Supporting Information

Poly(propylene succinate): A New Polymer Stereocomplex

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1. General Considerations

All manipulations of air and water sensitive compounds were carried out under dry nitrogen using a Braun Labmaster Glovebox or standard Schlenk line techniques. ^{1}H and ^{13}C NMR spectra were recorded on a Varian INOVA 400 (^{1}H, 400 MHz) or Varian INOVA 500 (^{1}H, 500 MHz) spectrometer. ^{1}H NMR spectra were referenced with residual non-deuterated solvent shifts ($CHCl_3$ = 7.26 ppm) and ^{13}C NMR spectra were referenced by solvent shifts ($CDCl_3$ = 77.16 ppm).

Gel permeation chromatography (GPC) analyses were carried out using an Agilent PL-GPC 50 integrated system (2 x PLgel Mini-MIX C columns, 5 micron, 4.6 mmID) equipped with UV and refractive index detectors. The GPC columns were eluted at a rate of 0.3 mL/min with tetrahydrofuran (30 ºC) and were calibrated relative to monodisperse polystyrene standards.

Differential scanning calorimetry (DSC) of polymer samples was performed on a Mettler-Toledo Polymer DSC instrument equipped with a Julabo chiller and autosampler. DSC experiments were prepared in crimped aluminum pans and standard experiments were conducted with a heating rate of 10 ºC/min from -70 ºC to +200 ºC or from -20 ºC to +130 ºC.

Stereocomplex crystallization experiments were conducted with a heating rate of 2 ºC/min from -20 ºC to +130 ºC. Data were processed using StarE software.

Gas chromatography was performed using an HP6890 Series GC System. Propylene oxide enantiomers were separated using a Chiraldex α-cyclodextrin trifluoroacetyl column. The separation method comprised holding at 40 ºC for 20 minutes, followed by heating at 20 ºC/min to 150 ºC, and then holding at 150 ºC for 28 minutes. Methyl ester derivatives were separated with a Supelco Chiraldex 225 column. The separation method for these compounds comprised holding at 50 ºC for 15 minutes, heating from 50 ºC to 60 ºC at a rate of 10 ºC/min, holding at 60 ºC for 50 minutes, heating from 60 ºC to 180 ºC at a rate of 10 ºC/min, and finally holding at 180 ºC for 10 minutes. (*S*)-propylene glycol diacetate shows a retention time of around 58.1 minutes and (*R*)-propylene glycol diacetate shows a retention time of around 59.5 minutes.

X-ray diffraction patterns were recorded on a Scintag Powder X-Ray Diffractometer in 2θ medium resolution Brag Brentano geometry employing Cu Kα line focused radiation at 40 kV, 44 mA power and equipped with a Ge crystal detector fitted with a 1.0 mm radiation entrance slit. Samples were mounted on zero background sample holders by dropping powders from a wide-blade spatula and then leveling the sample surface with the back of the spatula. No sample grinding was used prior to analysis unless otherwise noted. Samples were observed using a step scan from 7–30º, integrating at each point for 5 seconds (Omega = 1.0º).

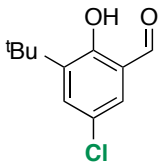
Optical rotations were measured with a digital polarimeter at a concentration of 1 g/100 mL in chloroform at 20 °C with a path length of 1 dm.

2. Materials

Calcium hydride (Strem, 90%) was used as received for drying propylene oxide. All solvents were used as received unless otherwise noted. Propylene oxide was purchased from Sigma-Aldrich, dried over calcium hydride for 3 days, vacuum transferred to a flame-dried thick-walled Schlenk-adapted flask under inert atmosphere, degassed via 3 freeze-pump-thaw cycles, and stored in the glove box. Succinic anhydride was purchased from Acros Organics (99% purity), recrystallized from $CHCl_3$, dried at 60 ºC under reduced pressure, and stored in the glove box. HPLC grade CH_2Cl_2 for metallation was purchased from Fischer Scientific and filtered through a solvent purification system under inert atmosphere and degassed with N_2 for 1h. Ethanol for metallation was purchased from Koptec, stored over 3 Å sieves and degassed with N_2 for 1h. Metal precursor $Co(NO_3)_2{\cdot}6H_2O$ (>99% purity) was purchased from Strem and stored in a desiccator until use. Bis(triphenylphosphine)iminium chloride was purchased from Sigma-Aldrich and recrystallized by layering CH_2Cl_2/Et_2O. NMR solvents were purchased from Cambridge Isotopes and stored over 3 Å molecular sieves. All other reagents were purchased from commercial sources and used as received.

3. Synthesis of Catalyst and Cocatalysts

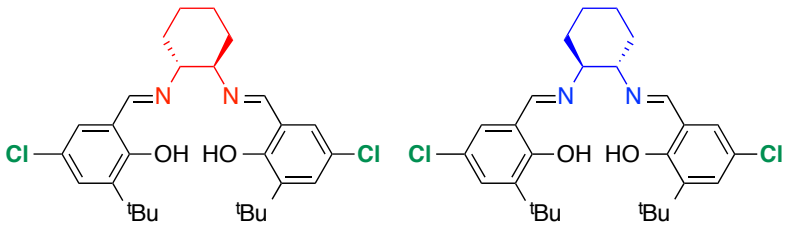
3.1 Salicylaldehyde Synthesis



The ligand precursor 3-*tert*-butyl-5-chlorosalicylaldehyde has been previously reported, and ^{1}H NMR assignments are included that match well with those in the literature.[1] The precursor to the salicylaldehyde, 2-*tert*-butyl-4-chlorophenol, was synthesized according to literature

procedure.[2] 4-Chlorophenol (Combi-Blocks, 8.00 g, 62.2 mmol) was dissolved in *tert*-butyl alcohol (Aldrich, 11.9 mL, 124 mmol), and 7.50 mL of concentrated H_2SO_4 was added dropwise over 5 minutes, turning the solution from a pale yellow to a light orange. The solution was stirred for 2 days, neutralized with Na_2CO_3 (aq), and then extracted into diethyl ether and dried over Na_2SO_4. The product was concentrated and purified by column chromatography (95:5, hex:EtOAc) resulting in a yellow oil (71% isolated yield). Using a modified Duff reaction, 2-*tert*-butyl-4-chlorophenol was formylated as reported by Jacobsen et al.[1] The product was purified by column chromatography (90:10, hex:EtOAc) to yield a crystalline yellow solid (24% isolated yield). ^{1}H NMR spectrum in ppm ($CDCl_3$, 400 MHz): δ 11.72 (s, 1H); 9.82 (s, 1H); 7.46 (d, J = 2.6 Hz, 1H); 7.38 (d, J = 2.6 Hz, 1H); 1.41 (s, 9H). HR/MS: calculated 211.0526 g/mol; found 211.0523 g/mol and matched well with the literature value.[1]

3.2. *N,N'*-Bis(3-*tert*-butyl-5-Cl-salicylidene)-1,2-cyclohexadiimine Synthesis



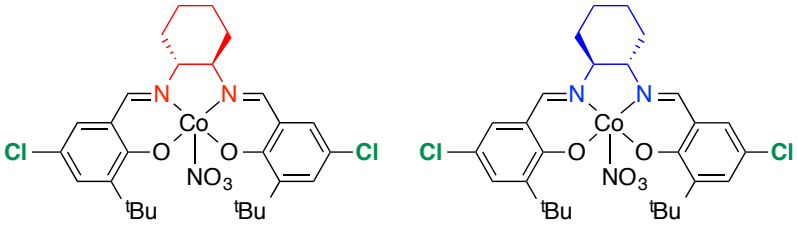
N,N'-Bis(3-*tert*-butyl-5-Cl-salicylidene)-1,2-cyclohexadiimine has been previously reported, and ^{1}H NMR assignments are included that match well with those in the literature.[3] Both the (*R,R*) and (*S,S*) enantiomers of this ligand were prepared. Only preparation of the (*R,R*)-enantiomer is described, as the only difference between the two is that the opposite enantiomer of tartaric acid is used to prepare the (*S,S*)-ligand.

(*R,R*)-1,2-Diaminocyclohexane was prepared according to literature procedure.[1] In a round bottom flask, (L)-(+)-tartaric acid (2.25 g, 15.0 mmol) was added to 7.50 mL deionized H_2O.

Trans-1,2-diaminocyclohexane (3.60 mL, 30.0 mmol) was added via syringe, followed by 1.50 mL acetic acid, resulting in the formation of a precipitate. The reaction was stirred in an ice bath for 3 h, and the precipitate collected by filtration, rinsed with cold H_2O and methanol, and dried under reduced pressure to give a white powder.

N,N'-Bis(3-*tert*-butyl-5-chloro-salicylidene)-1,2-cyclohexadiimine was prepared according to literature procedure and the ^{1}H NMR spectrum of the product matched well with the literature.[3] (*R,R*)-1,2-diaminocyclohexane (0.270 g, 1.02 mmol) and K_2CO_3 (0.282 g, 2.04 mmol) were dissolved in 1.36 mL deionized H_2O. Ethanol (5.50 mL) was added and the reaction mixture was heated to 80 ºC with vigorous stirring. 3-*tert*-Butyl-5-chlorosalicylaldehyde was dissolved in 3.30 mL ethanol and added slowly to the reaction mixture via syringe. The reaction mixture was then stirred for 2 h at 80 ºC. Upon cooling and addition of minimal H_2O, the ligand precipitated. The precipitate was collected by filtration and dried under vacuum (80% isolated yield). ^{1}H NMR spectrum ($CDCl_3$, 400 MHz): δ 13.81 (s, 2H); 8.18 (s, 2H); 7.18 (d, J = 2.5 Hz, 2H); 6.95 (d, J = 2.5 Hz, 2H); 3.31 (m, 2H); 1.99 (bm, 2H); 1.90 (bm, 2H); 1.75 (bm, 2H); 1.48 (bm, 2H); 1.39 (s, 18H). HR/MS: calculated 501.2076 g/mol; found 501.2079 g/mol.

3.3 (Cl-salcy)Cobalt(III)NO_3 Complex Synthesis



(*R,R*)-(Cl-salcy)$CoNO_3$ **(*S,S*)-(Cl-salcy)$CoNO_3$**

Both the (*R,R*) and (*S,S*) enantiomers of this catalyst were prepared. Only preparation of the (*R,R*) catalyst is described, as the only difference between the two is that the opposite enantiomer

of the ligand is used to prepare the (*S,S*) catalyst. The yield represents average isolated yield. In a flame-dried Schlenk flask, (1*R*,2*R*)-*N,N'*-bis(3-*tert*-butyl-5-chloro-salicylidene)-1,2-cyclohexadiimine (0.500g, 0.914 mmol) was dissolved in anhydrous, degassed dichloromethane under N_2 flow. In a second flame-dried Schlenk flask, $Co(NO_3)_2 \cdot 6H_2O$ (0.293 g, 1.01 mmol) was dehydrated under reduced pressure until the color changed from red to light pink and subsequently dissolved in anhydrous, degassed ethanol. The metal solution was then transferred to the ligand solution via cannula and the reaction mixture was stirred overnight while oxidizing under dry air with a drying tube charged with a Drierite agent. Next the reaction mixture was evacuated to dryness and the resulting dark brown powder was rinsed with pentane and dried under reduced pressure at 60 ºC and then stored in a glove box (78% isolated yield). ^{1}H NMR spectrum (C_5D_5N, 400 MHz): δ 8.60 (2H); 7.66 (2H); 7.43 (2H); 3.94 (1H); 3.04 (1H); 2.10 (2H); 1.78 (2H); 1.66 (2H); 1.55 (2H); 1.44 (18H) (Figure S1). ^{13}C NMR spectrum (C_5D_5N, 500 MHz): δ 167.73; 162.82; 146.47; 133.87; 132.18; 120.36; 119.20; 71.68; 36.51; 30.95; 30.01; 25.20 (Figure S2). HR/MS: calculated 559.1329 g/mol; found 559.1339 g/mol.

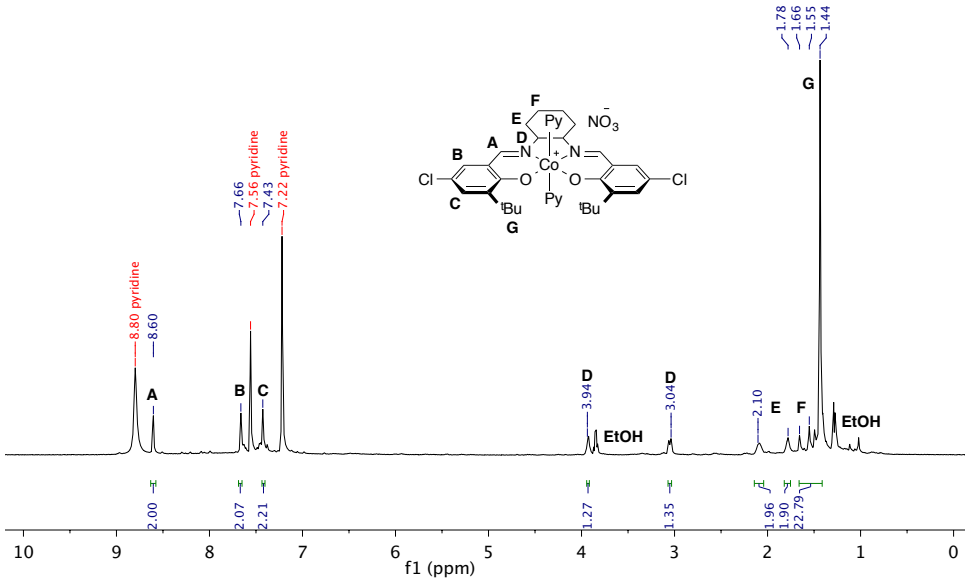


Figure S1. ^{1}H NMR spectrum of (*R*,*R*)-(Cl-salcy)$CoNO_3$ in C_5D_5N.

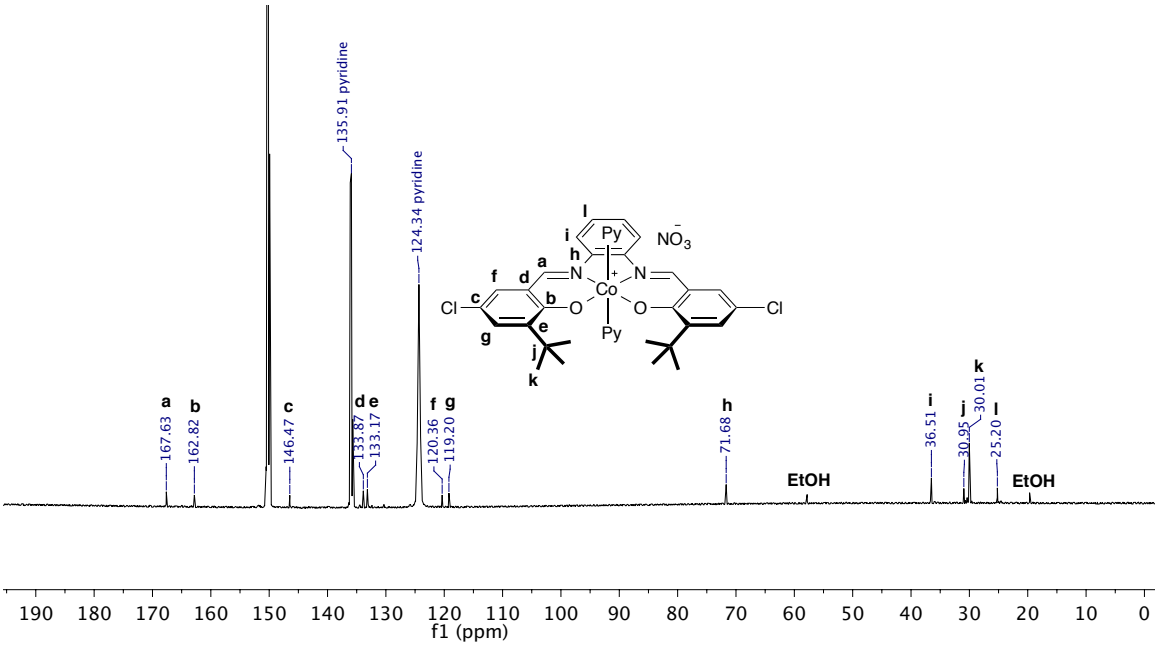


Figure S2. ^{13}C NMR spectrum of (*R*,*R*)-(Cl-salcy)$CoNO_3$ in C_5D_5N.

3.4 Synthesis of [PPN][X] Salts

3.4.1 [PPN][NO_3]

Bis(triphenylphosphine)iminium chloride ([PPN]Cl) (3.00 g, 5.22 mmol) was dissolved in 70 ºC deionized H_2O (75.0 mL), HNO_3 was added (0.360 mL, 5.74 mmol), and the reaction was slowly cooled to 25 ºC. A white precipitate formed immediately and the slurry was stirred for 1 h. The resulting solid was collected by filtration, washed with warm water to remove residual acid and PPNCl and dried under reduced pressure at 60 ºC for 24 h (95% yield). Purity was assessed by ^{1}H NMR spectroscopy to ensure removal of water and the presence of only one set of aryl peaks. A melting point of 230 ºC was measured using differential scanning calorimetry, which

matched well with the literature value.[4] ^{1}H NMR spectrum ($CDCl_3$, 400 MHz): δ 7.62 (m, 6H); 7.43 (m, 24H) (Figure S3). ^{13}C NMR spectrum ($CDCl_3$, 500 MHz): δ 133.89, 133.02, 129.57, 127.32/126.46 (d, J_{CP} = 108 Hz) (Figure S4). HR/MS: [NO_3] calculated 61.9878 g/mol; found 61.9870 g/mol.

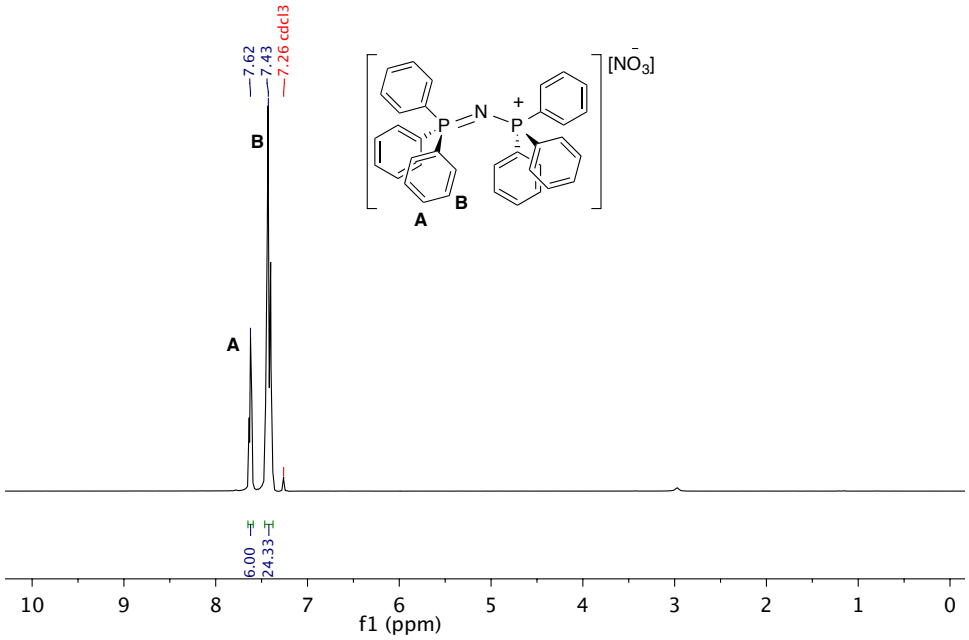


Figure S3. ^{1}H NMR spectrum of [PPN][NO_3] in $CDCl_3$.

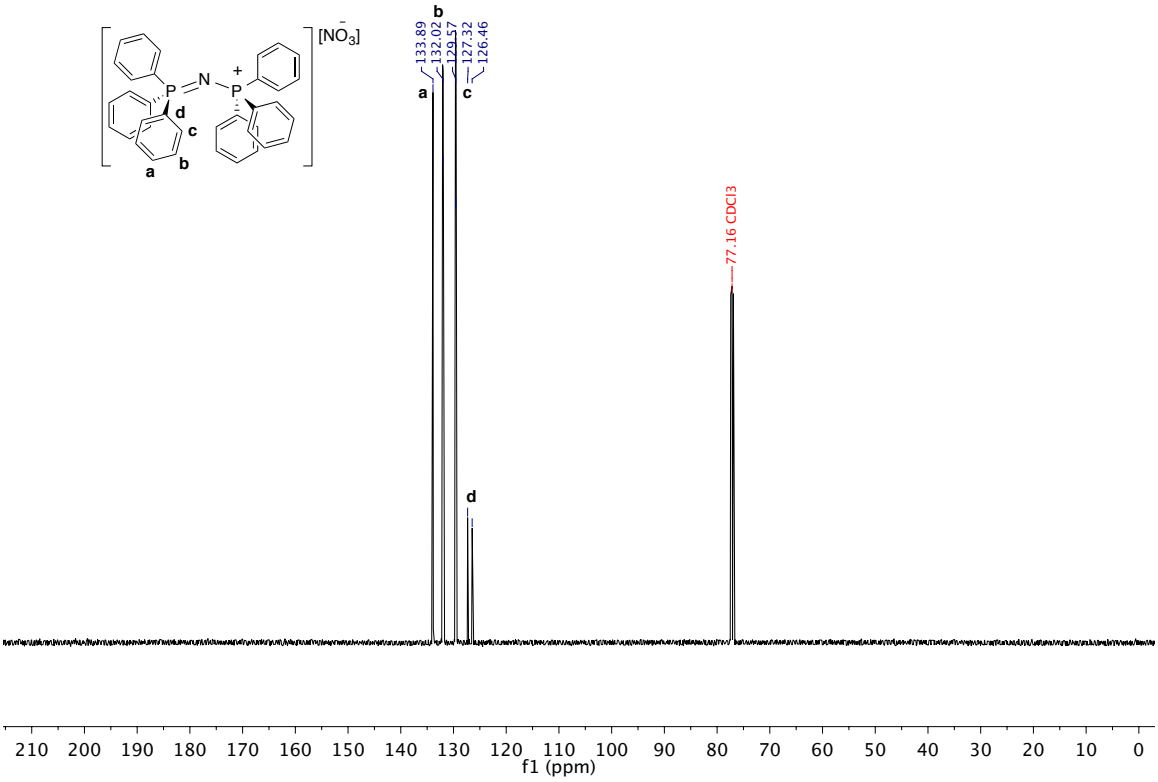


Figure S4. ^{13}C NMR spectrum of [PPN][NO_3] in $CDCl_3$.

3.4.2 [PPN][1-Adamantate]

1-Adamantanecarboxylic acid (0.314 g, 1.74 mmol) and NaOH (69.7 mg, 1.74 mmol) were added to a large vial and dissolved in 7.00 mL H_2O and 3.00 mL methanol by stirring with gentle heating. In a round bottom flask, [PPN]Cl (1.00 g, 1.74 mmol) was dissolved in 30.0 mL H_2O with stirring and the solution of 1-adamantanecarboxylic acid and NaOH was added to the flask and stirred while refluxing until the reaction was homogeneous. The reaction mixture was then cooled to room temperature with slow stirring. White crystals formed which were collected by filtration, rinsed with 0 ºC H_2O, and dried at 40 °C under reduced pressure (82% yield). A melting point of 147 ºC was measured using differential scanning calorimetry. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz): δ 7.60 (m, 6H); 7.40 (m, 24H); 1.92 (m, 6H); 1.81 (m, 3H); 1.61-

1.59 (m, 3H), 1.53-1.51 (m, 3H) (Figure S5). ^{13}C NMR spectrum ($CDCl_3$, 500 MHz): δ 182.80, 133.89, 132.97, 129.56, 127.29/126.43 (d, J_{CP} = 108 Hz), 41.80, 40.44, 37.45, 29.13 (Figure S6). HR/MS: [1-Adamantate] calculated 179.1072 g/mol; found 179.1061 g/mol.

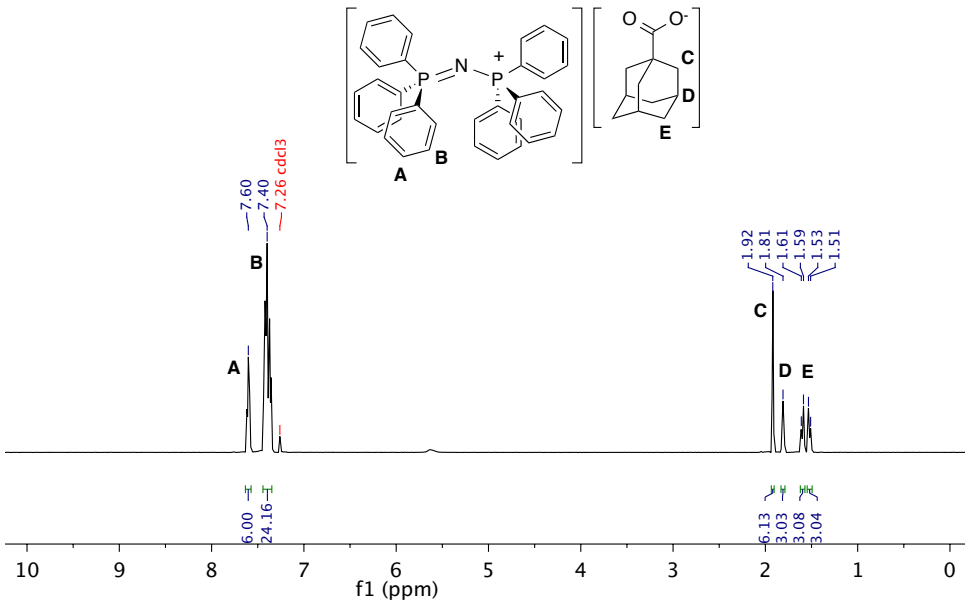


Figure S5. ^{1}H NMR spectrum of [PPN][1-Adamantate] in $CDCl_3$.

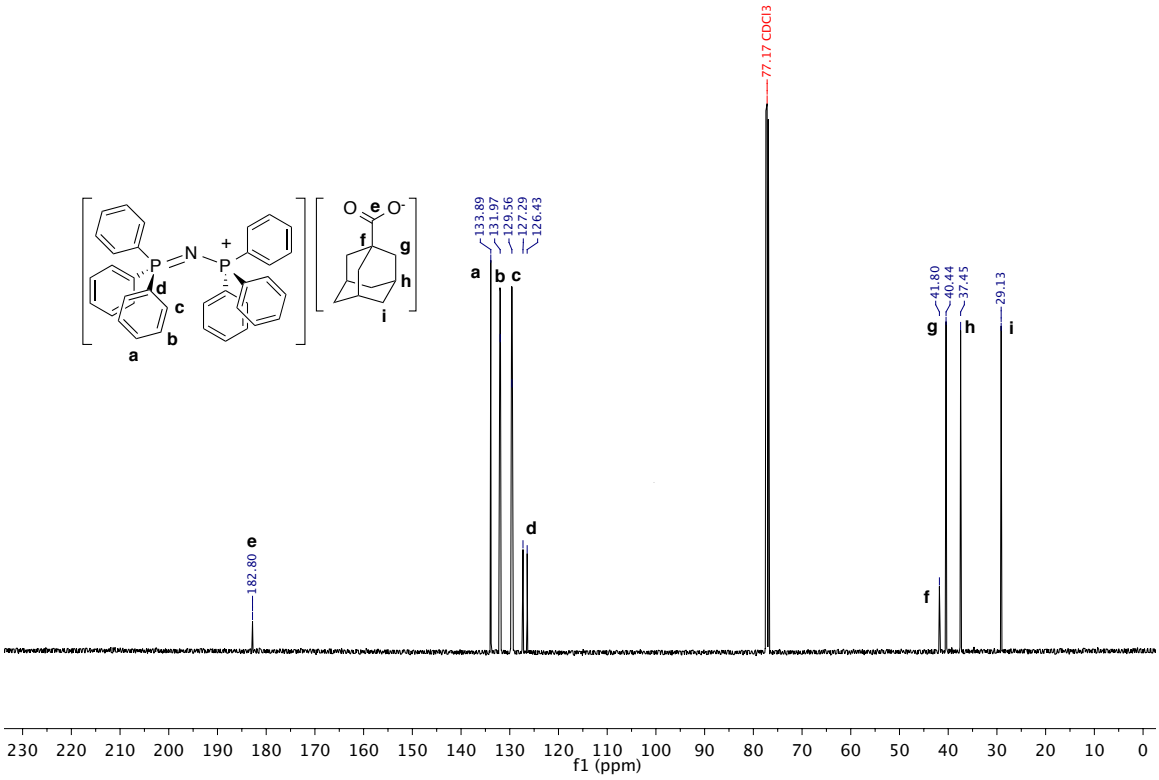


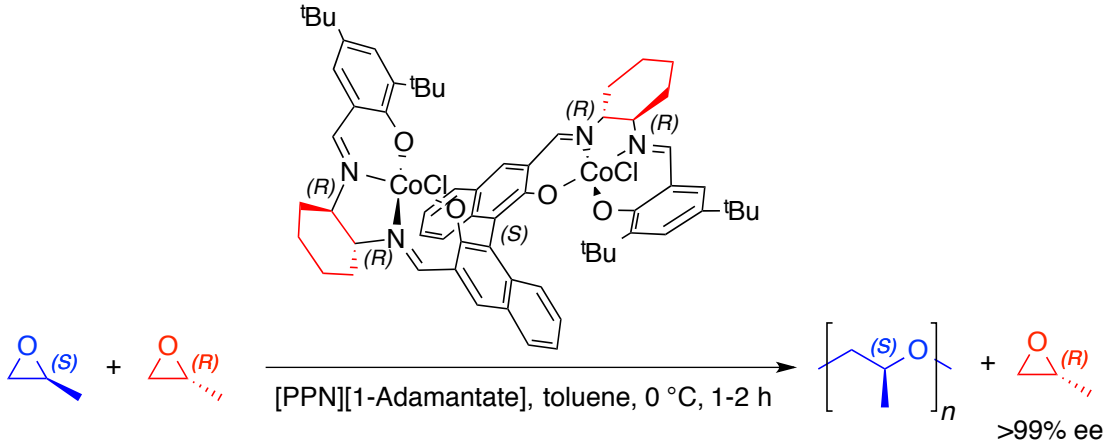
Figure S6. ^{13}C NMR spectrum of [PPN][1-Adamantate] in $CDCl_3$.

4. Resolution of (*S*)-Propylene Oxide and (*R*)-Propylene Oxide

Both (*S*)- and (*R*)-propylene oxide were resolved from racemic propylene oxide using a bimetallic cobalt salen catalyst that enantioselectively polymerizes only one enantiomer of epoxide, allowing the other enantiomer to be collected in high enantiomeric excess (ee) (Scheme S1).[5] Both the (*R,R,S,R,R*) and (*S,S,R,S,S*) versions of this catalyst were synthesized as reported in previous literature, where the former was used to prepare (*R*)-propylene oxide and the latter to prepare (*S*)-propylene oxide from racemic propylene oxide. In a glove box, the appropriate enantiomer of the catalyst (6.60 mg, 5.75 μmol) and [PPN][1-Adamantate] (8.30 mg, 12.0 μmol) were added to a flame-dried vial equipped with a Teflon coated stir bar. The solids were then dissolved in 11.5 mL toluene (to form a 2M solution), and the vial capped with a Teflon-lined,

puncturable top. The racemic epoxide was measured out in an airtight syringe, sealed with a rubber septum, and removed from the glove box along with the catalyst solution.

Scheme S1. (*R,R,S,R,R*)-Bimetallic Salen Cobalt Catalyst for the Resolution of (*R*)-Propylene Oxide from Racemic Propylene Oxide via Enantioselective Polymerization of (*S*)-Propylene Oxide.



The vial containing the catalyst/cocatalyst solution was cooled in an ice bath for 15 minutes and then the epoxide was injected into the reaction mixture. The reaction mixture was then stirred for 1-2 h in the ice bath, and aliquots were analyzed for conversion via ^{1}H NMR spectroscopy. Both enantiomers of this bimetallic catalyst are very highly enantioselective, so once >50% conversion to polymer was attained, the remaining enantiopure epoxide starting material was collected via vacuum transfer into a small, thick-walled Schlenk flask cooled with liquid N_2. The propylene oxide was then analyzed by gas chromatography as described above. Both (*S*)- and (*R*)-propylene oxide were obtained with >99% ee.

5. Representative Synthesis of Isotactic Poly((*S*)-propylene succinate) with (*R,R*)-(Cl-salcy)$CoNO_3$

In a glove box, a flame-dried 30 mL vial equipped with a Teflon coated stir bar was charged with (*R,R*)-(Cl-salcy)$CoNO_3$ (3.11 mg, 5.00 μmol), [PPN][NO_3] (3.00 mg, 5.00 μmol), and succinic anhydride (200 mg, 2.00 mmol). (*S*)-Propylene oxide (0.280 mL, 4.00 mmol) was added via syringe with care to wash all solids from the side of the vial. The vial was sealed with a Teflon lined cap, removed from the glove box, and placed in an aluminum heat block preheated to 30 ºC. Initially, the reaction mixture was heterogeneous, with the solid succinic anhydride dissolving over time until the mixture became homogeneous, around 24 hours after the reagents were combined. Over the course of 48 hours, the reaction mixture became viscous, at which point the vial was removed from the heat block, and the mixture was dissolved in 4 mL dichloromethane and precipitated into 20 mL hexanes. The hexanes were decanted and the polymer dried in vacuo. The polymer was then dissolved again in 4 mL dichloromethane and 20 mL methanol was added dropwise over 5-10 minutes with vigorous stirring until a white precipitate formed. After allowing time for the solid to settle, the methanol was decanted and the polymer dried *in vacuo*. Poly((*R*)-propylene succinate) was synthesized in the same manner, substituting (*R*)-propylene oxide for the (*S*)-propylene oxide.

6. NMR Spectra and Peak Assignments for Isotactic (*S*)-Poly(propylene succinate)

^{1}H NMR spectrum ($CDCl_3$, 500 MHz): δ 5.12 (m, 1H); 4.17-4.14 (dd, *J* = 3.8, 11.5 Hz, 1H); 4.08-4.05 (dd, *J* = 6.3, 11.5 Hz, 1H); 2.61 (bm, 4H); 1.22 (d, *J* = 6.3, 3H) (Figure S7). ^{13}C NMR spectrum ($CDCl_3$, 500 MHz): δ 172.08; 171.73; 68.60; 66.24; 29.18; 28.92; 16.49 (Figure S8).

^{1}H and ^{13}C NMR spectra of poly((*R*)-propylene succinate) look identical to those of the poly((*S*)-propylene succinate) pictured below.

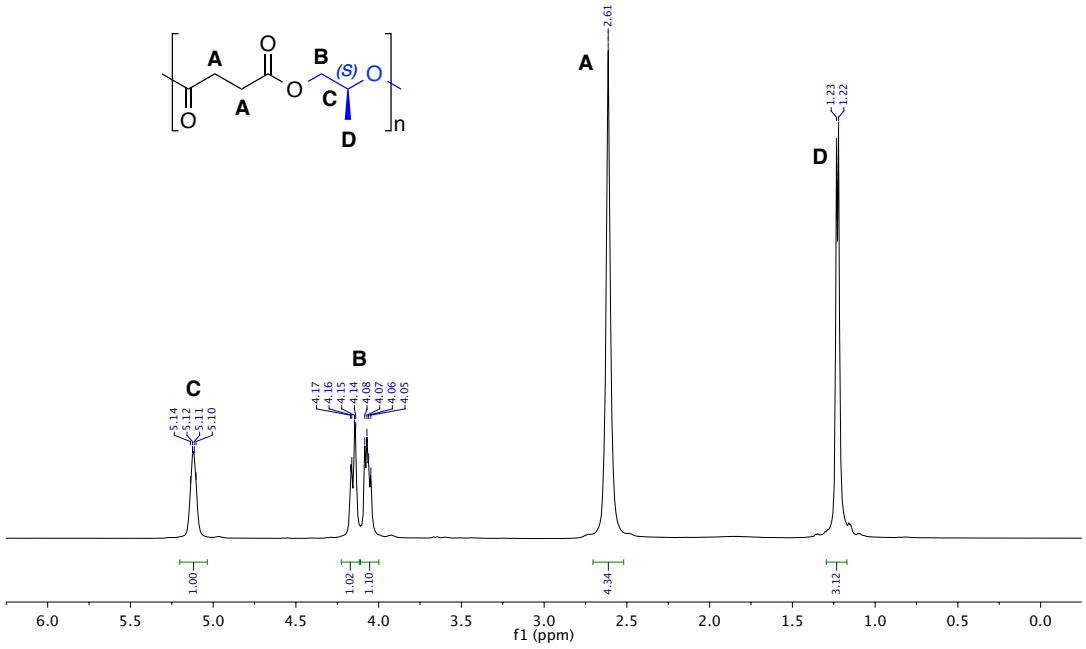


Figure S7. ^{1}H NMR spectrum of poly((*S*)-propylene succinate) in $CDCl_3$.

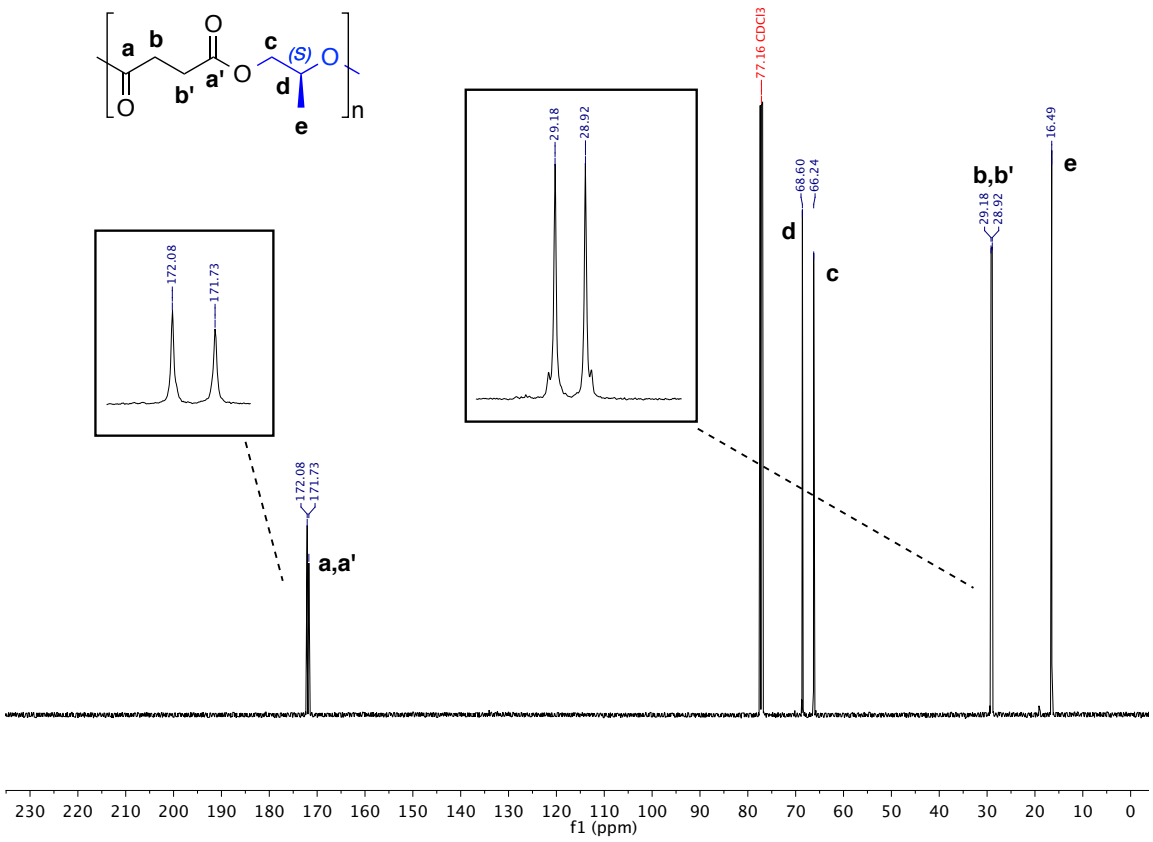


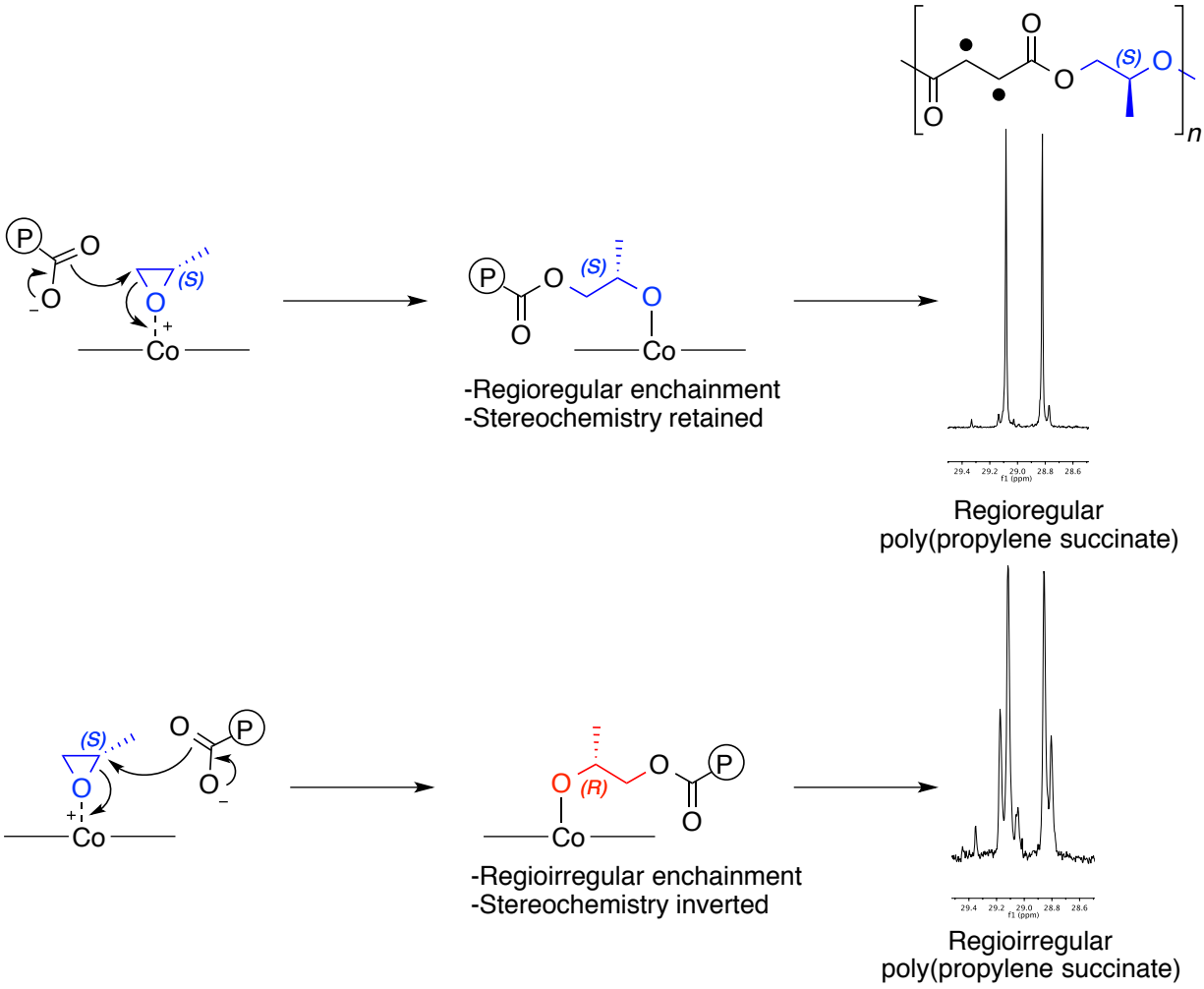
Figure S8. ^{13}C NMR spectrum of poly((*S*)-propylene succinate) in $CDCl_3$.

7. Determination of Regioregularity via Gas Chromatography

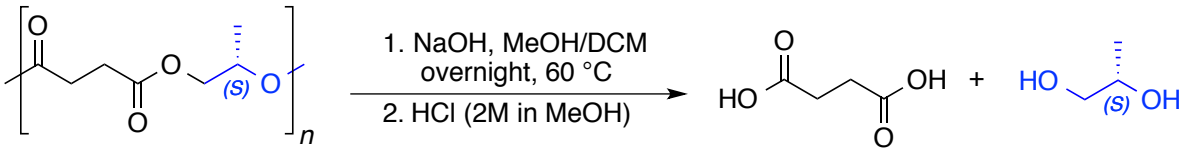
In the ring-opening alternating copolymerization of succinic anhydride and propylene oxide, the regioregularity of the polymer is determined by the regioselectivity of the ring-opening of the epoxide. In general, the epoxide is opened at the less sterically hindered methylene carbon, and a regioerror occurs when the epoxide is opened at the methine carbon instead (Scheme S2). Because of the S_N2 nature of the ring-opening step, attack at the methine carbon not only results in a regioerror but a stereoerror as well.[6] This means that the regioregularity of the polymerization can be assessed by determining the enantiopurity of polymers synthesized from enantiopure starting materials. The regioregularity of poly(propylene succinate) polymers

synthesized with (Cl-salcy)$CoNO_3$ was analyzed using gas chromatography after degradation and derivatization as described below. Poly(propylene succinate) regioregularity can be analyzed qualitatively by the methylene ^{13}C NMR spectroscopy signals, as shown in Scheme S2.

Scheme S2. Regio- and Stereochemistry of the Epoxide Ring-Opening Step and the Methylene ^{13}C NMR Spectroscopy Signals Resulting from Regioregular and Regioirregular Enchainment

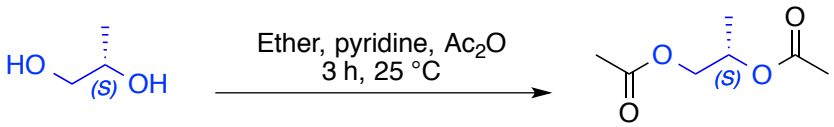


7.1 Degradation of Poly(propylene succinate)



Approximately 200-300 mg of (*S*)- or (*R*)-poly(propylene succinate) were dissolved in 3.0 mL dichloromethane, 15 mL methanol and 200 mg NaOH were added, and the reaction mixture was stirred at 60 ºC for 12 hours. The reaction mixture was then neutralized with acidic methanol (2M HCl in MeOH) and the solvent evacuated under reduced pressure. Diethyl ether (40 mL) was added to the resulting off-white powder and the slurry was vigorously stirred for 1 h, followed by filtration and removal of the solvent to yield propylene glycol.

7.2 Derivatization of Diols resulting from Degradation



Into a small vial equipped with a Teflon lined stir bar was added 1 mL diethyl ether and equal amounts (5-10 drops) propylene glycol, pyridine, and acetic anhydride. The reaction mixture was stirred 3 h at room temperature, washed with deionized H_2O (3 x 1 mL) and dried over Na_2SO_4. The derivatized product was then analyzed via gas chromatography (*vide supra*). The diacetate was obtained with an ee of 97% when (*R,R*)-(Cl-salcy)$CoNO_3$ was used, and with an ee of 96% when (*S,S*)-(Cl-salcy)$CoNO_3$ was used, indicating that both enantiomers produced highly regioregular poly(propylene succinate).

The enantiomeric ratio, calculated from the % ee, can in turn be used to determine the percent head-to-tail linkages (%HT) in the polymer chains. For every stereoerror present (indicating a regioerror is also present), there will be one head-to-head (HH) and one tail-to-tail

(TT) linkage. With this information, the %HT can be calculated, and in fact it corresponds with the %ee. For example, a sample with 0% ee has an enantiomeric ratio of 50:50. In 100 repeat units of this polymer (100 possible HT linkages), there will be 50 stereoerrors, corresponding to 50 HH linkages and 50 TT linkages, and therefore 0% HT linkages.

8. Determination of Catalyst Enantiomer/Epoxide Enantiomer Combinations

To determine which enantiomer of catalyst should be used to copolymerize each enantiomer of propylene oxide with succinic anhydride, racemic propylene oxide was polymerized with both (*R,R*)-(Cl-salcy)$CoNO_3$ and (*S,S*)-(Cl-salcy)$CoNO_3$ as described above, except that a puncturable Teflon-lined cap was used. When the reaction mixtures became viscous, the excess epoxide was collected via vacuum transfer into a small, thick-walled Schlenk flask cooled with liquid N_2. The propylene oxide was then analyzed by gas chromatography. For (*R,R*)-(Cl-salcy)$CoNO_3$, a slight preference for (*S*)-propylene oxide was observed, as the starting material collected was enriched in (*R*)-propylene oxide, while the opposite was observed when (*S,S*)-(Cl-salcy)$CoNO_3$ was used. In both cases, a k_{rel} of around 4 was observed where the catalyst showed slightly greater activity for polymerizing the opposite enantiomer of propylene oxide.

Additionally, both (*S*)-propylene oxide and (*R*)-propylene oxide were polymerized using both (*R,R*)-(Cl-salcy)$CoNO_3$ and (*S,S*)-(Cl-salcy)$CoNO_3$, and the regiochemistry of the resulting poly(propylene succinate) was analyzed as described above. For both enantiomers of propylene oxide, polymerization with the opposite enantiomer catalyst gave higher regioregularity, around 97% HT linkages, as opposed to 86% HT linkages when the matching enantiomer of catalyst and epoxide were used.

9. Polymer Precipitation and DSC Procedures

Poly(*S*)- and poly((*R*)-propylene succinate) both show no crystallinity from the melt by differential scanning calorimetry (DSC). Crystallinity, and therefore a melting temperature (T_m) of these polymers, is seen only if the polymer is precipitated with methanol, a method that is impractical for industrial applications as the resulting polymer is a very fine powder. For this method, each polymer was dissolved in 4.0 mL dichloromethane and 20.0 mL methanol was added dropwise over 5-10 minutes with vigorous stirring until a white precipitate formed. After allowing time for the precipitate to settle, the solvent was decanted and the polymer dried *in vacuo* at 60 ºC. DSC thermograms of the precipitated polymers show that after precipitation, the T_m for both samples can be seen to be 78 ºC, with ΔH values of 68 J/g and 78 J/g for poly((*S*)-propylene succinate) and poly((*R*)-propylene succinate), respectively (Figure S9). The T_m, however, is only observed on the first heat, with no immediate recrystallization upon cooling. Regardless of the rate of heating/cooling (10 ºC/min or 2 ºC/min) or the temperature to which the sample was heated (90 ºC, 130 ºC, or 200 ºC), the T_m remained the same and no recrystallization was observed.

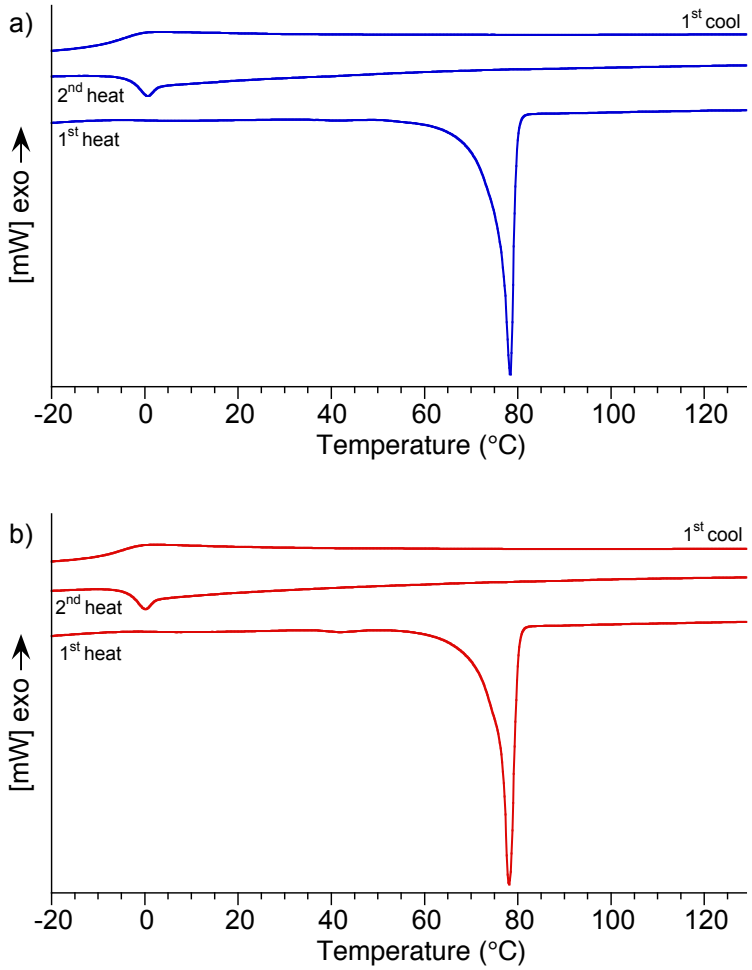


Figure S9. DSC thermograms of a) poly(*S*)- and b) poly((*R*)-propylene succinate) after precipitation by methanol into solutions of the polymers in dichloromethane.

10. Crystallization of poly(*S*)- and poly((*R*)-propylene succinate)

To determine the amount of time required for poly(*S*)- and poly((*R*)-propylene succinate) to crystallize from the melt, approximately 200 g of each polymer were melted at 130 ºC. The samples were then allowed to sit at room temperature, and DSC was performed on aliquots from these samples with a heating rate of 10 ºC/min several times over the course of 19 days (Figure S10). For both samples, the T_m first reappeared after 7 days, although at a lower temperature than is seen before melting (around 40–50 ºC). Over time, a higher melting polymorph (around 70 ºC)

returns to some extent in both samples, although much more of this polymorph is observed in the poly((*S*)-propylene succinate) sample. It is currently unclear why the poly((*S*)-propylene succinate) and poly((*R*)-propylene succinate) recrystallized differently from the melt, although precipitation of both of these polymers with methanol gave the same T_m. Plotting ΔH versus time allowed a $T_{1/2}$ to be extrapolated for the recrystallization time of each enantiopure sample and for the stereocomplex. Initial data suggests that the stereocomplex recrystallizes approximately three orders of magnitude faster than either poly((*S*)-propylene succinate) or poly((*R*)-propylene succinate). Further kinetic studies on the recrystallization rate of both species are ongoing.

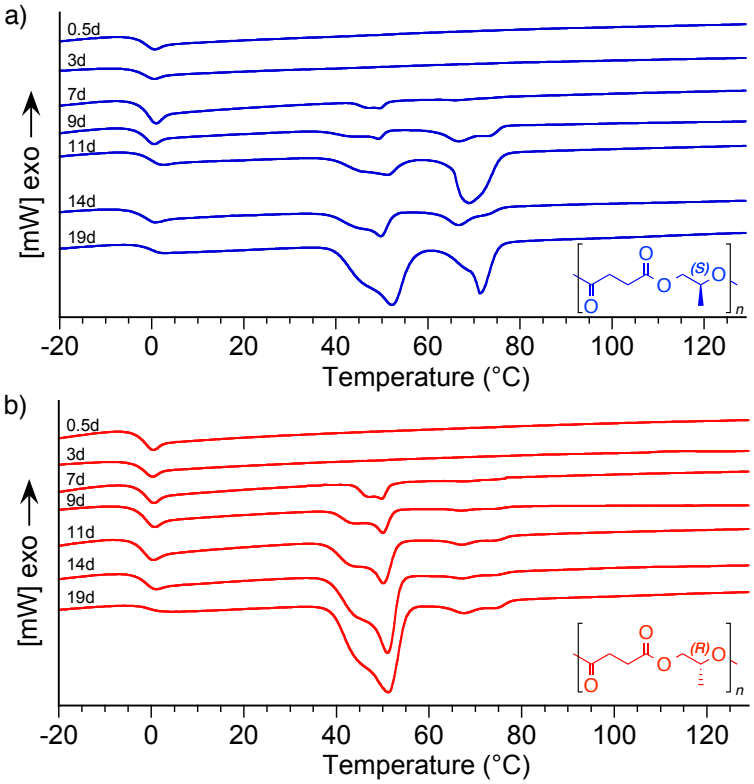


Figure S10. Crystallization of a) poly((*S*)-propylene succinate) and b) poly((*R*)-propylene succinate) over time at 25 ºC.

11. Stereocomplex Formation and DSC Analysis

The poly(propylene succinate) stereocomplex was formed via two methods which were compared by DSC and powder X-ray diffraction. For method 1, 40–50 mg each of poly(*S*)- and poly((*R*)-propylene succinate) were dissolved in ~1.5 mL dichloromethane and mixed together by shaking in a small vial. The top of the vial was then covered with Parafilm, punctured with one hole, and the solvent was allowed to evaporate slowly and completely. The material was then dried *in vacuo* to ensure all solvent was removed. For method 2, the stereocomplex was made as in method 1, dissolved in minimal dichloromethane, and precipitated again by adding methanol dropwise with vigorous stirring.

With a heating rate of 10 ºC/min and heating to 200 ºC, the polymer stereocomplex of poly(*S*)- and poly((*R*)-propylene succinate) exhibited an increased T_m in comparison to the enantiomerically pure polymers (119 ºC, ΔH = 88 J/g). However, as shown in Figure S11, no recrystallization is observed upon cooling and no T_m is seen on the second heat. To induce crystallization in the polymer stereocomplex, the polymer was first precipitated with methanol as described above for the enantiomerically pure polymers, and then the sample was heated at a rate of 10 ºC/min to only 130 ºC and subsequently cooled at the same rate. Figure S12 shows that with this procedure, recrystallization is observed as well as melting during the second heat. The recrystallization temperature of the stereocomplex can be further optimized by heating and cooling at a rate of 2 ºC/min and heating only to 130 ºC, as shown in Figure S13. In this case, again, the T_m remains the same but the recrystallization temperature increases from 80 ºC to 90 ºC.

Additionally, when the stereocomplex recrystallizes upon cooling, no glass transition (T_g) is observed during the second heat. It is expected that the slower the rate of heating (2 ºC/min

versus 10 ºC/min) will result in smaller T_g. However, when the stereocomplex is cooled slowly at 2 ºC/min to induce recrystallization, and subsequently heated at 10 ºC/min, there is still no visible T_g, suggesting that the crystallized stereocomplex has a high degree of crystallinity. Determination of the percent crystallinity of the poly(propylene succinate) stereocomplex is currently underway.

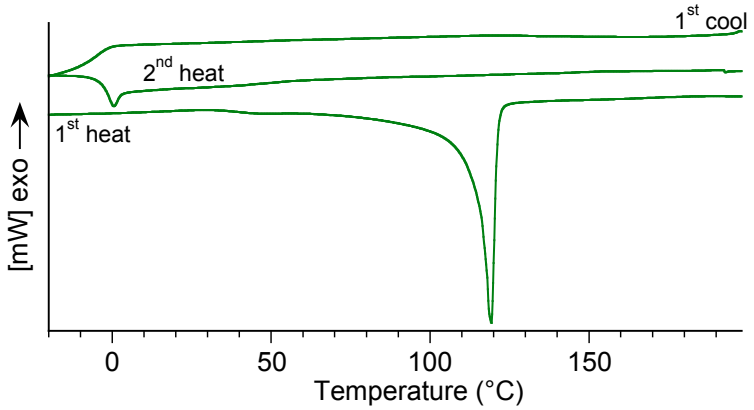


Figure S11. DSC thermogram of the poly(propylene succinate) stereocomplex formed by solvent evaporation, with a heating rate of 10 ºC/min and heating to 200 ºC.

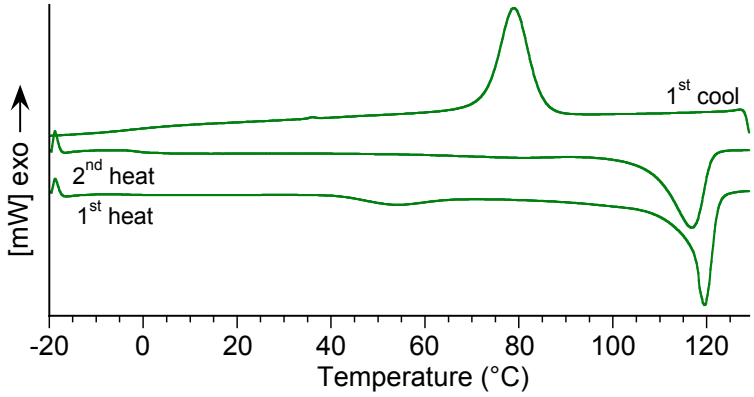


Figure S12. DSC thermogram of the poly(propylene succinate) stereocomplex formed by precipitation with methanol, with a heating rate of 10 ºC/min and heating to 130 ºC.

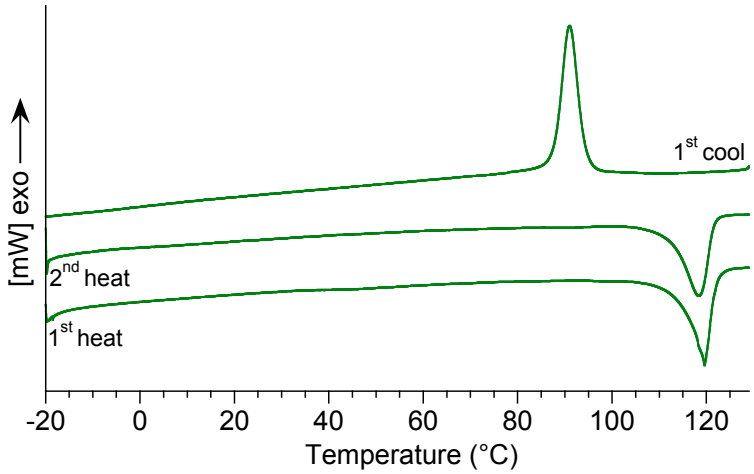


Figure S13. DSC thermogram of the poly(propylene succinate) stereocomplex formed by precipitation with methanol, with a heating rate of 2 ºC/min and heating to 130 ºC.

12. Powder X-ray Diffraction of PPS Stereocomplex

The powder X-ray diffraction profile for the poly(propylene succinate) stereocomplex varied depending on the method of stereocomplex formation, via solvent evaporation or precipitation from methanol as described above (Figure S14). When solvent evaporation (method 1) was used, six peaks were observed at 14.3º, 17.6º, 18.8º, 21.0º, 21.9º, and 24.6º. In contrast, when precipitation from methanol (method 2) was used for stereocomplex formation, only four peaks were observed at 16.2º, 17.9º, 20.8º, and 24.1º. As can be seen in Figure S14, while the exact locations of the major peaks differ for the two methods, the general locations and relative intensities of the peaks are the same. Both profiles are different from those of poly(*S*)- and poly((*R*)-propylene succinate) alone, and we predict that the doubling of the peaks when method 1 is used for stereocomplex formation is a result of the presence of two polymorphs in the sample.

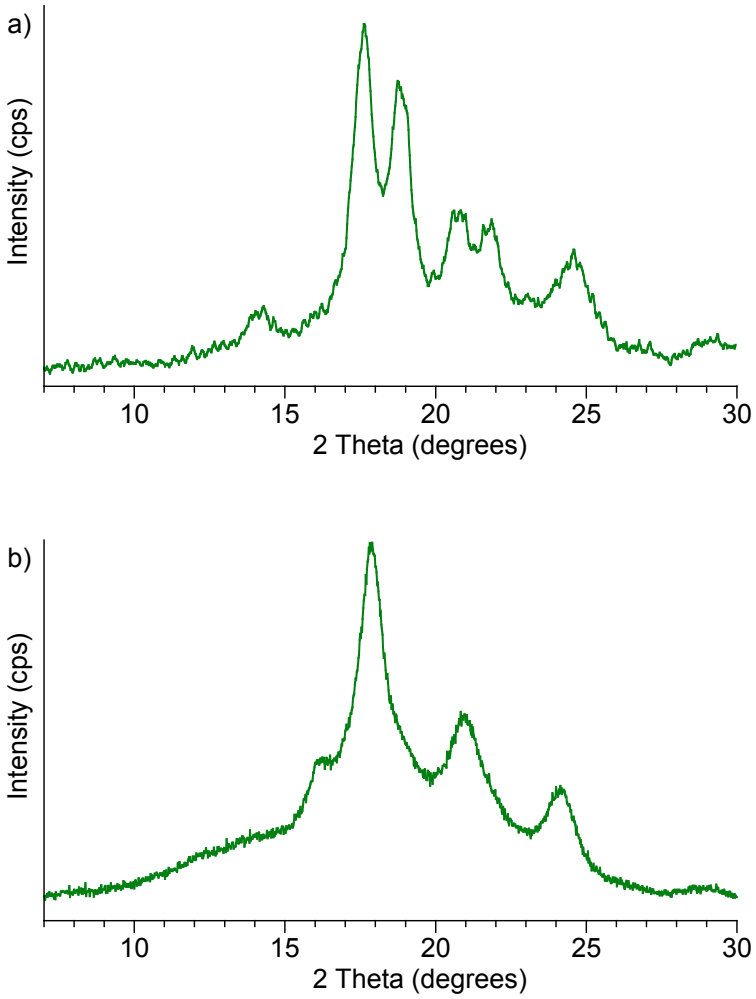


Figure S14. Powder X-ray diffraction profiles for the poly(propylene succinate) stereocomplex formed by a) mixing and solvent evaporation (method 1) and b) solvent evaporation and subsequent precipitation into methanol (method 2) as described above.

Percent crystallinity of the parent polymers and the stereocomplex was investigated by profile fitting and peak decomposition of the powder XRD data. As shown in Figure S15, an approximation of the amorphous region of the polymers can be subtracted from an approximation of the crystalline peak area. Both the parent polymers and the stereocomplex (precipitated with methanol) show a crystallinity of 50–60%. While there is not a large

difference in percent crystallinity based on these calculations, the parent polymers only exhibit significant crystallinity from solution, while the stereocomplex shows this crystallinity from solution and from the melt.

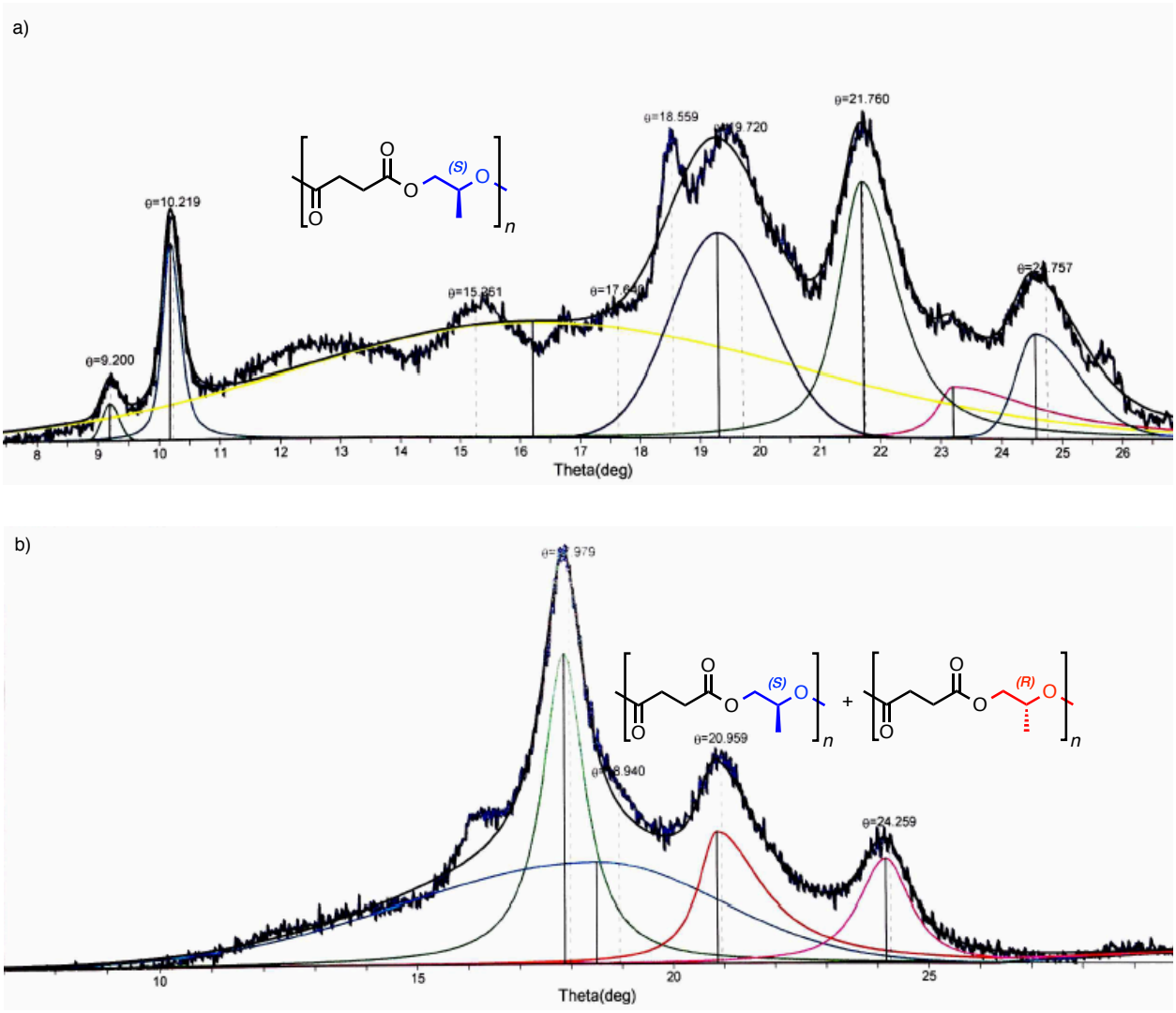


Figure S15. Peak profiles for a) poly((*S*)-propylene succinate) and for b) the poly(propylene succinate) stereocomplex. The fit of the amorphous curve is subtracted from the fit of the crystalline peaks to give a percent crystallinity of 50–60% for both samples.

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