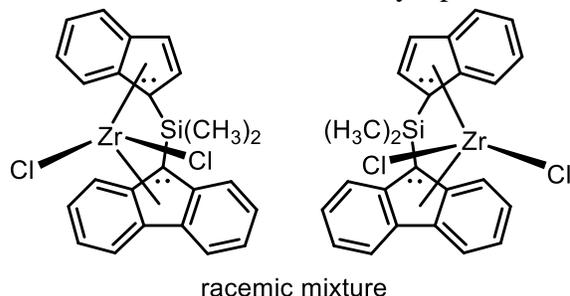


1. Consider the metallocene catalyst pictured below:



- a) Characterize the active sites of this catalyst with regard to topicity (homotopic, enantiotopic, or diastereotopic) and selectivity (enantioselective or nonselective).

Diastereotopic
NS, E

- b) Characterize the tacticity of the polymer that this catalyst would be expected to produce from a 1-substituted ethylene monomer. Explain.

Hemiisotactic. One site of each enantiomer has local symmetry and is thus non-selective. The other site is asymmetric and is expected to coordinate exclusively either the re or si face. Assuming migratory insertion and no back skip, then monomer additions will alternate between random and isoselective. The result is referred to as hemiisotactic.

2. a) What two functions does the Group I-III metal compound perform in traditional Ziegler-Natta polymerizations?

1. Reduces the transition metal to the correct oxidation state. Usually this involves reduction of TiCl_4 to TiCl_3 . 2. Supplies the initiating species, i.e., the group that satisfies the valence at the head of the polymer chain. Typically this is an ethyl group from triethylaluminum.

What two functions does methylaluminoxane perform in a metallocene polymerization?

1. Behaves as a Lewis acid to remove a halide (usually chloride) from the catalyst precursor; this yields a positively charged catalyst with a counteranion derived from MAO. 2. Supplies the initiating species, which for MAO, is a methyl group.

3. Polymerization of propylene is carried out with a certain metallocene catalyst. NMR analysis shows that the overwhelming majority of dyads are meso (m). However, a small fraction of racemic (r) dyads is observed, and they are observed to occur as adjacent pairs along the chain (for example, ...m m m m m m m m m r r m m m m m m m m m m m m m m r r m m m m m...).

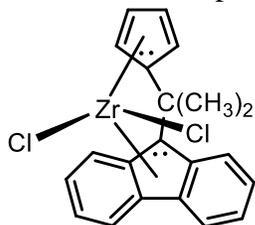
a) What is the probable type of catalyst being used (C_{2v} , C_2 , etc.)?

Probably C_2 , but possibly could be C_1 .

b) What is the probable mechanistic origin of these occasional stereoerrors?

Probably epimerization.

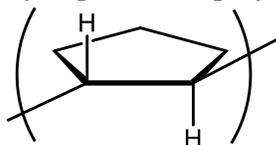
4. For metallocene polymerization of propylene using the catalyst below,



explain in detail the mechanism of propagation and the stereochemical result (tacticity) of the resulting polypropylene.

The catalyst pictured is a C_s type. The active sites are each enantioselective due to local asymmetry. But the two active sites are also mirror images of each other (enantiotopic); therefore if one is selective for the *re* face of monomer, then the other will be selective for the *si* face of monomer. This leads to syndiotactic polymer by the following mechanism: Let us begin the mechanism with the growing polymer chain attached to, for example, the left side of the catalyst (as pictured above). Monomer approaches and coordinates to the vacant (right) side of the catalyst with, for example, its *re* face directed to the transition metal. Migratory insertion occurs, and now the growing chain resides on the right side of the catalyst as pictured. Next, monomer approaches and coordinates to the left side of the catalyst, which is now the vacant site. However, on the left side, monomer must approach with its *si* face directed to the transition metal (because the two sites are mirror images). Migratory insertion occurs and we are back to our starting point. In this cycle of two propagations, we see that a racemic dyad has been produced. If each succeeding cycle of two propagations occurs similarly, the polymer will consist solely of racemic dyads ($r = 1$). This is by definition a purely syndiotactic polymer.

5. Cyclopentene is polymerized to yield the following structure:



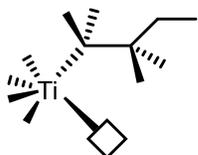
Which type of ditacticity is displayed?

First, we know that it must be diisotactic; because we require only one repeating unit to define the tacticity. Were it syndiotactic, we would be obliged to show two consecutive repeating units to so signify. Since, in the planar zig-zag representation of this polymer, there is a syn arrangement of like groups, the type of diisotacticity is threodiisotacticity.

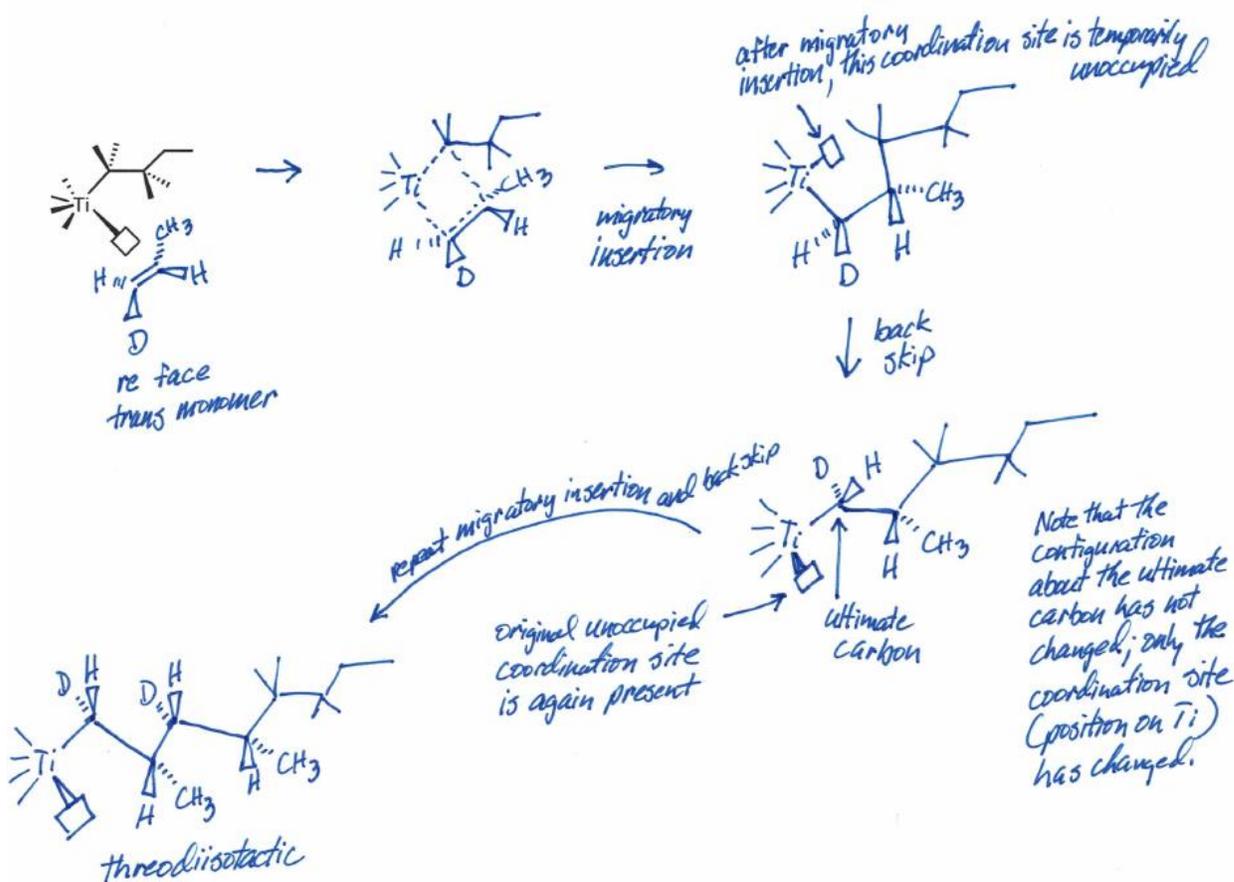
6. The anionic polymerization of methyl methacrylate in toluene with lithium counterion gives highly isotactic polymer; in THF with sodium counterion, the result is moderate syndiotacticity similar to free radical (syndiotacticity increases as temperature decreases). Explain the role of the solvent and counterion in determining the stereoregularity of polymerization.

The combination of toluene/lithium counterion (non-polar solvent and less electropositive alkali metal) tends to produce predominantly contact ion pairs. The strongly coordinating counterion promotes catalyst site control and isotactic placement. The combination of THF/sodium counterion tends to produce predominantly solvent-separated pairs or free anions. Under these conditions, a tendency toward syndiotacticity results from chain end control.

7. Starting from my diagram, show the detailed mechanism of traditional Ziegler-Natta polymerization of trans-1-d-propylene, assuming that monomer always directs its re face (priority decreases clockwise) toward Ti. What type of diastereotacticity is produced (threo means the two stereocenters have opposite configuration, erythro the same)?



The mechanism would proceed as follows to yield threodiisotactic polymer.



8. Compare and contrast the properties of cis-1,4-polyisoprene and trans-1,4-polyisoprene.

Cis-1,4-polyisoprene is an elastomer. It is soft and flexible. It possesses a low glass transition and very little crystallinity (except at high strains, where so-called strain-induced crystallinity is observed). The cis double bonds do not pack well, and this is the principle reason for low crystallinity. In comparison, trans-1,4-polyisoprene is a semi-crystalline plastic. It is harder and less flexible and has higher T_g than cis-1,4-polyisoprene. It has a melting point. The trans double bonds facilitate chain packing, and this is the principle reason for the tendency to crystallize.