Supporting Information for
Highly Regioselective and Alternating Copolymerization of Carbonyl Sulfide with Phenyl Glycidyl Ether

EXPERIMENTAL

Materials and Methods. Unless otherwise specified, all syntheses and manipulations were carried out on a double-manifold Schlenk vacuum line under an atmosphere of argon or in an argon-filled glovebox. Following purification, materials were stored in an argon-filled glovebox prior to use unless otherwise specified. Phenyl glycidyl ether was purchased from TCI and distilled under reduced pressure over CaH₂. Carbonyl sulfide (99.0%, 0.756 lbs) was purchased from Specialty Gases of America Inc., and used directly. (R,R)-N,N'-bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediamino chromium(III) chloride, (salen)CrCl, was purchased from Strem and used as received. Dichloromethane and toluene were purified by an MBraun Manual Solvent Purification System packed with Alcoa F200 activated alumina desiccant.

Nuclear Magnetic Resonance (NMR). ¹H and ¹³C NMR spectra were recorded on Mercury 300 MHz and Inova 300 MHz spectrometers. The peak frequencies were referenced versus the internal standard (TMS) shift at 0 ppm for ¹H NMR and against the solvent chloroform-d at 77.0 ppm for ¹³C NMR.

Gel Permeation Chromatography (GPC). Molecular weight determinations (Mₙ and Mₘ) were carried out with a Malvern modular GPC apparatus equipped with ViscoGEL I-series columns (H+L) and Model 270 dual detector composed of RI and light scattering detectors. The curve was calibrated using monodisperse polystyrene standards covering the molecular weight range from 580 to 460,000.
Da. In addition, THF was used as eluent for all GPC measurement, the flow-rate is 1 ml/min.

**Differential Scanning Calorimetry (DSC).** The glass transition temperature ($T_g$) of the resultant copolymer was determined by using a Mettler Toledo differential scanning calorimetry. The sample was heated from room temperature to 150°C at a rate of 10°C/min, then cooled to 0°C at a rate of -10°C/min, finally heated from 0°C to 150°C at a rate of 5°C/min. $T_g$ was determined from the third run.

**Copolymerization of Carbonyl Sulfide and Phenyl Glycidyl Ether.** The copolymerization of carbonyl sulfide (COS) and phenyl glycidyl ether (PGE) was performed in a 10 mL autoclave equipped with a magnetic stirrer and a barometer. In a typical experiment (entry 1 in Table 1), the autoclave was first dried in an oven for 24 hours and transferred into the glovebox. (Salen)CrCl, PPNCl and 2.22 mmol PGE were added into the autoclave successively. The autoclave was pressurized to 1 MPa pressure with COS and put into an oil bath of 20 °C, and the reaction mixture was stirred for 2 hours. After copolymerization, an aliquot was taken from the crude product for the determination of the conversion rate of PGE and the percentage of polymer versus cyclic product as shown by the $^1$H NMR spectrum. Subsequently, the crude product was dissolved in dichloromethane (2 mL) and precipitated from methanol (20 mL) three times. The yellow precipitate was collected and dried in vacuum at 40 °C overnight, and the resulting copolymer was analyzed by $^1$H NMR, $^{13}$C NMR and GPC.

**Schemes and figures:**
Scheme S1. The structure of the binary (salen)CrCl/PPNCl catalyst.

Figure S1. The $^{13}$C NMR spectrum of the crude product of entry 1 in Table 1.

Figure S2. The $^1$H NMR spectrum of the crude product of entry 2 in Table 1.
Figure S3. The $^1$H NMR spectrum of the crude product of entry 3 in Table 1.

Figure S4. The $^1$H NMR spectrum of the crude product of entry 4 in Table 1.
Figure S5. The $^1$H NMR spectrum of the crude product of entry 5 in Table 1.

Figure S6. The DSC curve of the copolymer of entry 1 in Table 1.

Figure S7. The MALDI-TOF spectrum of the copolymer from COS and PGE.
Figure S8. The GPC curve of the copolymer from entry 1 in Table 1.

Figure S9. The GPC curve of the copolymer from entry 2 in Table 1.
**Figure S10.** The GPC curve of the copolymer from entry 4 in Table 1.

**Figure S11.** The GPC curve of the copolymer from entry 5 in Table 1.

**Figure S12.** The GPC curve of the copolymer from entry 6 in Table 1.
**Figure S13.** The GPC curve of the copolymer from entry 7 in Table 1.

**Figure S14.** The thermogravimetric analysis (TGA) trace of the COS/PGE copolymer (entry 1, Table 1).