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FI Catalysts: A Molecular Zeolite for Olefin Polymerization

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Abstract: A bis(phenoxyimine) group 4 transition metal catalyst (now known as FI catalysts) can discern ethylene from a mixture of ethylene and propylene at more than 99% selectivity. Denisty function theory (DFT) calculations revealed a spatially confined reaction site in the transition states of the migratory insertion which is just the right size for an ethylene molecule but too small for a propylene one. The substituents adjacent to the phenoxy-oxygens are of crucial importance in developing the size/shape-selectivity.

Keywords: ligand design; polymerization; size selectivity; substituent effects; zeolites

Improvements in transition metal-catalyzed olefin polymerization performance can roughly be attributed to selectively increased or suppressed rates of specific elementary reaction(s), i.e., initiation, propagation, chain transfers, and irreversible terminations. Due to the inherent characteristics of polymerization reactions, where any errors tend to leave significant and sometimes fatal consequences in the polymer products, any selectivity involved in these elementary reactions needs to be extremely high for the synthesis of macromolecules with desired structures, while such errors will simply reduce the yield for the synthesis of small molecules. For example, ultra-high molecular weight polyethylene having molecular weights in the millions can be prepared with high efficiency, which means that the propagation reaction is about 99.999% selective relative to any possible side reactions that can interrupt its chain growth. In another example, stereospecific propagation of α-olefins achieves ~99.9% enantioselectivity to give either isotactic or syndiotactic polypropylene with extremely high melting temperatures (T_m), which are readily degraded with only the slightest microstructural errors.

However, in the field of olefin copolymerization catalysis, the selectivity among the comonomers has not been considered important, or rather the research efforts have been directed towards widening the scope of comonomer variety and increasing comonomer uptake (which of course have yielded an incredibly rich variety of polyolefin products) and towards a less selective direction. This trend has been accelerated by the advent of well-defined single-site catalysts,[1] because they surpass, based on the rational understanding of polymerization mechanisms and molecular design, the limited performance attainable with the classical heterogeneous Ziegler–Natta catalysts regarding comonomer incorporation. Thus, olefin copolymerizations have rarely been perceived as a selective catalysis and have not been directed towards the other end of the spectrum, that is, a substrate-selective catalysis to enchain a particular monomer from among a mixture of more than two monomers. Such selectivity among small molecules has been known to exist in catalysis by zeolites, in which the molecules are discerned by uniform pore size and topologies.[2] To the best of our knowledge, in transition metal-catalyzed olefin polymerizations or any transition metal-catalyzed organic reactions, there are few examples that exhibit a high selectivity based on the size or shape of the substrates in a similar way that zeolites or related catalysts do for simple alkanes or alkenes,[3] which have no directing functional groups to aid the selective reactions through complementary non-covalent interactions as seen in enzymatic catalysis.

Our continuing research into bis(phenoxyimine) group 4 transition metal catalysts (now known as FI catalysts) has revealed that the appropriate choice and design of phenoxyimine ligands, metal, cocatalysts, and polymerization conditions make FI catalysts very selective in almost all aspects of polymerization and polymer structures. FI catalysts are (i) extraordinarily active for ethylene polymerization (TOF = 64,900 $s^{-1} atm^{-1}$),[4] and (ii) very selective about chain propagation to yield UHMWPE,[4] ultra-high molecular weight ethylene/α-olefin copolymers

($>$10,000,000 Da)[5] and atactic polypropylenes (8,300,000 Da),[6] and also various living olefin polymers, which represent ultimate selectivity in propagation over any termination reactions that do not exist.[7] FI catalysts can be (iii) highly iso- and syndiospecific for both propylene[8] and styrene[9] polymerizations, and (iv) can be selective in chain end structures to produce exclusively vinyl-[10] or R_2Al-terminated[11] olefin polymers (R = alkyl).

Here we would like to report on another unique selectivity pertaining to FI catalysts, namely, the substrate-selectivity in ethylene/propylene copolymerizations, where only ethylene is enchained into polymers out of ethylene/propylene mixtures at $>$99% selectivity with high efficiency. In addition, this remarkable selectivity based on molecular size/shape has resulted in unique characteristics for the obtained polyethylenes, or can be used for new olefin polymerization and other processes. We would also like to touch on these new and emerging applications based on this unique substrate-selective catalysis.

The selectivity between ethylene and propylene in copolymerizations can be quantitatively estimated by monomer reactivity ratios (MRR). In this study, we assume the first-order Markov chain, where the reactivity of the propagating species depends on the last-inserted monomer unit (terminal model).[12] On this assumption, there are four propagating reactions as shown in Scheme 1, and the MRR (r_1, r_2) are defined as the ratios of the propagation rate constants, $r_1 = k_{11}/k_{12}$, $r_2 = k_{22}/k_{21}$ (M_1 = ethylene; M_2 = propylene).

A prototypical metallocene, Cp_2ZrCl_2, and a constrained geometry catalyst, $Me_2Si(Me_4C_5)(N\text{-}t\text{-}Bu)TiCl_2$ (CGC), were examined in ethylene/propylene copolymerization as a benchmark. Comonomer uptake of Cp_2ZrCl_2 is modest or relatively low, while CGC is known as one of the most efficient catalysts for incorporating higher α-olefins in ethylene/α-olefin copolymerization.[13]

The MRR were evaluated using the Fineman–Ross method, and the conversions of propylene were kept below 10% for almost all runs to minimize the change from the initial monomer compositions.[14] However, the comonomer incorporation ability of CGC was so high that the monomer conversions easily exceeded this limit. Therefore, the MRR for CGC could not be accurately evaluated under the conditions examined. Nevertheless, the monomer compositions in feed and in the copolymer are very close to each other (Table 1), which suggests an even smaller r_1 value than the r_1 (= 4) estimated previously for ethylene/1-octene copolymerization using the same complex.[13] The r_1 of Cp_2ZrCl_2 was estimated at 13; meaning that the ethylene last-inserted species ($Cp_2Zr\text{-}CH_2CH_2\text{-}$polymer) is 13 times more reactive toward ethylene relative to propylene.

$$L_nZr{\cdot}M_1\text{-}M_i\text{-}M_i\text{-}M_i\text{-}\text{-} \xrightarrow[M_1]{k_{11}} L_nZr{\cdot}M_1\text{-}M_1\text{-}M_i\text{-}M_i\text{-}M_i\text{-}\text{-}$$

$$L_nZr{\cdot}M_1\text{-}M_i\text{-}M_i\text{-}M_i\text{-}\text{-} \xrightarrow[M_2]{k_{12}} L_nZr{\cdot}M_2\text{-}M_1\text{-}M_i\text{-}M_i\text{-}M_i\text{-}\text{-}$$

$$L_nZr{\cdot}M_2\text{-}M_i\text{-}M_i\text{-}M_i\text{-}\text{-} \xrightarrow[M_1]{k_{21}} L_nZr{\cdot}M_1\text{-}M_2\text{-}M_i\text{-}M_i\text{-}M_i\text{-}\text{-}$$

$$L_nZr{\cdot}M_2\text{-}M_i\text{-}M_i\text{-}M_i\text{-}\text{-} \xrightarrow[M_2]{k_{22}} L_nZr{\cdot}M_2\text{-}M_2\text{-}M_i\text{-}M_i\text{-}M_i\text{-}\text{-}$$

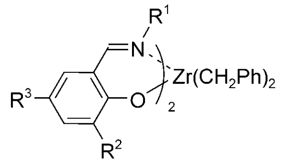
Scheme 1. Propagation reactions in the first order Markov chain (L: ancillary ligand; i = 1 or 2).

FI catalysts **2**–**4** are substantially more ethylene-selective than Cp_2ZrCl_2 or CGC. In particular, FI catalyst **4**, that has cumyl groups adjacent to the phenoxy-oxygen (R^2 substituents), exhibited a more than 150 times higher reactivity towards ethylene than propylene, i.e., a remarkable selectivity of $>$99%, despite the difference of only one carbon in the substrates. On the other hand, the fact that **1** (R^2 = cyclooctyl) showed the lowest selectivity demonstrates that the R^2 plays a vital role in determining the selectivity of ethylene monomers from a mixture of ethylene and propylene and that the steric bulk of R^2 near the α-carbon (to the phenoxy ring) is more important rather than the bulk of the entire R^2.

The r_1 values of **2** and **3** (R^2 = *t*-Bu), which are similar to each other and in between those of **1** and **4**, indicate that the substituents on the imine-nitrogen (R^1 substituents) have a smaller effect on monomer selectivity,[15] although considerable differences in polymer molecular weights are observed for these catalysts,[14] showing that polymer molecular weight and the substrate selectivity are determined independently as previously suggested.[4] These observations are qualitatively consistent with an assumed octahedral *cis*-N, *trans*-O, *cis*-X (the reaction site) configuration of these FI catalysts, where the R^2 is located above and below the reaction site, while the R^1 is positioned at the slightly skewed backside of the reaction site, and thus does not directly interact with a coordinating monomer.

The DFT calculations further reinforce the argument described above. Figure 1 compares the computed transition state structures for the migratory insertions of ethylene and propylene to the alkyl complexes of **1** and **4**, where the alkyl chain is represented by an *n*-propyl group, [hereafter, TS(**1**, E) and TS(**1**, P) denote the transition states of ethylene and propylene insertion to the cationic propyl derivative of **1**, respectively]. The bond lengths and geometry of the four-membered metallacycles are very similar to each other for these complexes.[14] However, the environments around these metallacycles are significantly different due to the R^2 that is situated close to the reaction site. The cyclooctyl groups of **1** can ease steric tension by directing the smallest hydrogen on the α-

Table 1. Monomer reactivity ratios in ethylene/propylene copolymerizations.[a]



FI catalysts **1** – **4**

1: R^1 = 2-Me-cyclohexyl, R^2 = cyclooctyl, R^3 = Me
2: R^1 = 2-Me-cyclohexyl, R^2 = *t*-Bu, R^3 = Me
3: R^1 = Ph, R^2 = *t*-Bu, R^3 = H
4: R^1 = 2-Me-cyclohexyl, R^2 = cumyl, R^3 = Me

Catalyst precursor	Propylene in feed [mol%][b]	Propylene conversion [%]	Propylene in polymer [mol%][c]	r_1
Cp_2ZrCl_2	32.25	11.4	2.87	13
Cp_2ZrCl_2	58.84	6.1	4.63	
CGC[d]	36.69	16.6	31.77	–
1	32.25	8.6	2.39	16
1	58.84	3.1	3.52	
1	72.70	8.3	5.12	
2	58.84	7.7	1.79	69
2	72.70	2.0	2.48	
2	85.40	3.3	5.23	
3	58.84	7.6	2.59	45
3	72.70	6.0	3.84	
3	85.40	3.9	5.12	
4	58.84	0.42	0.88	152
4	72.70	3.2	1.95	
4	85.40	6.2	3.02	

[a] *General conditions:* 5.0 mL of hexane, Al(dMAO)/Zr = 300, 100 °C, 10 min, 7.0 atm gauge pressure maintained by continuous ethylene supply.

[b] Calculated initial monomer composition.

[c] Determined either by IR or ^{13}C NMR.

[d] 5.0 mL of toluene, $(i\text{-Bu})_3Al/Ph_3CB(C_6F_5)_4/CGC = 300/2/1$, 100 °C, 5 min, 7.0 atm gauge pressure maintained by ethylene supply.

carbon (to the phenoxy ring) toward the metallacycles (Figure 1 a,b). Considering that the van der Waals radius of hydrogen is 1.20 Å, TS(**1**, E) and TS(**1**, P) have no significant constraint between R^2 substituents and the reaction site. On the other hand, one of the methyl groups in the cumyl group of **4** needs to protrude into the reaction sphere, and besides, the conformation of the cumyl group is much more rigid than that of the cyclooctyl group because of the high rotational barrier around the two C(quaternary)–C(*ipso* carbons in phenyl and phenoxy groups) bonds. This geometry and rigidity of the cumyl group considerably confine the space around the reaction site as can be clearly seen in the shortest distances between R^2 and the reaction site (Figure 1 c,d). The structure of TS(**4**, E) demonstrates that even the ethylene molecule seems to be close-fitting in the confined space formed by the cumyl groups. With regard to TS(**4**, P), the spatial constraints between the cumyl groups and the transition state metallacycle seem to be critically large, apparently verified by the very short H–H distances (Figure 1 d). From the calculated rate constants (k_{11}, k_{12}), the r_1 values were estimated at 125.5 and 57.5 for **4** and **1**, respectively, which are in appreciably good agreement with the experiments.

Kretschmer, Kempe and their co-workers reported a similar ethylene selective polymerization using zirconium complexes bearing aminopyridinato ligands.[3a] Under the given conditions in their report, the selectivity seems to roughly correspond to the level of **2** (propylene mole fraction in the reaction media: 43.5%; propylene content in polymer: < 1 mol%) at 80 °C (*vs.* 100 °C for our experiments), which implies that the ethylene selectivity of **4** will exceed that of their catalysts under comparable conditions. In addition, despite the significant steric difference in their ligands, the ethylene selectivity did not vary for their two complexes, from which they concluded that this selectivity is electronic in nature. This is in sharp contrast to the FI catalysts that exhibit a clear structure-selectivity relationship where the origin of the selectivity is primarily steric in nature and thus tunable.

This remarkably high ethylene-selectivity of the FI catalysts has resulted in applications that have not been possible using catalysts with ordinary selectivity.

One of the consequences of the unique ethylene-selectivity is that FI catalysts can produce a completely linear polyethylene free from any short or long chain branches. Commercially available high density polyethylenes (HDPE) have methyl branches (0.2–0.6 Me/

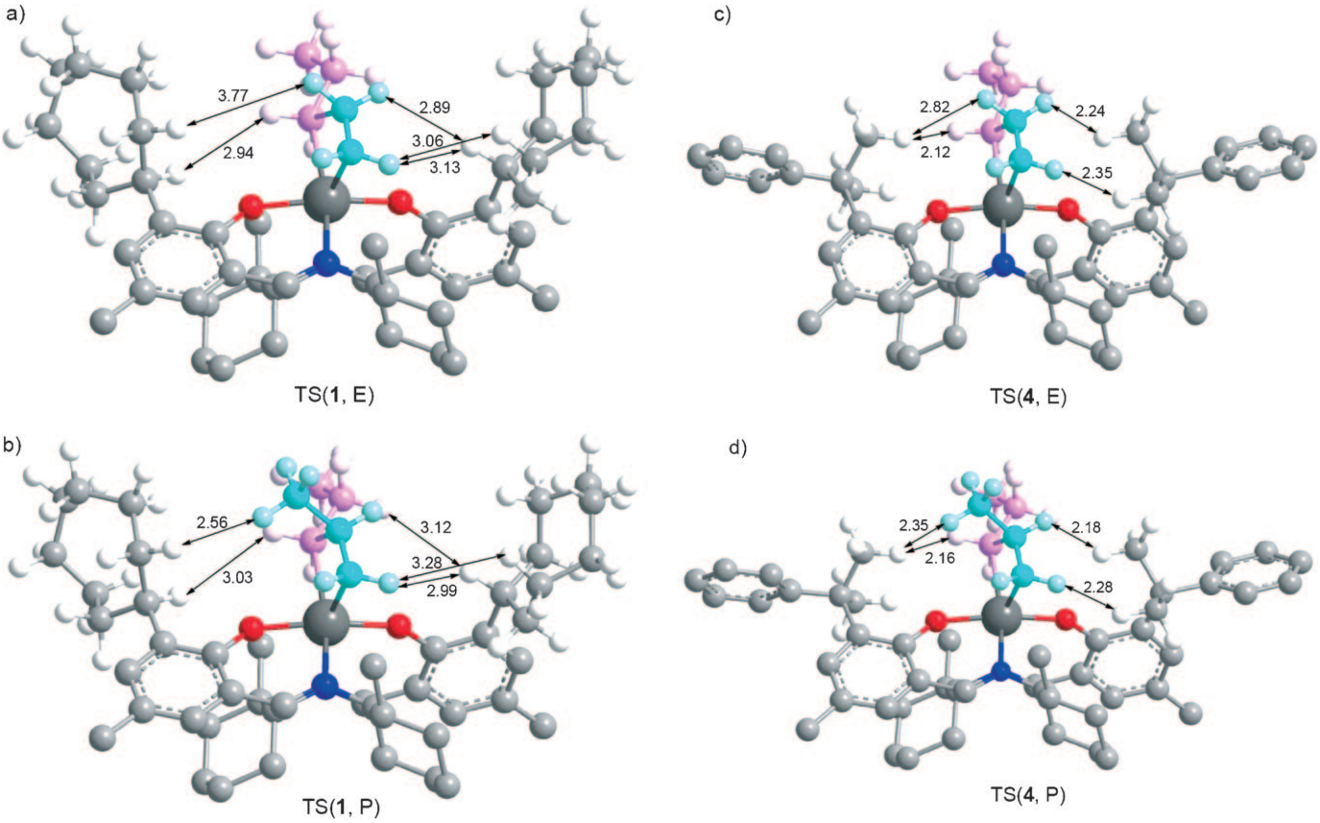
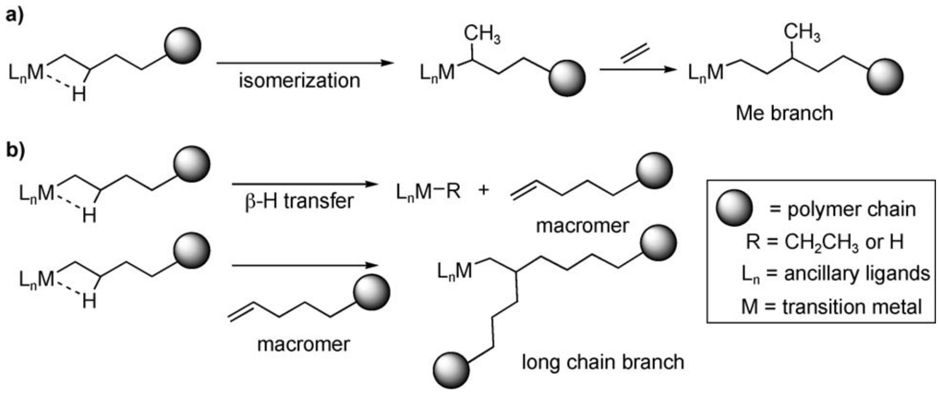


Figure 1. Calculated transition states of olefin insertion into Zr-propyl species of FI catalysts: **a)** TS(**4**, E); **b)** TS(**4**, P); **c)** TS(**1**, E); **d)** TS(**1**, P). The important distances are given in Å. The atoms highlighted in red and blue are oxygens and nitrogens, and in light blue and pink represent inserting monomers and propyl chains, respectively. Some hydrogen atoms are omitted for clarity.

1000 C) or longer branches that are not derived from α-olefin comonomers,[16] but presumably from chain-end isomerization (Scheme 2 a) or reinsertion of *in-situ* generated vinyl macromers (Scheme 2 b). For example, a heterogeneous Ziegler catalyst yielded polyethylene with 0.3 and 0.6 methyl branches per 1000 carbons in ethylene *homo*-polymerizations, while polyethylenes prepared by complex **2** under comparable conditions are truly linear and have virtually no branches (under the detection limit, < 0.1 branch/1000 C).[16] Since the highly ethylene-selective FI catalysts possess such a confined reaction site, the isomerization, which will generate a sterically demanding secondary α-carbon or the reinsertion of large macromers, is virtually impossible. The defect-free, completely linear PE is expected to show higher crystallinity, stronger intermolecular forces, and thus greater tensile strength. These features are most suitable for



Scheme 2. Probable pathways for the formation of **a)** methyl, and **b)** long chain branches.

UHMWPE having $>10^6$ molecular weights, whose applications range from lithium ion battery separators to bulletproof vests. In fact, complex **4** produces such UHMWPE under industrially relevant conditions.[14]

Scientists at Dow Chemical Company have recently revealed that the high ethylene-selectivity of FI catalysts can also be applied to make an olefin block copolymer in a continuous process.[17] The process includes two catalysts, one of which is a highly ethylene-selective FI catalyst (closely related to complex **2** in this work) that provides the block copolymers with crystalline segments with low comonomer contents and high melting temperatures (T_m). The hard crystalline segments produced with the FI catalyst form physical cross-linking points connecting the very elastic soft segments, which were simultaneously produced with the other catalyst, generating an infinite network and serving as a thermoplastic elastomer. The strength of the cross-linking points is directly related to the crystallinity of the hard segments, which in turn is attributed to the excellent ethylene-selectivity of the FI catalysts over 1-octene.

In conclusion, we have developed highly ethylene-selective FI catalysts based on the size/shape recognition in the substrates. An FI catalyst can polymerize only ethylene monomers from mixtures of ethylene and propylene at $>99\%$ selectivity, the highest selectivity ever reported. Zeolites are known to be highly selective in size and shape of substrates or products in the reactions of small molecules based on the size and topology of uniform pores. Similarly, the molecular size/shape selectivity of FI catalysts stems from the confined reaction site consisting of the metal center and the appropriate substituents on the phenoxyimine ligands, which is just right for ethylene but too small for propylene, allowing FI catalysts therefore to function as a molecular zeolite. As such, we envisage that the FI ligand framework, which is relatively rigid as an organometallic compound but significantly more flexible than inorganic zeolites, might be applicable for other reactions which require high selectivity at the molecular level.

Experimental Section

Ethylene/Propylene Copolymerization

Copolymerizations were carried out in a parallel, multi-reactor (Endeavor Catalyst Screening System®, Biotage AB) equipped with the reagent addition ports and automated system of gas delivery, heating and mixing control, and the entire system was placed in a nitrogen-filled glove box. Into thoroughly dried reactors, hexane (5 mL) was added *via* a gas-tight syringe through the reagent addition ports and saturated with propylene gas at 25 °C under vigorous stirring. In a separate vessel, a catalyst solution was prepared by mixing an FI ligand and $Zr(CH_2Ph)_4$ in 2:1 molar ratio in toluene. Propylene was introduced until the reactor pressure reached the predetermined value and the reactors were closed. The reactor temperature was raised to 100 °C and ethylene gas was applied so that the total gauge pressure of the reactors was maintained at 7 bar all the time. Through the reagent addition ports, a prescribed amount of dMAO in toluene, and then the catalyst solution were added to initiate the polymerization. After 10 min, the polymerization was quenched by adding isobutyl alcohol. After removal of volatiles, the obtained polymer was dried under vacuum at 100 °C for 12 h.

Elucidation of MRR

The initial monomer compositions in solution under the given conditions were calculated by using Aspen Plus® (Aspen Technology, Inc.) and the copolymer compositions were measured either by IR or ^{13}C NMR (Table 1). According to the Fineman-Ross equation [Eq. (1)], where F is the initial molar ratio of ethylene/propylene in reaction media and f is copolymer compositions (ethylene/propylene) in the obtained polymers, F(f - 1)/f was plotted against F^2/f and linear approximation of the plots (mean square correlation coefficient, $R^2=0.96$–0.99) gave the r_1 as slope of a line and the r_2 as a Y-intercept.

$$F(f-1)/f = F^2 r_1/f - r_2 \qquad (1)$$

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