# Literature Discussion on “*Oscillating Stereocontrol: A Strategy for the Synthesis of Thermoplastic Elastomeric Polypropylene”*

by Geoffrey W. Coates and Robert M. Waymouth, *Science,* **1995,** *267,* 217-219.

Questions for consideration:

1) In your own words, describe a thermoplastic elastomer.

2) a) Draw a molecule of propylene and label the carbons with “1” and “2” according to nomenclature rules. Write the series of reactions showing the 1,2-insertion of 3 propylene monomers into the growing polymer chain of a catalyst [Zr+] – P (where P denotes the polymer chain, not phosphorus). (Hint: the result of a 1,2-insertion is that the carbon #1 is bonded to the metal and carbon #2 is attached to P.)

b) Explain why the carbons with the methyl groups (labeled “2”) in the polymer backbone are chiral.

3) a) Refer to Figure 1 and footnote 17. What do the designations “m” and “r” denote in the polypropylenes depicted?

b) Sketch a segment of polypropylene that is syndiotactic (where the relative stereochemistry of the all methyl groups is “r”).

4) Refer to Figure 2. Only one enantiomer of the chiral *ansa*-zirconocene capable of synthesizing isotactic polypropylene is depicted. Sketch the other enantiomer.

5) a) Consider the pre-catalyst compound bis(2-phenylindenyl)zirconium dichloride, (2-PhInd)2ZrCl2 and the active catalyst, (2-PhInd)2Zr+-P (where P = growing polymer chain, not phosphorus). Use the covalent bond classification (CBC) method of electron counting to fill in the table below.

|  |  |  |
| --- | --- | --- |
|  | (2-PhInd)2ZrCl2 | (2-PhInd)2Zr+-P |
| 2-PhInd CBC ligand classification |  |  |
| Cl CBC ligand classification |  | N/A |
| P (growing polymer chain) CBC ligand classification | N/A |  |
| MLlXxZz classification |  |  |
| Valence number |  |  |
| Ligand bond number |  |  |
| Electron count from ligands |  |  |
| Electron count from metal |  |  |
| Total electron count |  |  |
| dn count for metal |  |  |

b) Use the data from the table above to explain why the propylene polymerizations using zirconocene-derived catalysts typically take place under rigorously water-free conditions.

6) a) Refer to Figure 3. Draw the isomer of the active catalyst, (2-PhInd)2Zr+-P, that is responsible for synthesizing the atactic blocks and isotactic blocks within a single polypropylene (PP) chain.

|  |  |
| --- | --- |
| Isomer that synthesizes atactic PP  | Isomer that synthesizes isotactic PP  |
|  |  |

b) Define the 4 rate constants in the figure.

c) Refer to Figure 3 and the equation on page 218. Why must *k*i be less than *k*pi[mon] in order for a block of isotactic polypropylene to be synthesized?

d) If the ligand were varied from 2-phenylindenyl to 2-methylindenyl, predict how the change would affect the rate constants *k*i and *k*-i. Would you predict that this catalyst could synthesize isotactic-atactic stereoblock polypropylene? Explain your answers.

7) Using the description at the end of page 217 and footnote (10), sketch the synthetic scheme for the synthesis of (2-PhInd)2ZrCl2 starting from 2-indanone.

8) How do the two crystal structures shown in Figure 4 support the proposed mechanism for isotactic-atactic stereoblock polypropylene formation in Figure 3?

9) According to Table 1, how is the isotactic pentad content, [mmmm], measured for polymer samples PP1-PP9?

10) The isotactic pentad content of atactic polypropylene is 6.25%. Show how this percentage is consistent with a probabilistic model of how propylene monomers insert into a growing polymer chain to form atactic polypropylene.

11) How did the authors use solvent fractionation (see second to last paragraph of the article) to demonstrate that a polypropylene sample similar to PP4 was an isotactic-atactic stereoblock polypropylene and not a mixture of isotactic and atactic polypropylene with [mmmm] = 16%?

12) Why did the authors cite the three articles listed in reference (18)?