SUPPORTING INFORMATION

for

Trivalent Cobalt Complex Mediated Formation of Stereoregular CO_2 Copolymer from Phenyl Glycidyl Ether

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1. General information

NMR ^{1}H and ^{13}C NMR spectra were recorded on a Varian INOVA-400 MHz type (^{1}H, 400 MHz; ^{13}C, 100 MHz) spectrometer. Their peak frequencies were referenced versus an internal standard (TMS) shifts at 0 ppm for ^{1}H NMR and against the solvent, chloroform-*d* at 77.0 ppm for ^{13}C NMR, respectively.

Gel Permeation Chromatography Molecular weights and molecular weight distributions of CO_2 copolymers were determined with a PL-GPC 220 high temperature chromatograph (Polymer Laboratories Ltd.) equipped with the HP 1100 series pump from Agilent Technologies. The GPC columns were eluted with tetrahydrofuran at 35 °C at 1.00 ml/min. The sample concentration was about 0.1%, and the injection volume was 100 μL. The curve was calibrated using monodisperse polystyrene standards covering the molecular weight rage from 580 to 460000 Da.

Differential scanning calorimetry (DSC) The analysis of DSC was carried out with a NETZSCH DSC 206 thermal analyzer.

2. Characterization of CO_2/phenyl glycidyl ether copolymers by ^1H NMR

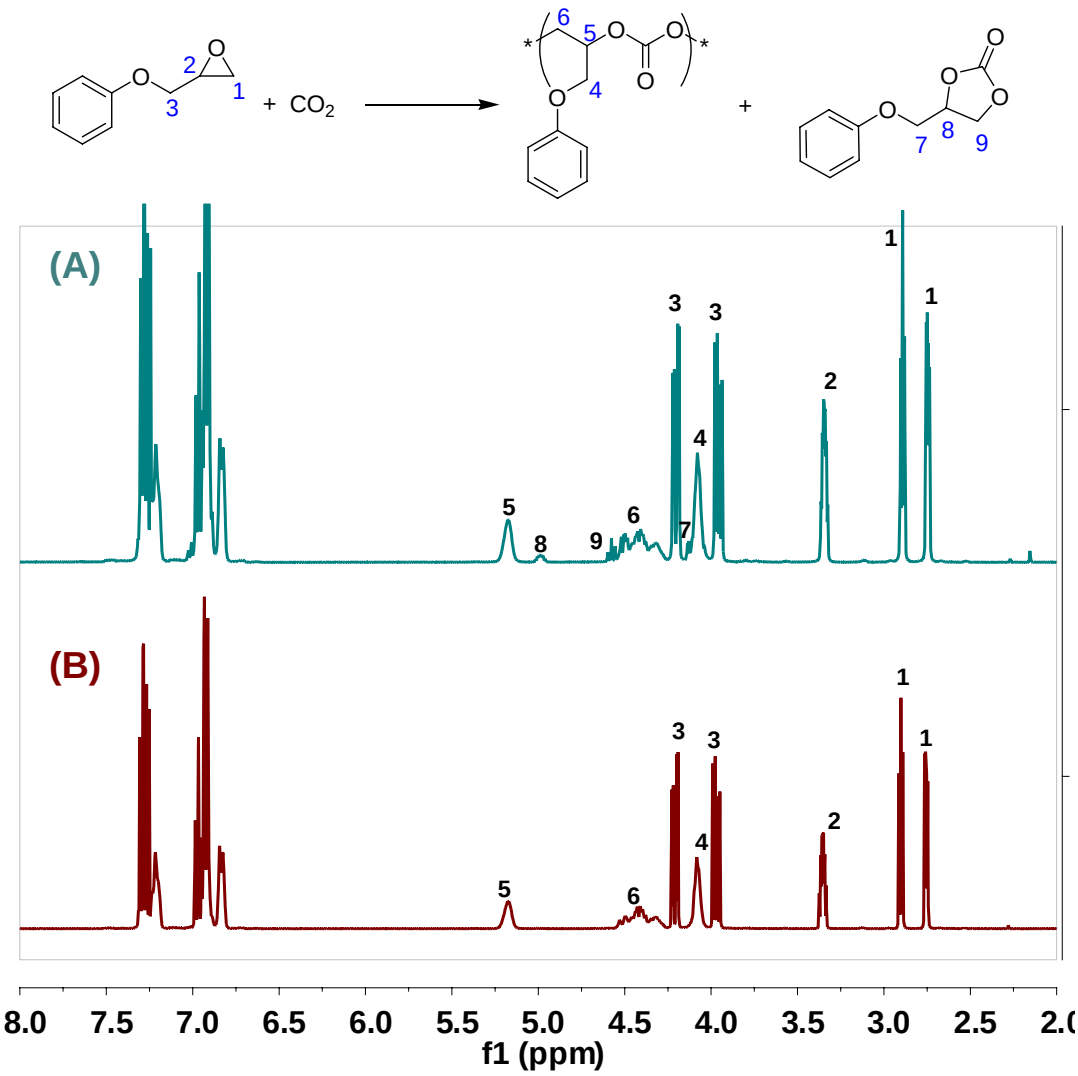

Figure S1. ^{1}H NMR spectra of the reaction mixture sampled directly from the coupling of CO_2 and phenyl glycidyl ether catalyzed by (A) binary **1**/MTBD system, and (B) single-component **3** under a [PGE]/[Catalyst] ratio of 2000 at ambient temperature.

3. Reaction rate data for CO_2/phenyl glycidyl ether coupling

Table S1. Reaction rate data for the coupling of CO_2 and phenyl glycidyl ether[a]

Catalyst system	Temperature (K)	Rate (abs/s × 10^6)	
		Copolymer	Cyclic carbonate
Binary **1**/PPNDNP (1/1)	293	1.54	2.57
	303	2.49	1.23
	313	4.27	0.55
	323	6.64	0.16
Single-component **3**	293	5.95	-
	303	8.32	0.17
	313	13.15	0.98
	323	18.02	2.01

[a] The reactions were performed in neat phenyl glycidyl ether (PGE) (18.0 g, 120 mmol) at 1.5~2.0 MPa CO_2 pressure. The molar ratio of catalyst to PGE was 2000/1.

4. Arrhenius plots for formation of polycarbonate and cyclic carbonate during CO_2/phenyl glycidyl ether coupling reactions

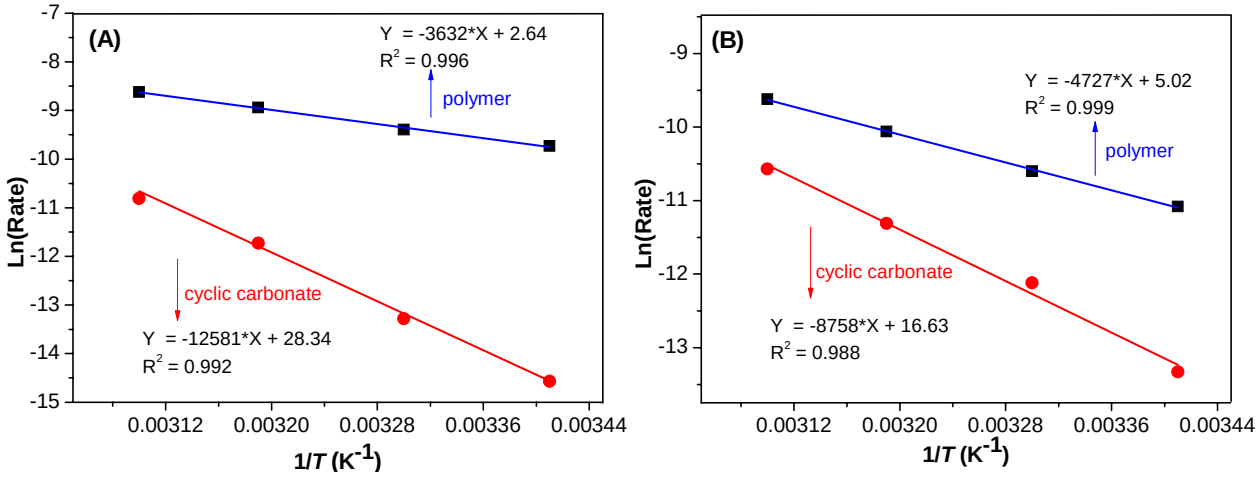

Figure S2. Arrhenius plots for formation of copolymer and cyclic carbonate during phenyl glycidyl ether/CO_2 copolymerization catalyzed by (A) the single-site catalyst **3**, and (B) the binary catalyst system consisting of complex **1** and PPNDNP.

5. Determination of enantiomeric purity of the resultant CO_2/phenyl glycidyl ether copolymers

The *ee* of the resulting copolymer (Table 2, entry 7) was determined by chiral HPLC analysis of the diol derivative from hydrolysis with 1M NaOH (OD-H, 8:2 hexane:*i*-PrOH, t_R(minor) = 7.17 min, t_R(major) = 13.85 min).