

SUPPORTING INFORMATION

Novel Chromium Complex with [OSSO]-type Bis(phenolato) Dianionic Ligand-mediated Alternating Ring-opening Copolymerization of Epoxides and Phthalic Anhydride

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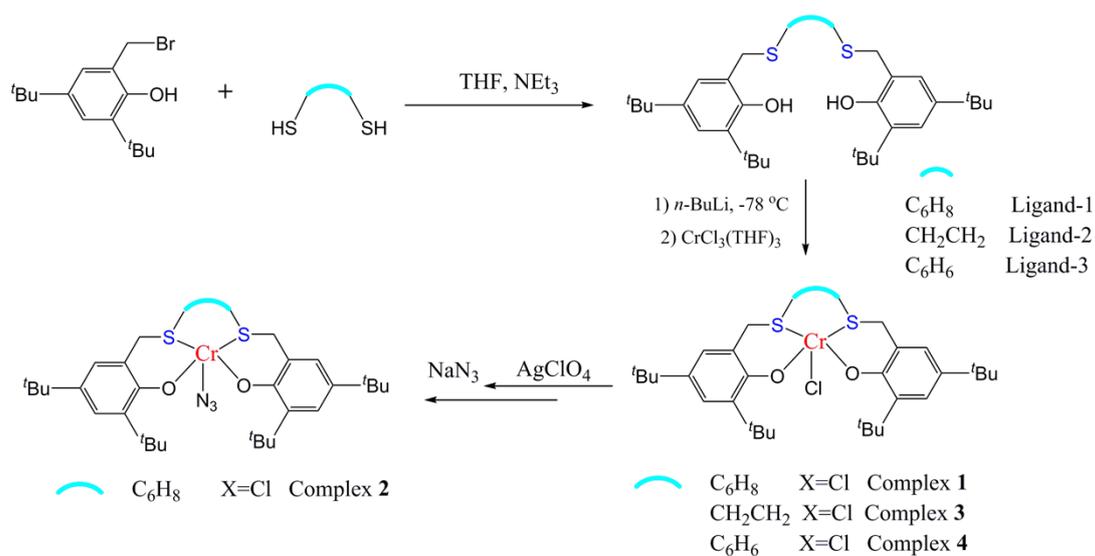
1. General Materials.

Unless otherwise special, 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. *Trans*-1,2-cyclohexanedithiol¹ and 3,5-*di-tert*-butyl-2-hydroxybenzylbromid² were synthesized according to literatures. Toluene and tetrahydrofuran (THF) was refluxed and distilled over Na-benzophenone under nitrogen. Dichloromethane (CH₂Cl₂) and acetonitrile (CH₃CN) were refluxed and distilled over CaH₂ before use. CrCl₃(THF)₃ (Aldrich, 98%), NaN₃(99%, Acros), and *n*-BuLi (2.5 mol/L in hexane, Beijing Ouhechem. Co. China).

2. Characterization

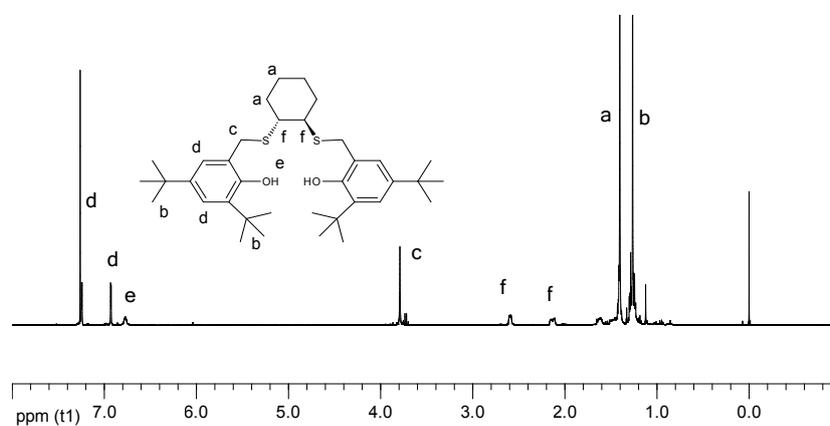
¹H spectra were recorded on a Bruker-400 spectrometer at frequencies of 400 MHz (¹H). Their peak frequencies were referenced versus an internal standard (TMS) shifts at 0 ppm for ¹H NMR and against the solvent. Infrared (IR) spectra were obtained on a Bruker Vector 22 spectrometer at a resolution of 4 cm⁻¹ (16 scans collected). The glass transition temperatures (*T*_g) of polymers were determined at a heating rate of 10 °C/min on Perkin-Elmer Diamond Differential Scanning Calorimetry instrument. Molecular weight determinations were performed using a PL-GPC 220 instrument with a refractive index detector. The columns used was MIXED-B 300×7.5mm columns held at 40 °C, using THF as eluent at a flow rate of 1.0 mL/min. ESI-MS were performed on a Thermo Finnigan LCQ Advantage spectrometer in ESI mode with a spray voltage of 4.8 kV and a spray current of 0.24 μA, capillary temperature 230 °C.

3. Synthesis of Ligands



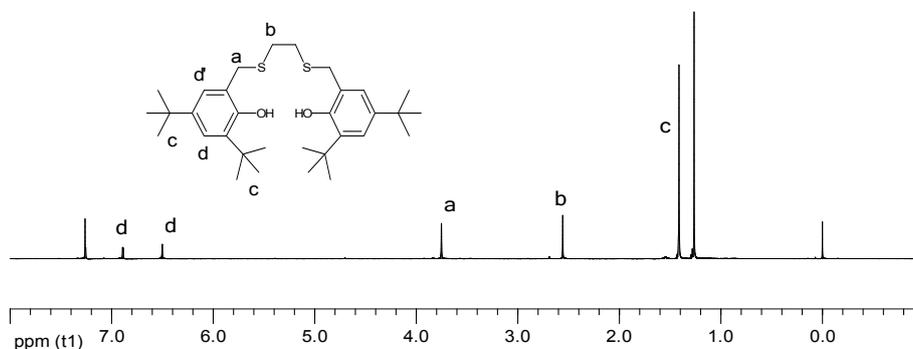
Ligand 1

It was synthesized according to the literature.^[3](A. Ishii, T. Toda, N. Nakata and K. Asajima, *Organometallics*. 30, 2011, 2947-2956) ¹HNMR (400MHz, CDCl₃) δ : 1.19-1.43 (*m*, 44 H), 2.09-2.15 (*m*, 2 H), 2.58-2.61 (*m*, 2 H), 3.79 (*s*, 4 H), 6.75 (*s*, 2 H), 6.93 (*d*, 2 H), 7.25 (*d*, 2 H) ppm. FT-IR: 1236 cm⁻¹($\nu_{\text{C-S}}$)



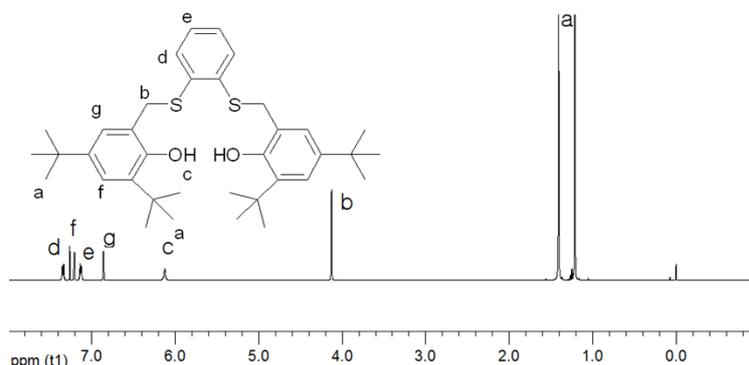
Ligand 2

^1H NMR (400MHz, CDCl_3) δ : 1.28 (s, 18H), 1.41 (s, 18H), 2.56 (s, 4H), 3.75 (s, 4H), 6.5(s, 2H), 6.89(s, 2H). FT-IR: $1238\text{ cm}^{-1}(\nu_{\text{C-S}})$



Ligand 3

^1H NMR (400MHz, CDCl_3) δ : 1.22 (s, 18H), 1.41 (s, 18H), 4.14 (s, 4H), 6.12 (d, 2H), 6.85 (d, 2H), 7.11-7.15 (c, 2H), 7.20 (d, 2H), 7.33-7.37 (c, 2H) ppm. FT-IR: $1230\text{ cm}^{-1}(\nu_{\text{C-S}})$



4. Synthesis of Complexes 1-4

4.1 Synthesis of Complexes 1, 3, 4

The chromium complexes were synthesized as previously described.⁴ *n*-BuLi (1.26ml, 3.15 mmol) was added dropwise to a stirred solution of ligand (1.5 mmol) in THF (15ml) at -78°C . The mixture was warmed to room temperature and further stirred 1h, and then drop to a flask containing $\text{CrCl}_3(\text{THF})_3$ (0.614g, 1.64 mmol). Following an immediate color change of the chromium starting material from purple to dark green, the reaction mixture was stirred for 48 h at room temperature. The resulting suspension was filtered, and the solid was collected and vacuum-dried. The solvent was removed in vacuo, and the resulting solid was redissolved in

dichloromethane. The mixture was filtered to remove LiCl, and solvent was removed in vacuo, yielding a dark green powder.

Complex 1

Yield: 96%. Negative ESI-MS (m/z): [M-Cr-Cl]⁻: 583.0, Found 583.27. FT-IR: 1245 cm⁻¹(ν_{C-S}).

Complex 3

Yield: 96%. Negative ESI-MS (m/z): [M-Cr-Cl]⁻: 528.90, Found 529.20. FT-IR: 1243 cm⁻¹(ν_{C-S}).

Complex 4

Yield: 93 %. Negative ESI-MS (m/z): [M-Cr-Cl]⁻: 576.90, Found 577.80. FT-IR: 1243 cm⁻¹ (ν_{C-S}).

4.2 Complex 2

The synthetic route is according to literature reported.⁵ 0.5 mmol of complex **1** was dissolved in 10 mL of CH₃CN. In another Schlenk flask, 0.5mmol of AgClO₄ was dissolved in an equal volume of CH₃CN. The [OSSO]CrCl solution was then cannulated into the silverperchlorate solution. Immediate precipitation of AgCl was observed, and the reaction was allowed to stir overnight. 1.5 mmol of NaN₃ was added under argon atmosphere. The reaction was stirred for an additional 24 h. The mixture was diluted with distilled diethyl ether and the organic portion washed with water to remove NaClO₄ and excess NaN₃, dried with Na₂SO₄ and the solvent removed in vacuum, yielding a dark green powder. Yield: 96%. Negative ESI-MS (m/z): [M+CH₃CN]⁻: 718.05, Found 718.13. FT-IR: 2104 cm⁻¹(ν_{N₃}) and 1245 cm⁻¹(ν_{C-S}).

References

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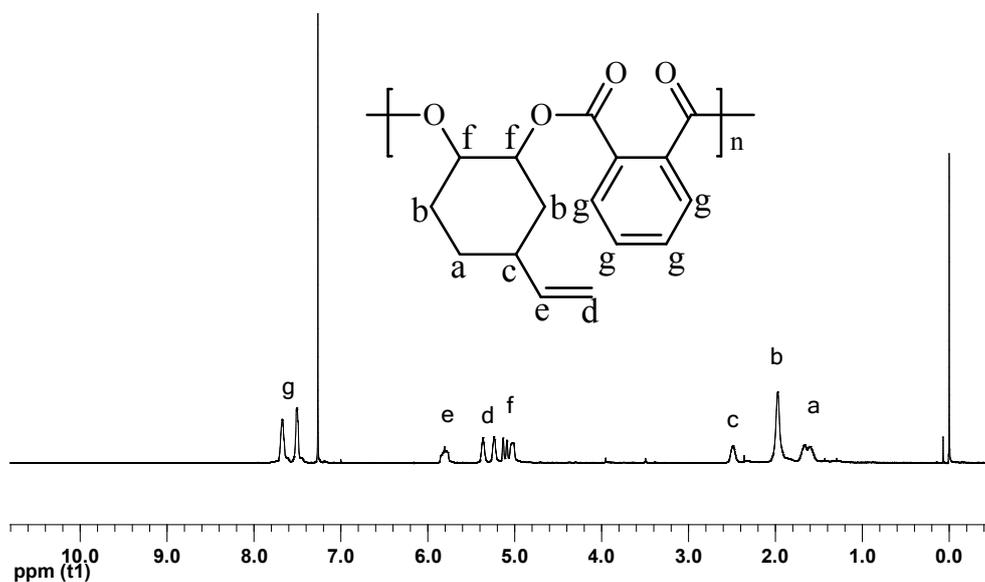


Figure S1. Representative ^1H NMR spectrum of the poly(4-VCHO-*alter*-PA) obtained from complex **1**

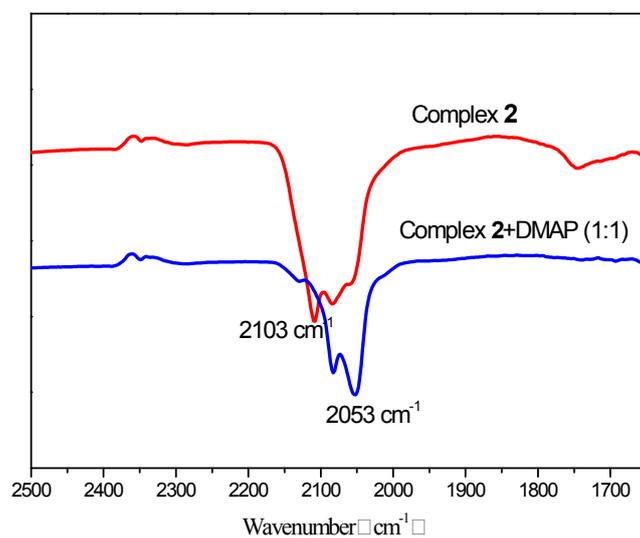


Figure S2. IR spectra of azide stretching vibration ($\nu(\text{N}_3)$) of complex **2** and its mixtures of complex **2**/DMAP (molar ratio 1:1)

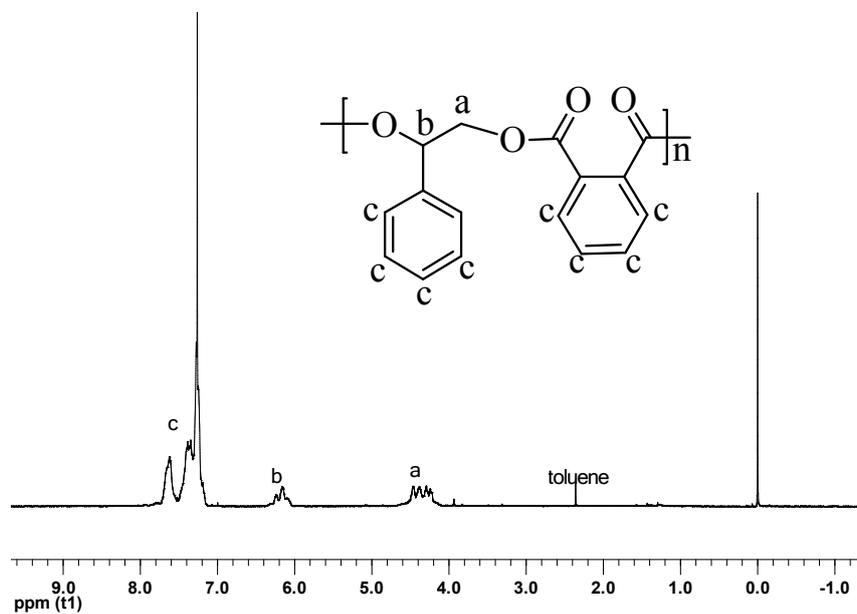


Figure S3. ¹H NMR spectrum of the poly(SO-*alter*-PA) (entry 7, Table 1)

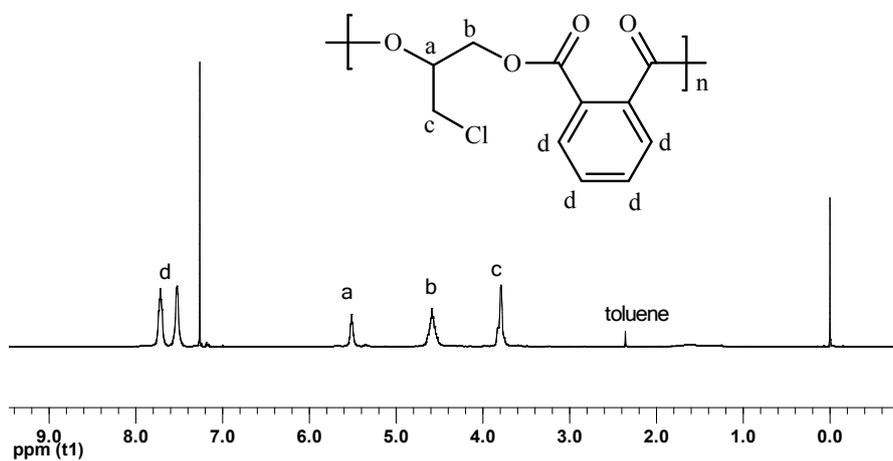


Figure S4. ¹H NMR spectrum of the poly(ECH-*alt*-PA) (entry 8, Table 1)

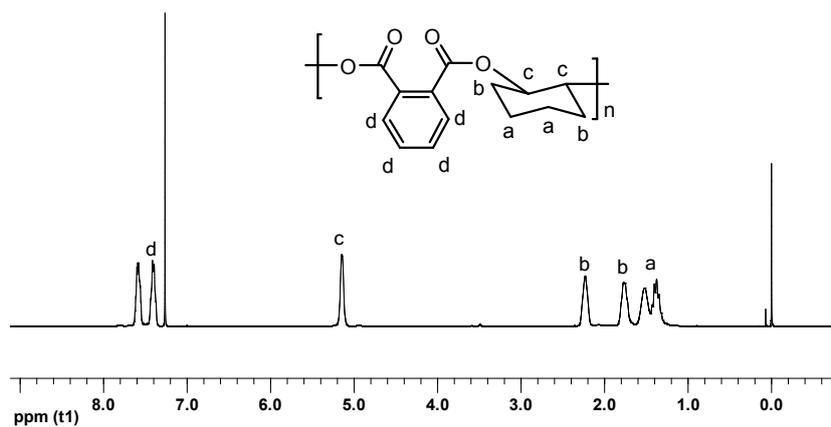


Figure S5. ¹H NMR spectrum of the poly(CHO-*alt*-PA) (entry 9, Table 1)

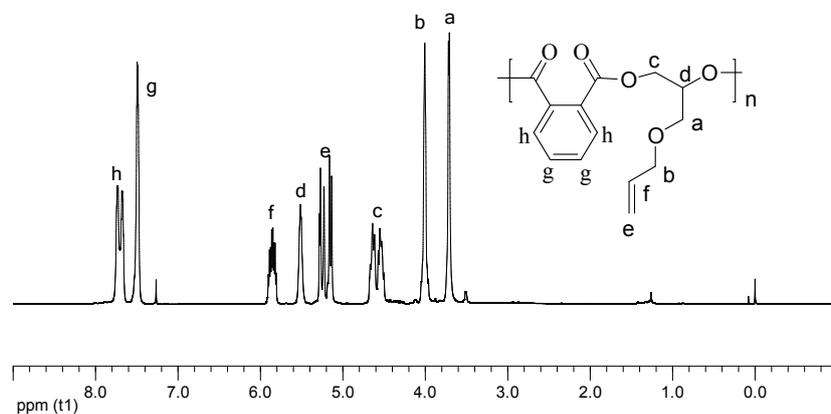


Figure S6. ¹H NMR spectrum of the poly(AGE-*alt*-PA) (entry 10, Table 1)

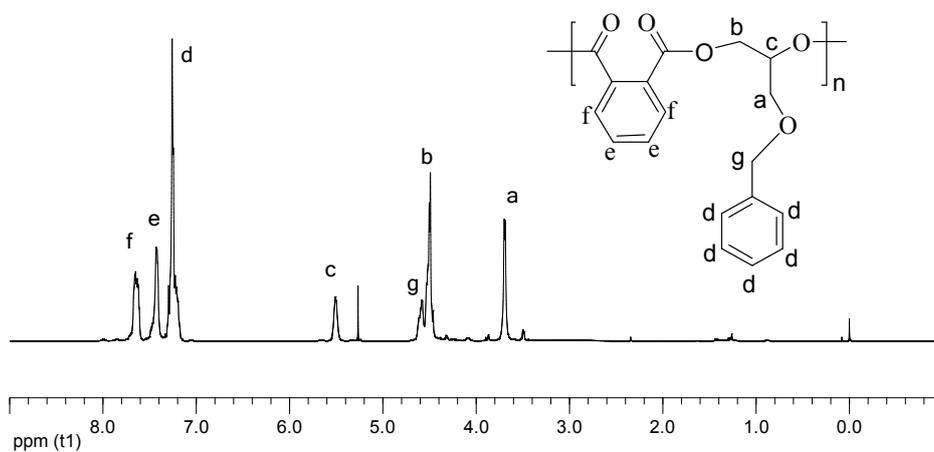


Figure S7. ¹H NMR spectrum of the poly(BGE-*alt*-PA) (entry 10, Table 1)

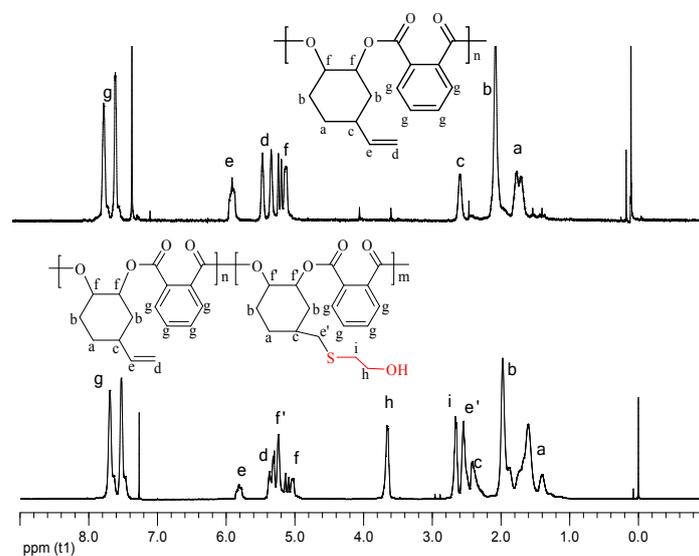


Figure S8. ¹H NMR spectra of polyesters obtained by 4-VCHO/PA and its post-modification by *thiol-ene* reaction with 2-mercaptoethanol

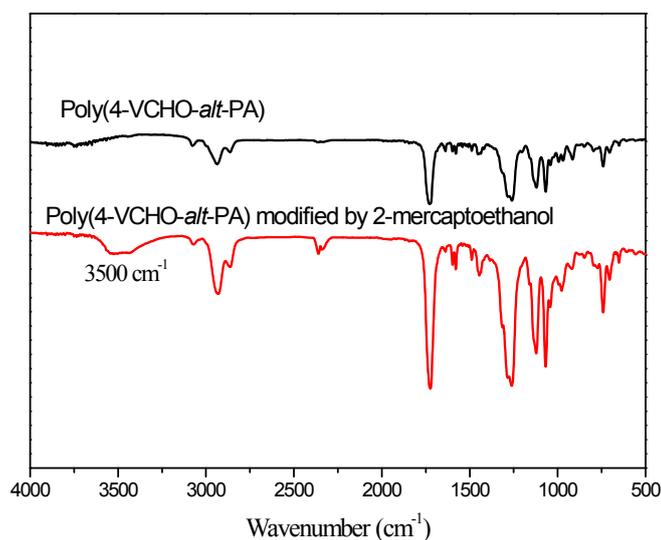


Figure S9. IR spectra of poly(4-VCHO-*alt*-PA) and its post-modification product by *thiol-ene* reaction with 2-mercaptoethanol