Recent Advances in Stereocontrolled Polymerization

Katie Stawiasz Literature Seminar November 7, 2019

Tacticity control in polymers offers the unique opportunity to understand structure-property relationships on a macroscopic scale. Polymers with stereorandom repeat units often yield materials with drastically different properties than their stereodefined counterparts. In some cases polymer tacticity manifests as minute changes in melting or glass transition temperatures while in others it constitutes a phase change or has considerable effects on mechanical properties (**Figure 1**).[1] The work presented herein will focus on main-chain optical stereochemistry involving stereogenic centers in the backbone of polyolefins as opposed to E/Z isomerism. Controlling optical stereochemistry in polymers is a non-trivial problem; many polymerization methods proceed through free radical or ionic intermediates which result in limited control over product stereochemistry. In small molecule synthesis, chiral organometallic catalysts have long been employed to affect asymmetric induction.[2] In stereocontrolled polymerization, the stereochemistry of the previously installed monomers exerts an inherent substrate bias that must be overcome to achieve further stereochemical control.

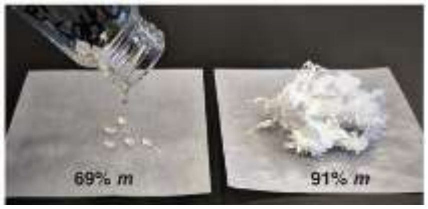

Figure 1. Differences in the percentage of meso diads have considerable effects on polymer properties.[1]

The 1950's experienced a rapid development in organometallic chemistry; Karl Ziegler had just published his finding that room temperature polymerization of polyethylene was possible using $TiCl_4/AlEt_3$.[3] Giulio Natta used these findings to develop a $TiCl_3/AlEt_3$ system which yielded isotactic polypropylene (*i*PP).[4] For this revolutionary work, Ziegler and Natta were awarded the 1963 Nobel Prize in chemistry. Concurrently, reports regarding the synthesis of transition metal "sandwich" compounds, such as ferrocene, were growing.[5] For stereocontrolled polymerization, the incorporation of a bridging group between cyclopentadienyl ligands was crucial for locking catalysts into specific conformations. Employment of C_2 and C_s symmetric metallocenes enabled the production of isotactic and syndiotactic polypropylene respectively (**Figure 2**).[6,7] In either case, the methyl group of the propylene is directed into a pocket of the metallocene while the polymer grows out of the less sterically hindered site. This catalyst configuration also favors a 1,2 insertion over a 2,1 insertion, allowing greater

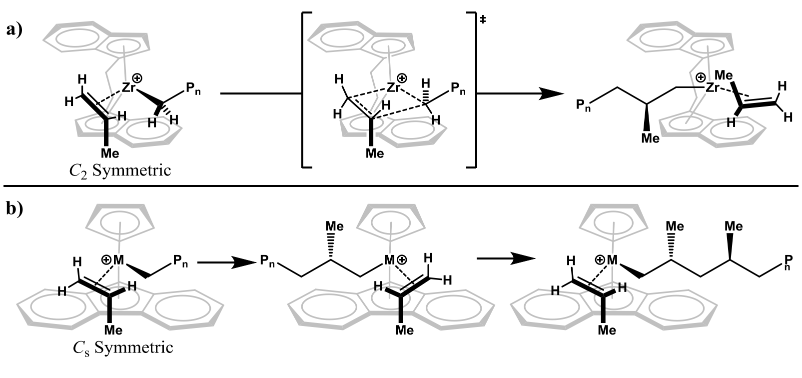

Figure 2. a) C_2 symmetry produces isotactic polypropylene[6] b) C_s symmetry produces syndiotactic polypropylene.[7]
Figures adapted from Coates, G. W. *Chem Rev.* **2000**, *100*, 1223.

stereochemical control. The isotactic polymer melts at 165 °C where its syndiotactic counterpart melts at 130 °C.[8] Catalysts lacking this bridge produced atactic polymers due to unrestricted rotation of the η^5-ligand. These studies made it clear that control of catalyst symmetry affords polymers with precisely controlled stereogenic centers in the main chain.

In 1995 Coates and Waymouth designed a system in which an unbridged metallocene rotates freely to isomerize between chiral and achiral geometries. This allows for the production of isotactic and atactic geometries respectively (**Figure 3**).[9] This work demonstrated the tuneable production of elastomeric polypropylene, a rubbery material with desirable properties that differ considerably from its isotactic and atactic counterparts. Where *i*PP is a highly crystalline polymer and *a*PP is amorphous, the length of these stereoblocks were modified using temperature and propylene pressure to produce semicrystalline thermoplastics with melting temperatures ranging from 52 °C to 145 °C.

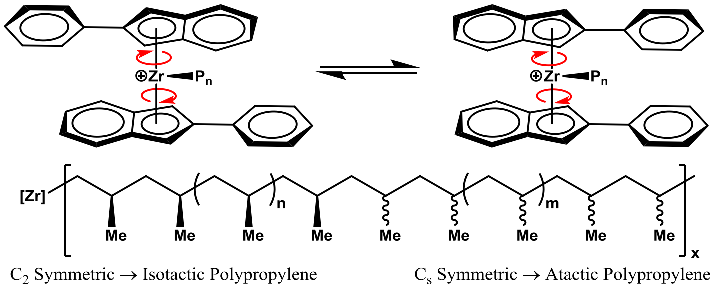

Figure 3. Conformational equilibrium of the unbridged metallocene.[9]

While metallocene chemistry has proven an effective method for stereoselective polymerization of nonpolar α-olefins such as propylene, there remains a great need for the development of stereocontrolled polymerization of polar monomers and epoxides. In 2010, Coates demonstrated isospecific polymerization of polyethers from racemic epoxides using a pseudo C_2 symmetric bimetallic cobalt catalyst and a bis(triphenylphosphine)iminium acetate cocatalyst.[10] These polymers contained *mm* diad sequences of 97% or higher for most of the tested epoxide substituents. Dispersities of approximately 2 indicated to the authors that this was single site catalysis. Analysis of ^{13}C NMR stereoerrors was consistent with an enantiomorphoric site control mechanism.

In 2017, Coates employed a very similar bimetallatic chromium catalyst to synthesize hydroxy-telechelic poly(propylene oxide) (PPO) from racemic monomers (**Figure 4**).[11] These polymers could be employed in products ranging from foams (polyurethanes) to adhesives due to their reactive hydroxyl end-groups. This attractive feature was missing with the formerly mentioned bimetallic cobalt system. The stereocontrolled polymers have very different physical properties compared to their atactic counterparts. Where atactic PPO has a glass transition temperature of -70 °C, isotactic PPO is semicrystalline with a melting temperature of 67 °C. It is

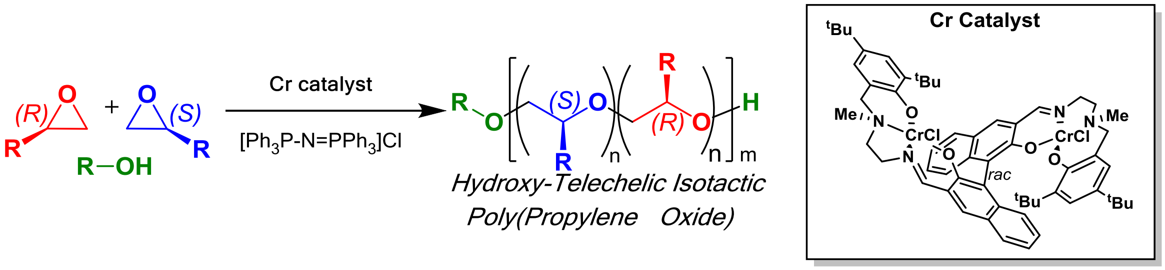

Figure 4. Isospecific polymerization of racemic epoxides involving a bimetallic chromium catalyst.[11]

proposed that the two metal centers are in close enough proximity that S_N2 type attacks of PO occur as the growing chain switches sites (**Figure 5**).

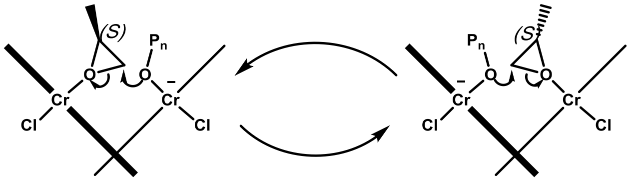

Figure 5. Propagation mechanism with a bimetallic species.[11]

Most recently the Leibfarth group demonstrated that cationic polymerization of *iso*-butyl vinyl ether with a BINOL based chiral anion biased the resulting polymer to contain 92% *meso* diads. Compared to its liquid 69% *m* counterpart, the solid (92% *m*) polymer exhibited properties comparable to low density polyethylene.[1] The authors further demonstrated high isotacticity for a range of vinyl ethers.

Stereocontrolled polymerization has evolved significantly since the inception of the Ziegler-Natta catalyst. While metallocene chemistry facilitated a rational way to control stereochemistry and thus properties such as melting temperature, bimetallic transition metal complexes and chiral anions have proven necessary for the incorporation of polar functionalities. These methods are critical for understanding the structure-property relationship for a diverse range of bulk polymeric materials.

References

[1] Teator, A. J., Leibfarth, F. A. Catalyst-controlled stereoselective cationic polymerization of vinyl ethers. *Science,* **2019**, *363*, 1439–1443.

[2] Cherney, A. H., Kadunce, N. T., Reisman, S. E. Enantioselective and Enantiospecific Transition-Metal-Catalyzed Cross-Coupling Reactions of Organometallic Reagents to Construct C-C bonds. *Chem. Rev*. **2015**, *115*, 9587−9652.

[3] Zielger, K., Holzkamp, E., Breil, H., Martin, H. Polymerisation von Äthylen und anderen Olefinen. *Angew. Chem.* **1955**, *67*, 426.

[4] Natta, G., Pino, P., Corradini, P., Danusso, F., Mantica, E., Mazzanti, G., Moraglio, G. Crystalline High Polymers of α-Olefins. *J. Am. Chem. Soc.* **1955**, *77*, 1708–1710.

[5] Eisch, J. J. Fifty Years of Ziegler-Natta Polymerization: From Serendipity to Science. A Personal Account. *Organometallics* **2012**, *31*, 4917–4932.

[6] Leclerc, M. K., Brintzinger, H. H. Ansa-Metallocene Derivatives. 31. Origins of Stereoselectivity and Stereoerror Formation in Ansa-Zirconocene-Catalyzed Isotactic Propene Polymerization. A Deuterium Labeling Study. *J. Am. Chem. Soc.* **1995**, *117*, 1651–1652.

[7] (a) Ewen, J. A., Jones, R. L., Razavi, A., Ferrara, J. D. Syndiospecific Propylene Polymerizations with Group IVB Metallocenes. *J. Am. Chem Soc.* **1988**, *110*, 6255–6256.
(b) Cavallo, L., Guerra, G., Vacatello, M., Corrandini, P. A Possible Model for the Stereospecificity in the Syndiospecific Polymerization of Propene with Group 4a Metallocenes. *Macromolecules* **1991**, *24*, 1784–1790.

[8] Maier, C., Calafut, T. Propylene: The Definitive User's Guide and Databook. **1998**, Willian Andrew Inc. pg. 14.

[9] Coates, G.W., Waymouth, R. M. Oscillating Stereocontrol: A Strategy for the Synthesis of Thermoplastic Elastomeric Polypropylene. *Science* **1995**, *267*, 217–219.

[10] Widger, P. C. B., Ahmed, S. M., Harahata, W., Thomas, R. M., Lobkovsky, E. B., Coates, G. W. Isospecific polymerization of racemic epoxides: a catalyst system for the synthesis of highly isotactic polyethers. *Chem. Commun*. **2010**, *46*, 2935–2937.

[11] Childers, M. I., Vitek, A. K., Morris, L. A., Widger, P. C. B., Ahmed, S. M., Zimmerman, P. M., Coates, G. W. *J. Am. Chem. Soc.* **2017**, *139*, 11048–11054.