

Co- and Cr-Catalyzed Stereoselective Epoxide Ring-Opening Polymerizations

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Poly(propylene oxide) (PPO) makes up 5% of the world's polymer production and is a critical building block for polyurethane synthesis.¹ These polyurethanes are used for a variety of applications, including elastomers, adhesives, and rigid foams.¹ Industrially, PPO is made from racemic propylene oxide (PO) via anionic ring-opening polymerization (ROP).² Anionic ROP is frequently catalyzed by achiral, nucleophilic, bases which randomly incorporate either enantiomer of epoxide, resulting in atactic polymers.² In contrast, polymerizing enantiopure epoxides leads to isotactic PPO, containing repeat units with the same stereochemistry.³ The difference in physical properties between atactic and isotactic PPO is stark; atactic PPO is amorphous, while isotactic PPO is semi-crystalline.³ Because of its superior properties, there is a need to make isotactic PPO for readily available racemic epoxides using stereoselective catalysis.

Since Pruitt and Baggett's first report of stereoselective Fe(III) halide salts in 1955, many stereoselective ROP catalysts utilizing transition metals; alkali and alkali earth metals; and main group elements have been developed.⁴ However, most of these catalysts suffer from poor selectivity stemming from chain-end control, a method of stereocontrol where the growing polymer determines the stereochemistry of the next monomer inserted.⁴ This method of control leads to repeated stereoerrors.⁴ In contrast, catalysts with enantiomorphic site control rely on a chiral environment around the metal center to preferentially insert one enantiomer of PO over the other.⁴ Under this method of stereocontrol, stereoerrors are not repeated.⁴

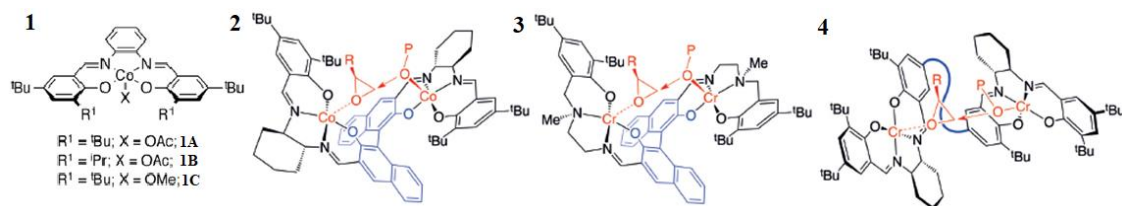


Figure 1. Stereoselective Co and Cr Catalysts.⁵⁻⁶

In 1983, Tsuruta and coworkers developed the first stereoselective Co epoxide ROP catalyst, supported by a salicy ligand.⁷ While this complex showed no selectivity for *rac*-PO, it was able to polymerize epichlorohydrin and *t*-butyl ethylene oxide with low stereo selectivity. The first highly stereoselective catalyst (**1A**) was reported by the Coates group in 2005.⁵ This catalyst could polymerize regioregular, isotactic PPO with virtually no stereoerrors with a turnover frequency (TOF) of 220 h⁻¹ from racemic PO.⁵ The lack of stereoerrors made it impossible to determine the method of stereocontrol, so the Coates group modified the *ortho-t*-butyl groups to less bulky isopropyl moieties on the salph ligand to reduce selectivity.⁸ PPO produced by these derivatives contained isolated

stereoerrors indicating an enantiomorphic site control mechanism.⁸ This result was surprising, considering that catalysts **1A-C** are achiral. Catalyst **1A** also exhibited unusual solvent and temperature sensitivity and had reactivity dependent on crystallization and oxidation conditions.⁸ This led the authors to postulate that the activity arose from undissolved crystals of the catalyst. Analysis of the X-ray crystal structure of **1C** revealed that neighboring **1C** complexes had a pseudo- C_2 relationship, creating a chiral environment.⁸ Each Co center was separated by 7.13 Å, where a PO molecule and alkoxide can coordinate in a favorable geometry for ring-opening, suggesting a bimetallic

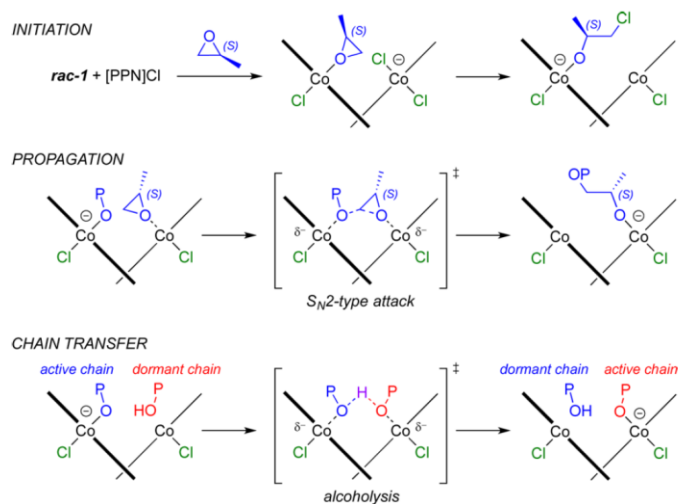


Figure 2. Proposed Basic Mechanistic Steps for Polymerization of PO by Bimetallic Catalyst¹¹

mechanism consistent with previous epoxide ROP mechanisms.^{4,8} Validation for a heterogeneous mechanism was provided by Blum and coworkers using *in operando* bright-field microscopy, where ethylene oxide polymers were observed growing from distinct loci on the crystal surfaces.⁹

Inspired by the crystal structure of **1C**, the Coates group designed a bimetallic cobalt catalyst **2**, by linking two Co(salcy) complexes with a binaphthol linker.¹⁰ While inactive by itself, in the presence of bis-(triphenylphosphine)iminium acetate, [PPN][OAc], as a cocatalyst, **2** was able to kinetically resolve *rac*-PO with high TOF (30,000 h⁻¹) and selectivity factors ($K_{rel} = 370$). **2** was also able to polymerize substituted PO, albeit with lower activities.¹⁰ The [PPN][OAc] cocatalyst plays an intricate role in this polymerization, with density functional theory (DFT) calculations supporting a dual function as an initiator and an activating ancillary ligand.¹² Additional modeling suggests that steric interactions between the anion and binaphthol ligand are responsible for **2**'s stereo- and regioselectivity.¹² Further calculations were utilized to propose a mechanism for the polymerization (Figure 2).¹² First, the dihalide precatalyst is activated by [PPN][X] to form an anion adduct with either the carboxylate or halide ligand in the endo position. This adduct coordinates a molecule of PO, which is attacked by the endo ligand. This forms the kinetic product, a chelate species with both the nucleophile and opened epoxide, which opens to form a new alkoxide, the thermodynamic product, on the adjacent cobalt. This species coordinates another molecule of PO and propagates.

While **2** was both highly active and selective for *rac*-PO ROP, two challenges remained – making dihydroxy telechelic PPO and controlling molecular weight. Dihydroxy telechelic PPO (PPO with two hydroxyl end groups) is required for polyurethane synthesis. The authors decided to add a diol chain-transfer agent (CTA), which facilitates transfer between enantiomers of a racemic catalyst, ending each chain with a hydroxyl group.¹¹ The CTA also allows multiple polymer chains to grow per catalyst, where the molecular weight is controlled by the ratio of CTA:PO. To accomplish these goals, the Coates group modified **2**, which suffered from slow initiation and was impractical to make in a racemic mixture to Cr catalyst **3** (Figure 1).¹¹ This catalyst had lower selectivity ($K_{rel} = 60$), but narrower dispersities ($\bar{D} \approx 1.7$), indicating better molecular weight control.¹¹ Introducing a flexible linker in catalyst **4**, allowed for the catalyst to adopt the ideal conformation for bimetallic cooperative ROP.⁶ This proved beneficial when controlling molecular weight, with **4** being able to polymerize PPO with $\bar{D} = 1.3$ without a CTA, and $\bar{D} = 1.02$ in the presence of a diol CTA, indicating a living polymerization.⁶

The Coates group has developed a family of highly selective catalysts capable of making isotactic PPO, and, in the presence of a CTA, do so in a living polymerization. Future efforts include increasing activity, scalability, and selectivity in the presence (of a CTA).

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