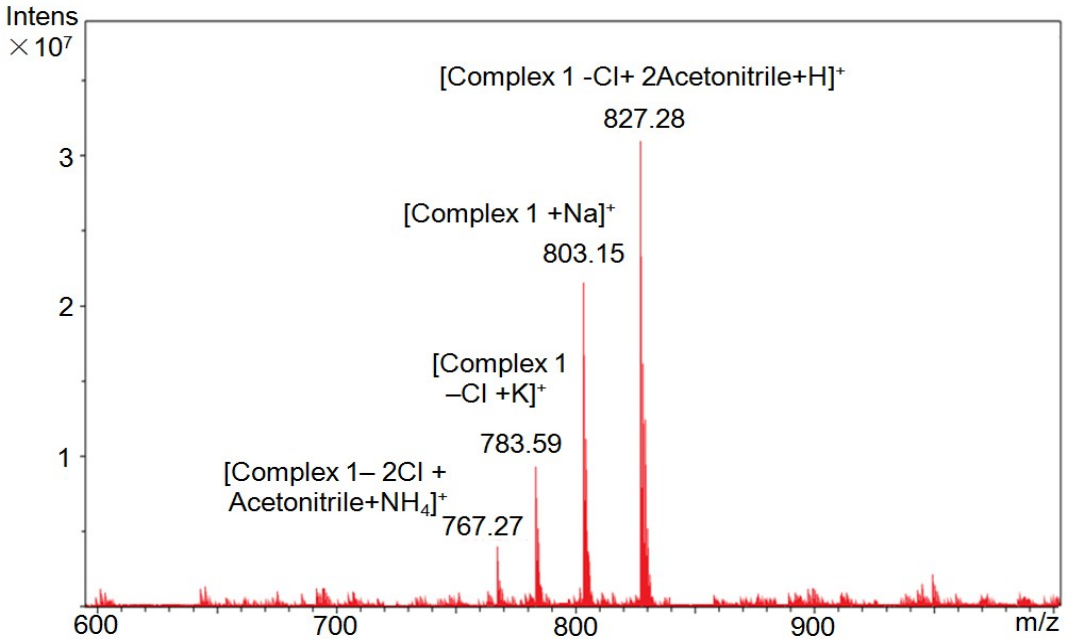


Fig. S1 ESI-MS spectrum of Complex **1**.

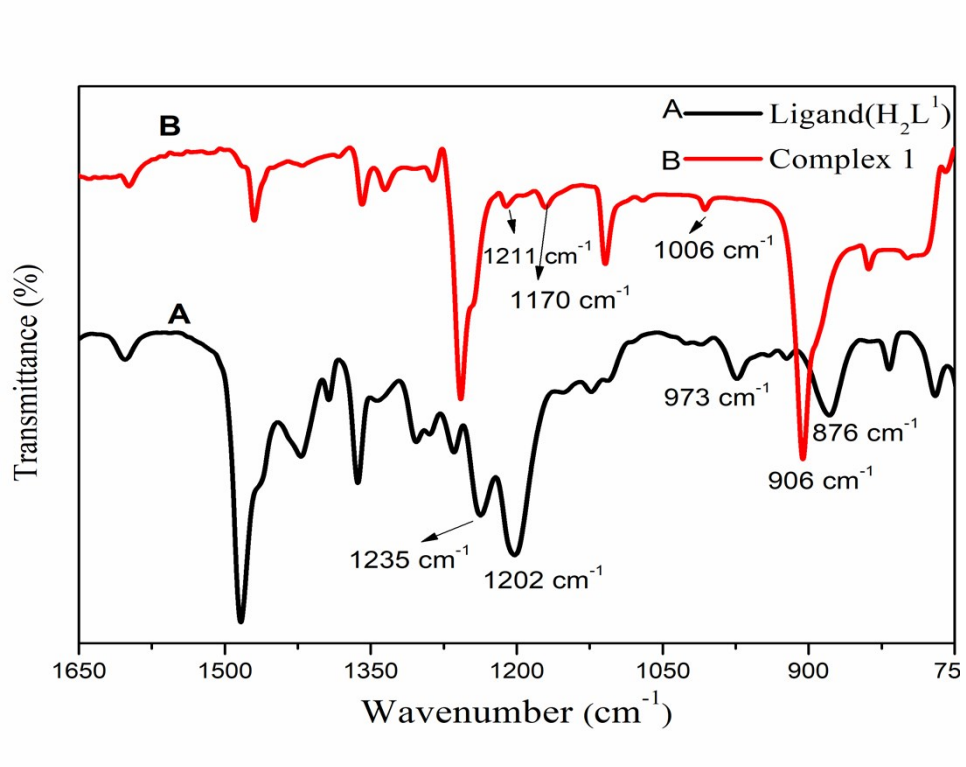


Fig. S2 IR spectra of Ligand (H_2L^1) and Complex **1**.

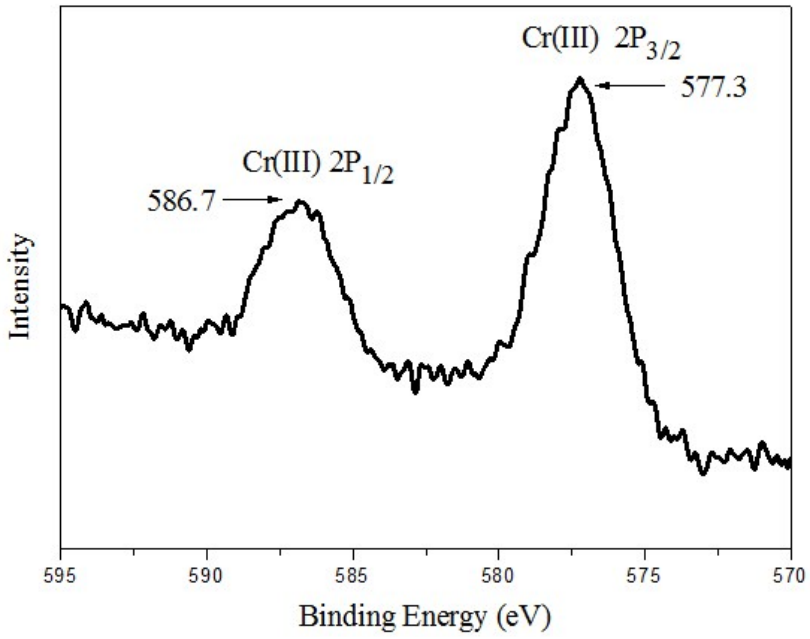


Fig. S3 XPS spectrum of Complex **1**.

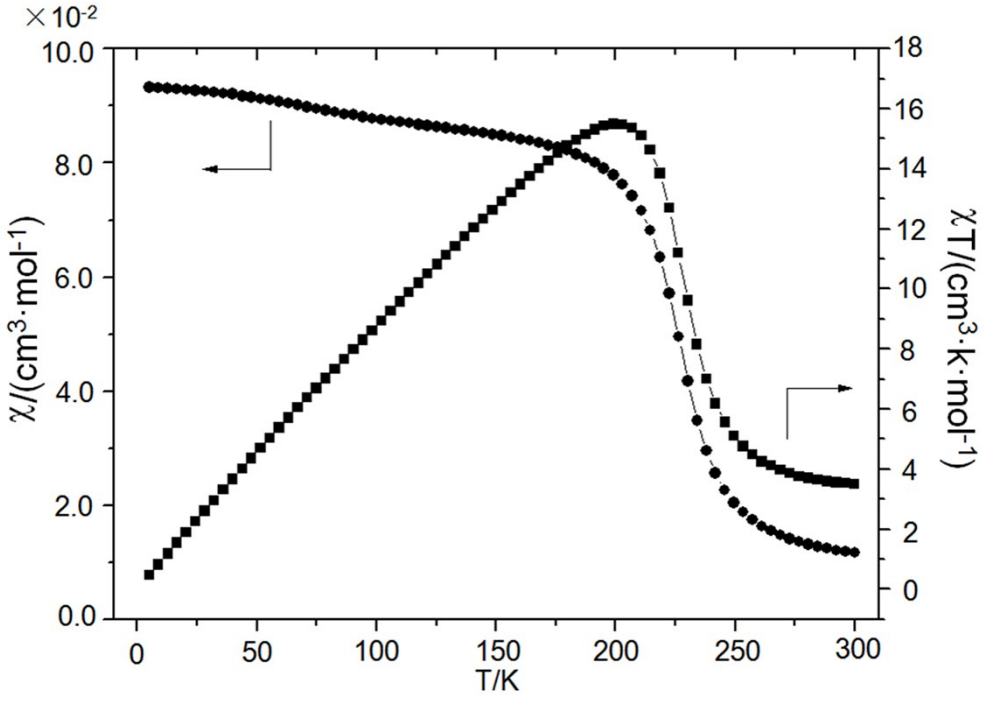


Fig. S4 Magnetic susceptibility (χ) and χT *vs* T Plots for Complex **1**.

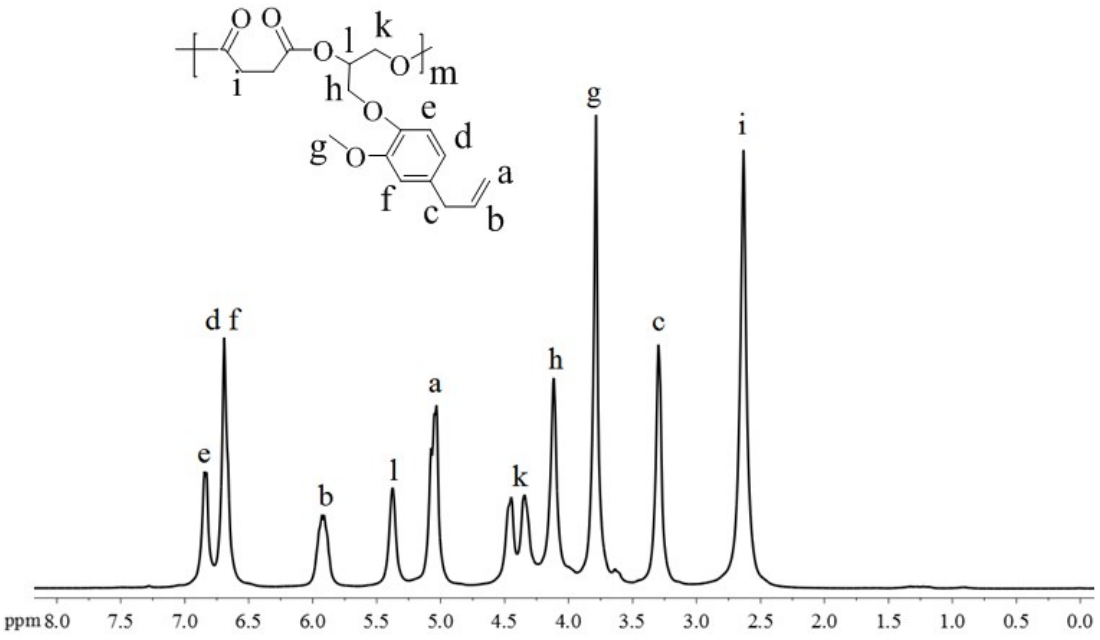


Fig. S5 ^{1}H NMR spectrum of poly(SA-*alt*-EGE) (Entry 6, Table 2).

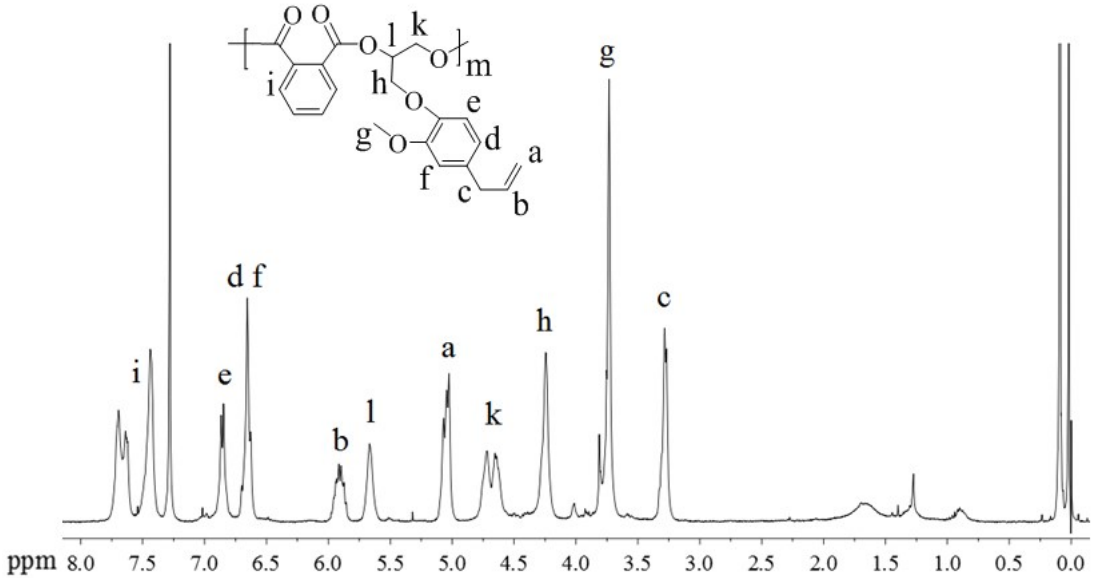


Fig. S6 ^{1}H NMR spectrum of poly(PA-*alt*-EGE) (Entry 5, Table 2).

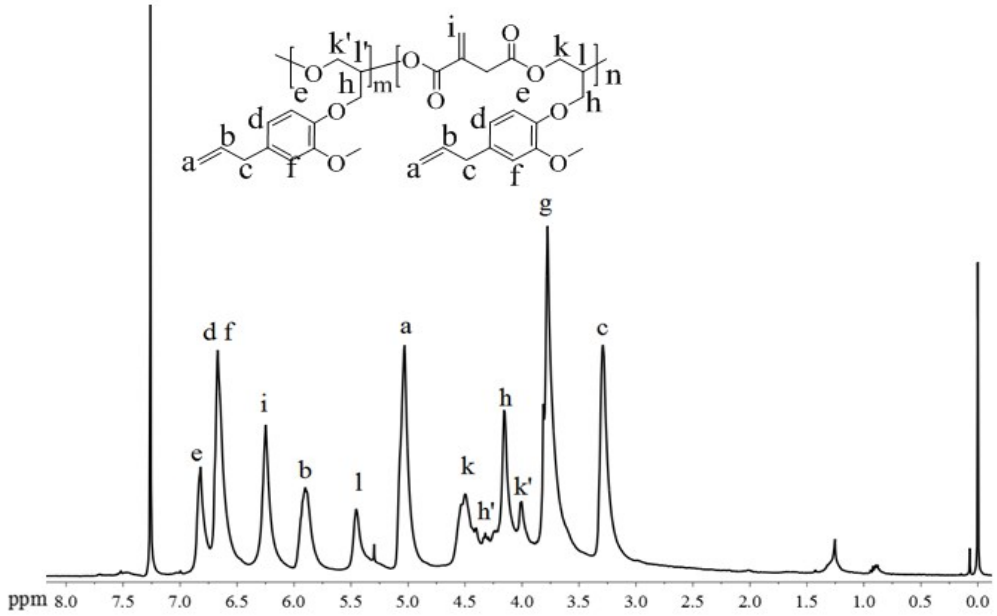


Fig. S7 ^{1}H NMR spectrum of poly(IA-*alt*-EGE) (Entry 1, Table 2).

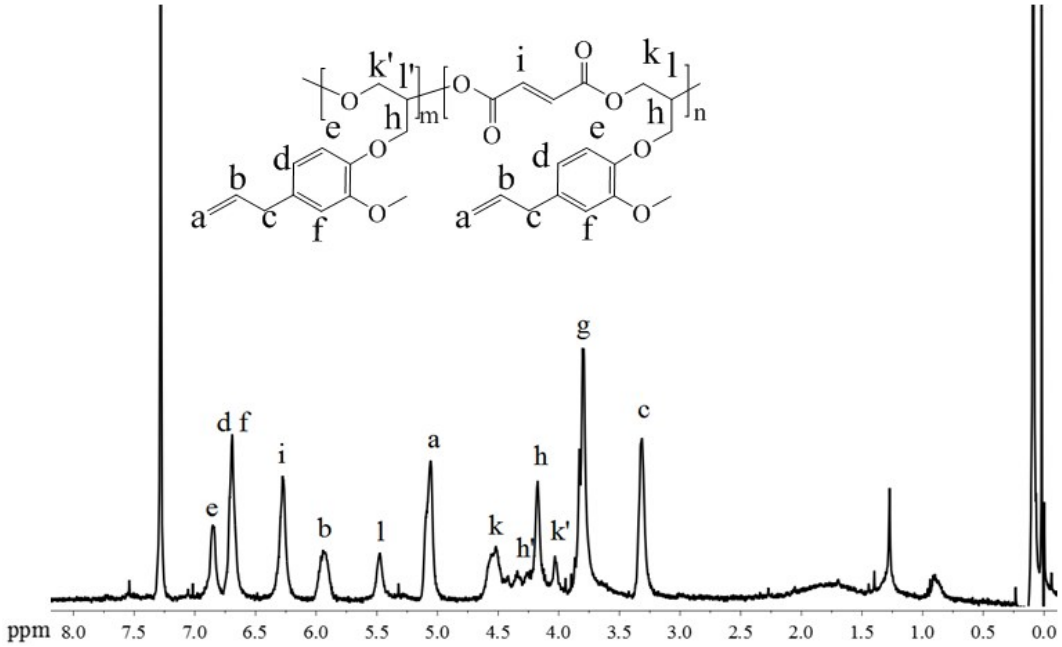


Fig. S8 ^{1}H NMR spectrum of poly(MA-*alt*-EGE) (Entry 2, Table 2).

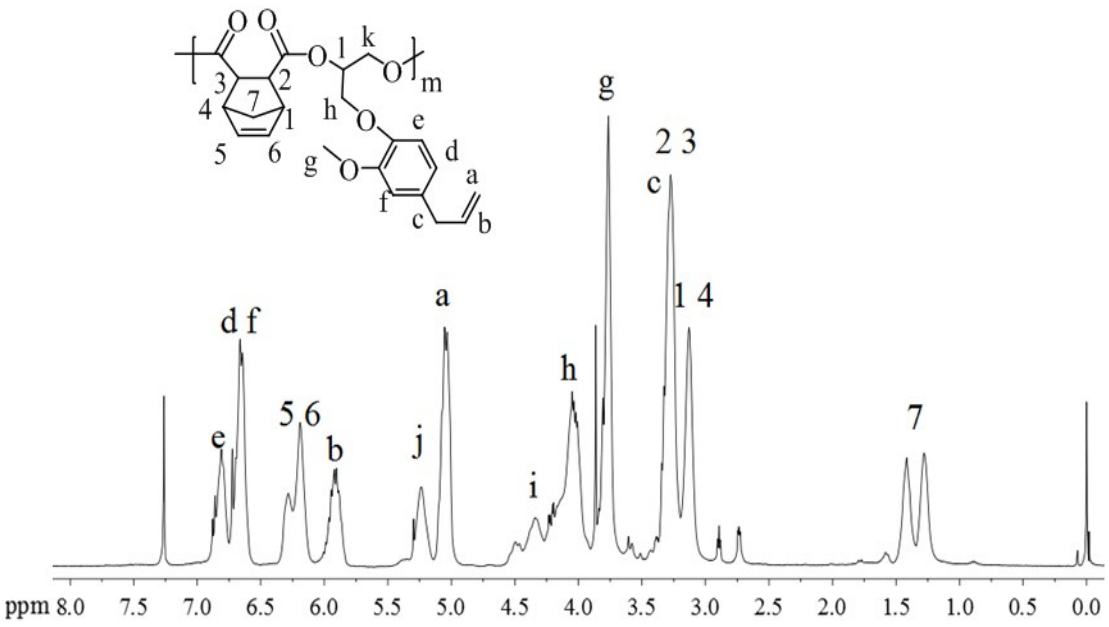


Fig. S9 ^{1}H NMR spectrum of poly(NA-*alt*-EGE) (Entry 4, Table 2).

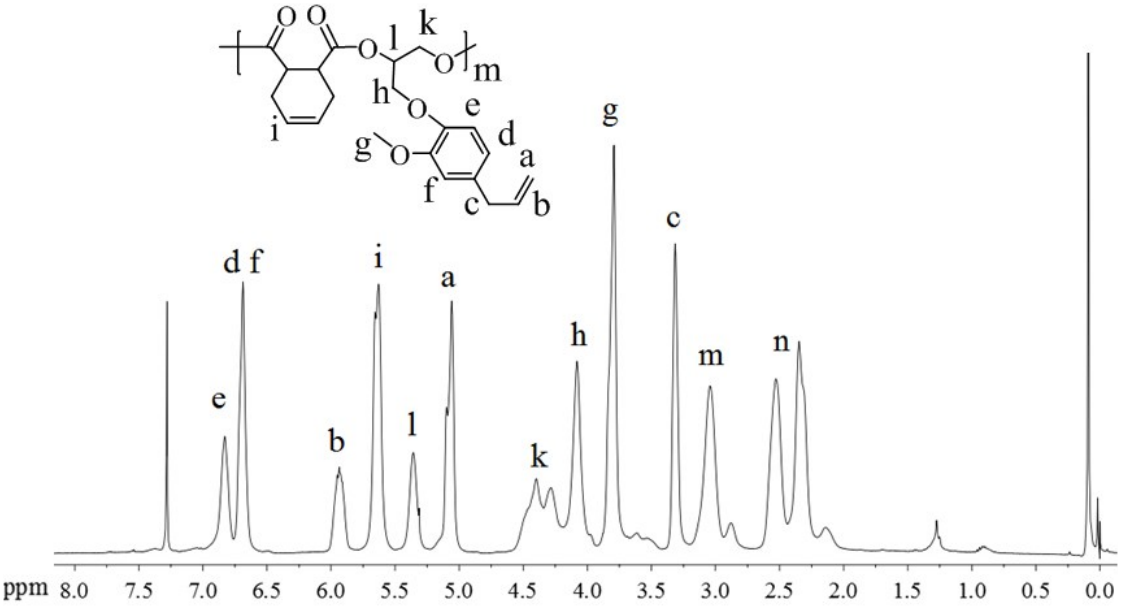


Fig. S10 ^{1}H NMR spectrum of poly(THPA-alt-EGE) (Entry 3, Table 2).

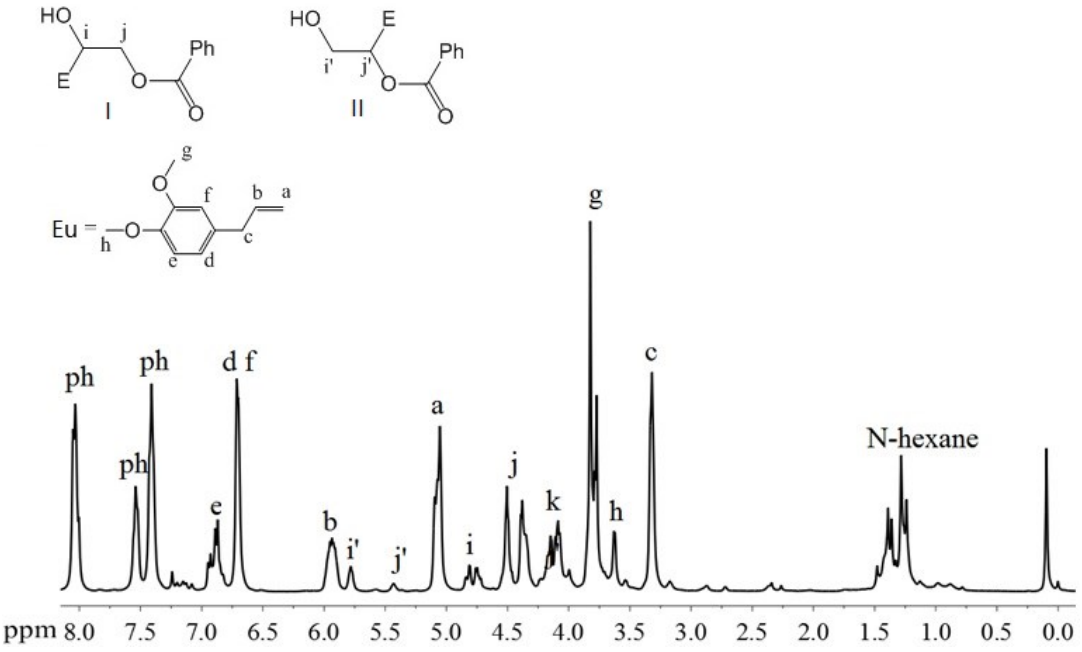


Fig. S11 ^{1}H NMR spectrum of the product obtained by the reaction of EGE with benzoic acid under EGE/Complex **1**/PPNCl=100:1:2 (molar ratio) at 90 ℃ for 48 h. Complex **1** (59 mg, 0.075mmol), PPNCl (86 mg, 0.15 mmol), EGE (1.5 mL, 75mmol), benzonic acid (0.915g, 75mmol), and toluene (1.0 mL).

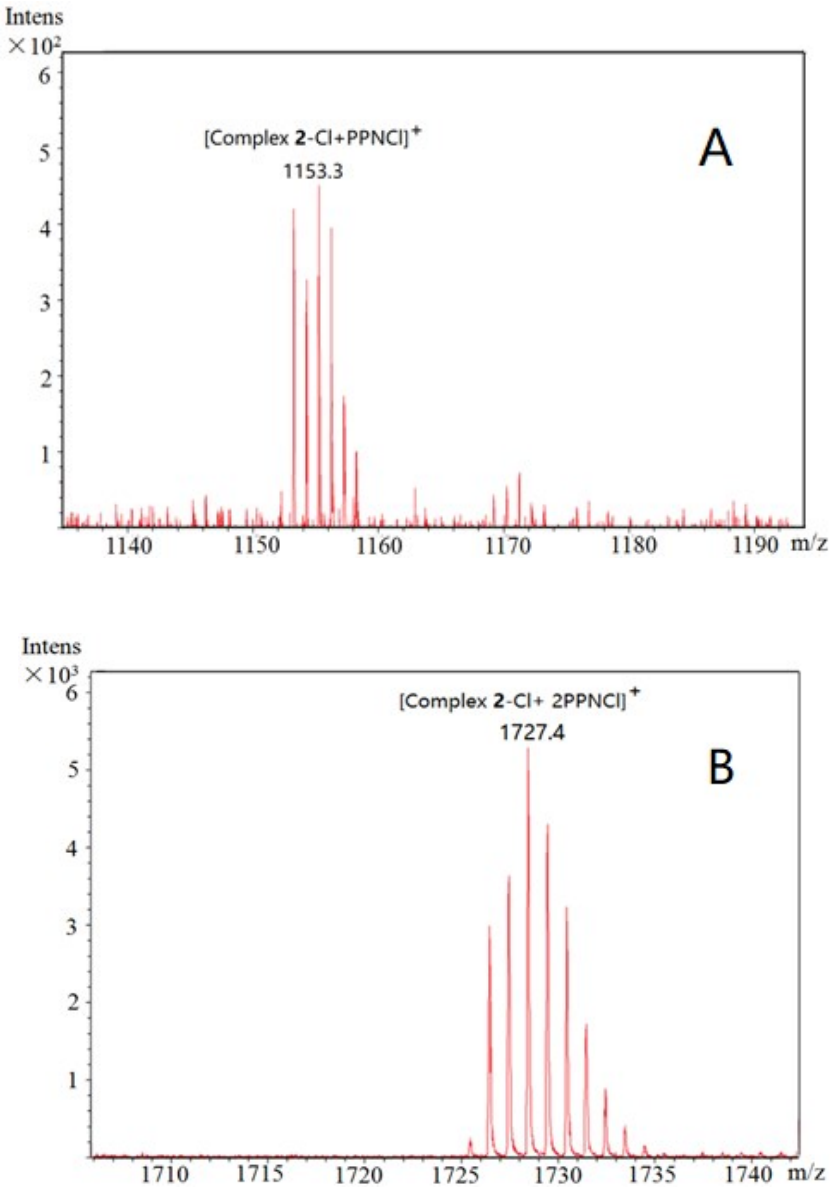


Fig. S12 ESI-MS spectra of products formed by reacting Complex **2** with 10 equivalents of PPNCl. (The theoretical distribution of isotope peak: 1153.3: 1154.3: 1155.3: 1156.3= 100: 80: 30: 20, found 537.2: 538.2: 539.2: 540.2= 100: 87: 39: 23; 1726.5: 1727.5: 1728.5: 1729.5: 1730.5: 1731.5= 78: 100: 73: 63: 24: 15, found 1726.4: 1727.4: 1728.4: 1729.4: 1730.4: 1731.4= 68: 100: 80: 60: 27: 16)

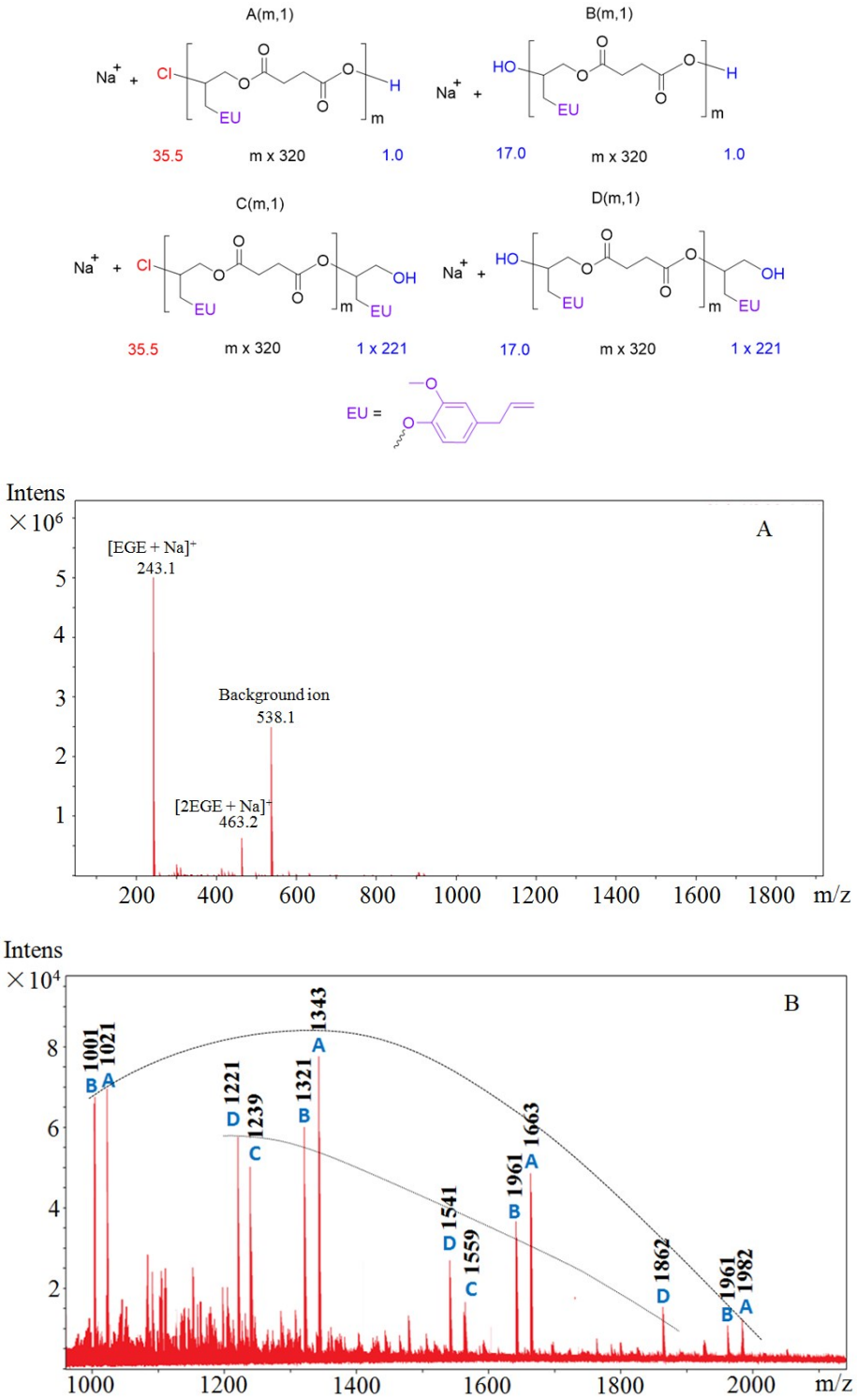


Fig. S13 The whole (A) and partial enlarged (B) view of ESI-MS spectrum of SA/EGE copolymer produced by ROCOP of EGE and SA. ([SA]/[EGE]/ Complex **1**[Cr]/[PPNCl]=250/250/1/1, Temperature: 90°C, Time: 2 h, toluene: 1.0 mL, Complex **1**: 0.0117 g (0.03 mmol Cr), EGE:1.65 g (7.5 mmol)).

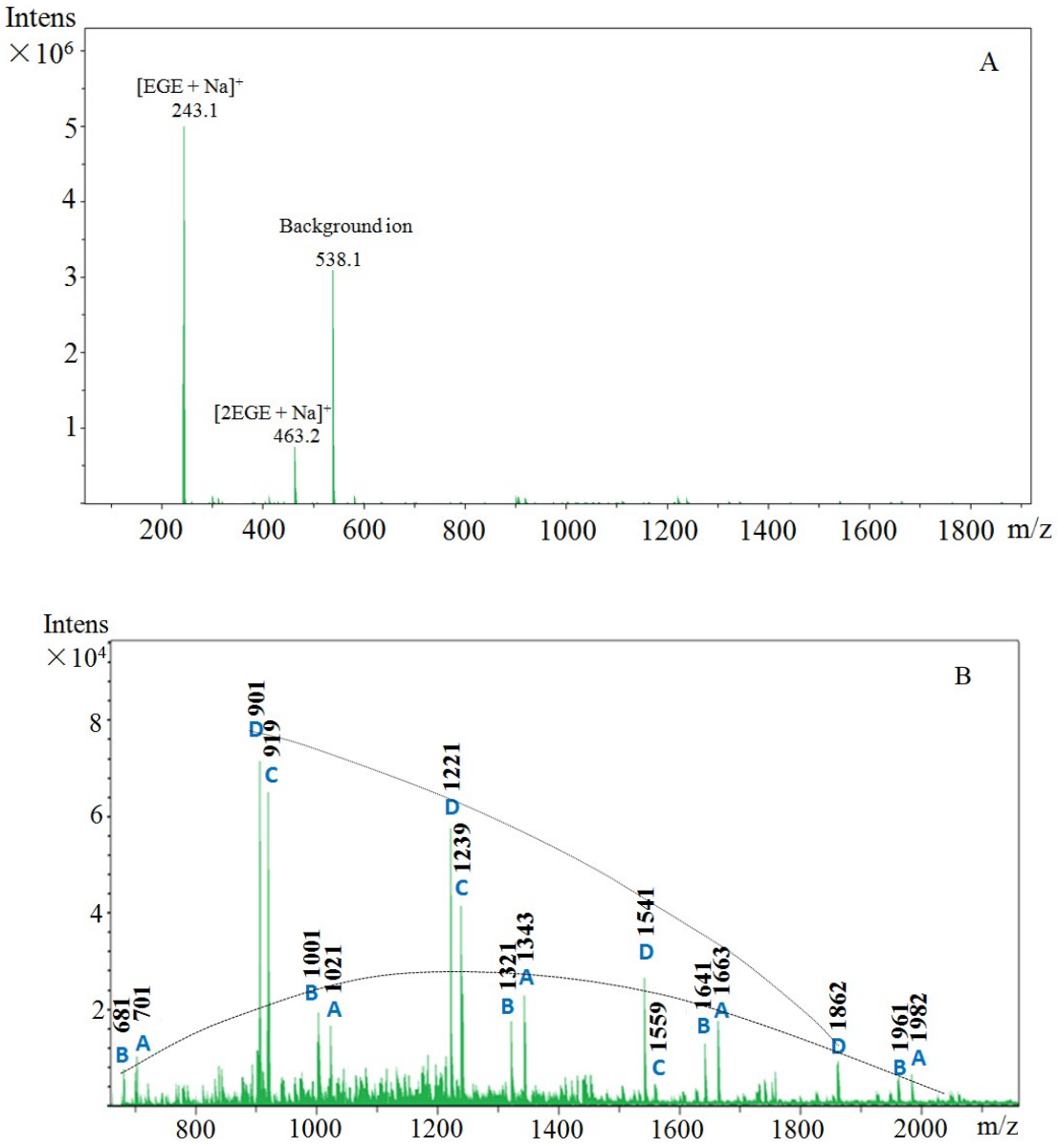


Fig. S14 The whole (A) and partial enlarged (B) view of ESI-MS spectra of SA/EGE copolymer under H_2O as chain transfer agent. ([SA]/[EGE]/Complex **1**[Cr]/[PPNCl]/H_2O=250/250/1/1/10, Temperature: 90°C, Time: 2.0 h, toluene:1.0 mL, Complex 1: 0.0117 g (0.03 mmol Cr), EGE:1.65 g (7.5 mmol)).

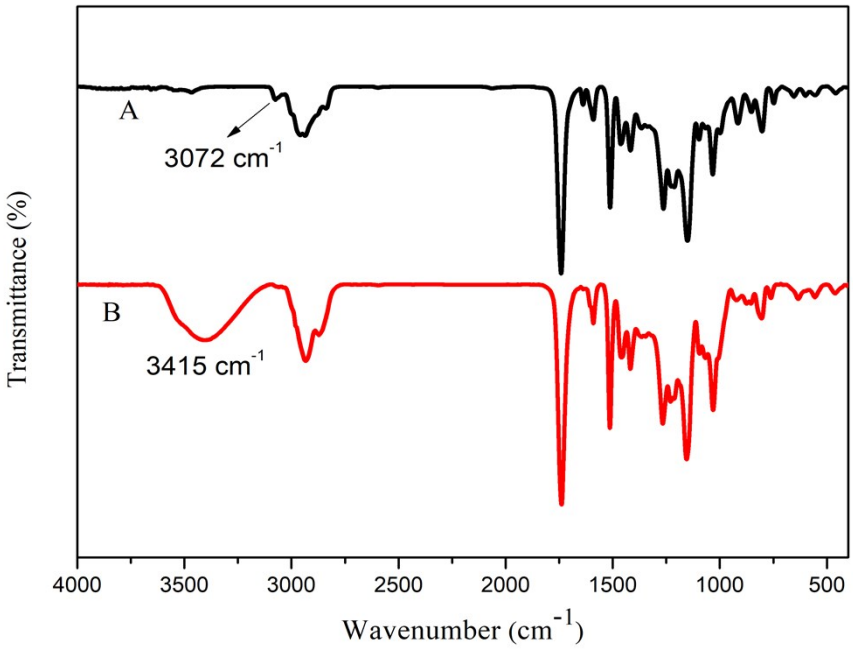


Fig. S15 IR spectra of poly(SA-*alt*-EGE) before (A) and after (B) modification by *thiol-ene* reaction.

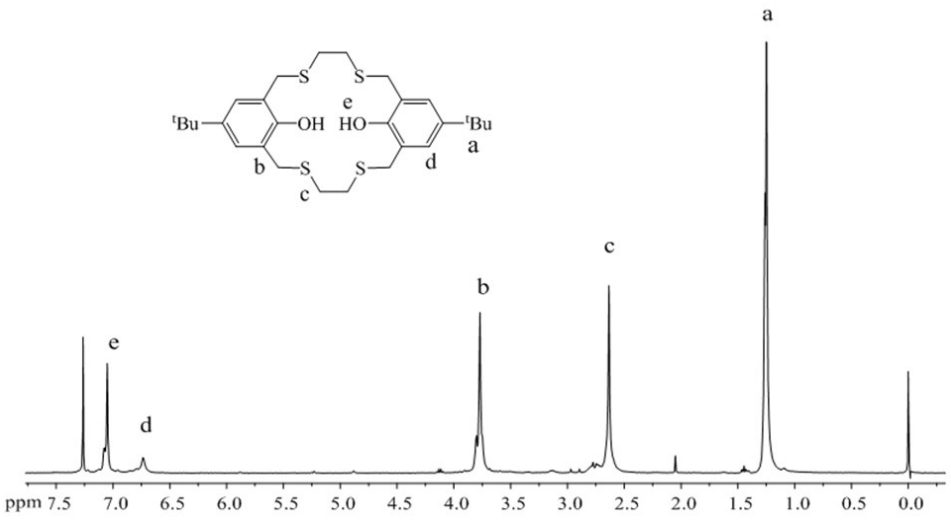


Fig. S16 ^{1}H NMR spectrum of H_2L^1.

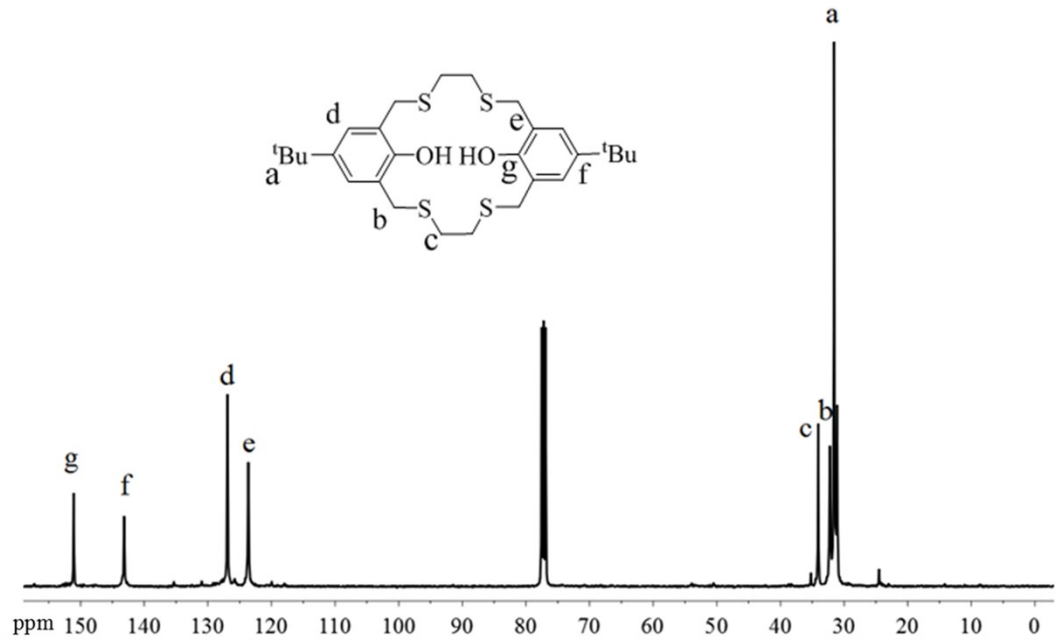


Fig. S17 ^{13}C NMR spectrum of H_2L^1.

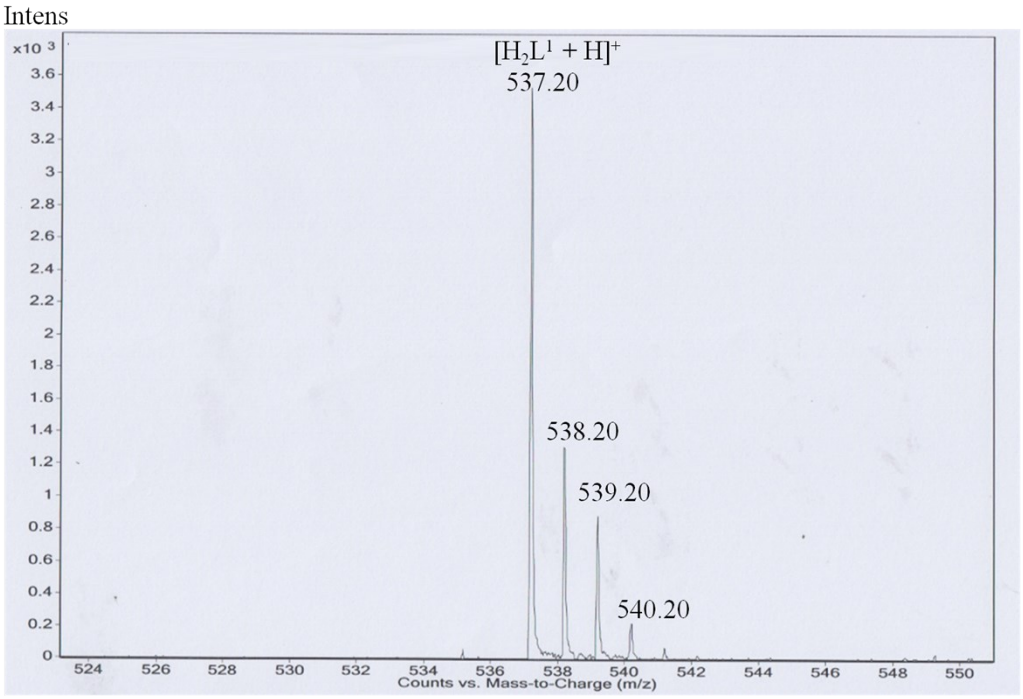


Fig. S18 ESI-MS spectrum of H_2L^1. (The theoretical distribution of isotope peak: 537.2: 538.2: 539.2: 540.2= 100: 33: 19: 6, found 537.20: 538.20: 539.20: 540.20= 100: 34: 22: 5).