

## Structure–Activity Relationship in Olefin Polymerization Catalysis: Is Entropy the Key?

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**Abstract:** Activation parameters for propene polymerization mediated by a bis(phenoxyamine)Zr-dibenzyl catalyst in combination with MAO have been measured experimentally and calculated by DFT; experiment and calculation consistently indicate that the entropic term is the most important reason for the low chain propagation rate with this system. Based on this finding and a review of literature data on a variety of olefin polymerization catalysts, we propose a strong correlation between the propagation rate and how catalysts deal with the entropy loss of monomer capture.

The relationship between structure and activity is the least understood aspect of olefin polymerization catalysts. The reaction rate can be expressed as<sup>1</sup>

$$v_p = -d[C_nH_{2n}]/dt = k_p x^* [M][C_nH_{2n}] \quad (1)$$

where [M] is the total concentration of the transition metal and  $x^*$  is the catalytically active fraction. There are reasons to believe that the latter is small not only for heterogeneous catalysts<sup>2</sup> but also for homogeneous ones.<sup>3</sup> Unfortunately, the only robust method to measure  $x^*$ , that is analyze the buildup of polymer molecular weight with time,<sup>4</sup> is difficult to apply with catalysts and monomers of industrial interest, because chain growth under practical conditions can be completed in a few milliseconds (which is too fast even for quenched-flow techniques). The available information is therefore quite limited.

**Table 1.** Activation Parameters for Olefin Polymerizations Mediated by Different Catalyst Systems (If Not Otherwise Specified,  $T = 273$  K)

#	Catalyst <sup>a</sup> (monomer) <sup>b</sup>	$k_p$ , L mol <sup>-1</sup> s <sup>-1</sup>	$\Delta H^\ddagger$ , kcal mol <sup>-1</sup>	$\Delta S^\ddagger$ , cal K <sup>-1</sup> mol <sup>-1</sup>	ref
1	1/B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> (H)	6.3 ± 0.6 <sup>c</sup>	6.4 ± 1.5	-33 ± 5	6
2	2/MAO/ TBP (P)	3.37 ± 0.07	4.97 ± 0.06	-44 ± 2	This work
3	3/AlEt <sub>2</sub> Cl (P)	0.012 <sup>d</sup>	4.4	-47	5a
4	4/[Ph <sub>3</sub> C] [B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ] (H)	9.2 ± 0.7	7.9 ± 0.4	-33.1 ± 1.1	5b
5	5 (H)	0.067	10.9 ± 0.5	-23 ± 2	5b
6	6/MAO (P)	0.017	9.3 ± 0.5	-33 ± 2	5c
7	7/MAO (E)	2.6 × 10 <sup>5</sup> <sup>c</sup>	10.7 ± 1.2	4 ± 4	3a

<sup>a</sup> 1, 2, and 7, see text; 3 = V(acac)<sub>3</sub>, 4 = [tBuNON]ZrMe<sub>2</sub>, 5 = {[MesNpy] HfR}[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], 6 = *rac*-( $\alpha$ -diimine)NiBr<sub>2</sub>, TBP = 2,6-di-*t*-butylphenol. <sup>b</sup> H = 1-hexene, P = propene, E = ethene. <sup>c</sup>  $T = 293$  K. <sup>d</sup>  $T = 208$  K.

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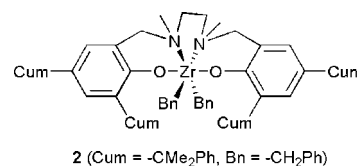
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Since slow processes are easier to study, one option is to deliberately retard fast polymerizations; an outstanding example is the study of Landis,<sup>6</sup> in which the prototypical *ansa*-zirconocene *rac*-C<sub>2</sub>H<sub>4</sub>(1-Indenyl)<sub>2</sub>ZrMe<sub>2</sub> (**1**) was activated with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, so as to moderate the active cation with the ‘sticky’ [MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sup>-</sup> anion, and used to polymerize 1-hexene (entry 1 of Table 1); however, it is not obvious that the information thus obtained can be extended to the cases of real interest. On the other hand, a number of catalysts are *inherently* slow even when used in combination with competent cocatalysts/activators to polymerize ‘fast’ monomers such as ethene or propene; we thought that understanding why might be revealing.

One such catalyst is obtained from the bis(phenoxyamine)Zr-dibenzyl precursor **2** (Chart 1). In previous papers,<sup>8</sup> we reported that propene polymerization with **2**/MAO/TBP (MAO = methylaluminumoxane, TBP = 2,6-di-*tert*-butylphenol<sup>9</sup>) in toluene yields a highly isotactic polymer with controlled kinetics for several minutes at RT.

**Chart 1**

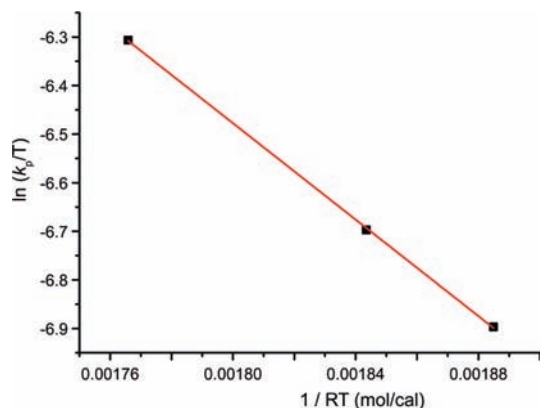


We have now carried out polymerization runs at three different temperatures (267, 273, 285 K), measured  $k_p$  and  $x^*$  independently from the time evolution of polymer molecular weight ( $M_n$ ) according to the classical method of Natta,<sup>4</sup> and estimated  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  from the Eyring plot (Table 2, Figure 1 and Supporting Information).

**Table 2.** Best-Fit Values of  $k_p$  and  $x^*$  for Propene Polymerization in the Presence of **2**/MAO/TBP

$T$ , K	10 $k_p$ , L mol <sup>-1</sup> s <sup>-1</sup>	$x^*$
267	2.7 ± 0.5	0.16 ± 0.04
273	3.37 ± 0.07	0.28 ± 0.01
285	5.2 ± 0.3	0.39 ± 0.05

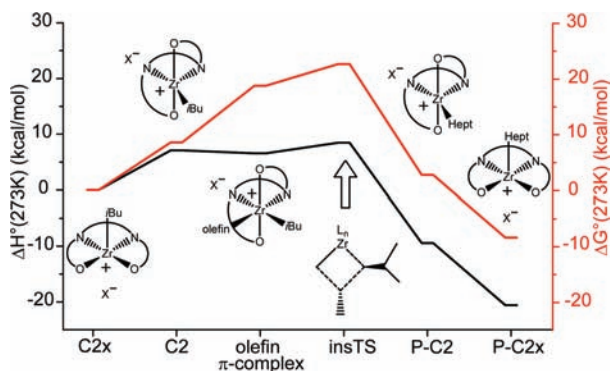
The results, summarized at entry 2 of Table 1, demonstrate that the low  $k_p$  is due primarily to a large negative  $\Delta S^\ddagger$ , overwhelming the modest  $\Delta H^\ddagger$ . The value of  $x^*$  is appreciably lower than 1.0 and increases with increasing temperature; therefore, an Eyring plot based on  $\{T, k_p x^*\}$  data would have led to a gross error on both  $\Delta H^\ddagger$  (12 instead of 5 kcal mol<sup>-1</sup>) and  $\Delta S^\ddagger$  (-15 instead of -44 cal K<sup>-1</sup> mol<sup>-1</sup>).



**Figure 1.** Eyring plot based on the  $\{T, k_p\}$  values in Table 2.

Recent solution NMR and DFT results<sup>10</sup> suggest that for this catalyst class the most stable isomer for the cation is the outer-sphere ion pair **C2x** of Figure 2, with the *cis*(*N,N*)-*cis*(*O,O*) ligand wrapped around the Zr center in a distorted square pyramidal configuration, the M–R bond in the apical position, and the anion *trans* to it. From this species, an intramolecular isomerization generates the active *trans*(*O,O*)-*cis*(*N,N*) isomer **C2** of Figure 2, another outer-sphere ion pair with an octahedral configuration, the anion at the back, and a coordination site *cis* to the Zr–R bond available for the monomer.

A DFT evaluation of the overall process of propene insertion is shown in Figure 2. The calculated  $\Delta H$  for the isomerization of **C2x** into **C2**<sup>11</sup> is 7.4 kcal mol<sup>-1</sup>, while the  $\Delta H^\ddagger$  for the 1,2 propene insertion into a Zr–*i*Bu bond, following the classical Cossee path,<sup>12</sup> is 8.5 kcal mol<sup>-1</sup> (relative to **C2x**); the latter is the rate-limiting step, due to the large negative entropic term (–47.5 cal K<sup>-1</sup> mol<sup>-1</sup>). All these DFT estimates are in good agreement with experiment.



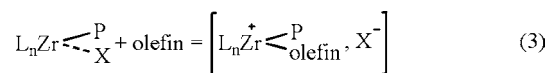
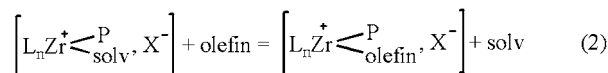
**Figure 2.** DFT-calculated propene insertion profile for a model of **2**-derived catalyst (see Supporting Information).

For a limited number of other similarly slow catalytic olefin polymerizations the activation parameters have been reported or can be calculated from available information (entries 3–6 of Table 1).<sup>5</sup> Notably, they all have in common the large negative  $\Delta S^\ddagger$  typical of a bimolecular process and a rather low  $\Delta H^\ddagger$  (5–10 kcal mol<sup>-1</sup>).

To the best of our knowledge, in the literature there is only one case in which the  $k_p X^*$  product has been factorized and the activation parameters were estimated from the temperature dependence of  $k_p$  for an industrially appealing system, and that is ethene polymerization in the presence of the last-generation *ansa*-zirconocene *rac*-Me<sub>2</sub>Si(2-Me-4-Ph-1-Indenyl)<sub>2</sub>ZrCl<sub>2</sub> (**7**) activated with MAO in toluene solution. From the results (entry 7 of Table 1) it can be seen that the exceedingly high  $k_p$  of this catalyst (almost 10<sup>5</sup> times

larger than that of **2**/MAO/TBP) is not due to a low  $\Delta H^\ddagger$  (which is in fact one of the largest in Table 1), but rather to a slightly *positive*  $\Delta S^\ddagger$ , which is definitely not what one would expect for a bimolecular reaction. This can be explained assuming that for **7**/MAO the active species is an outer-sphere ion pair (due to the frontal phenyl substituents on the indenyls that prevent the anion approach) with a solvent molecule coordinated to the metal and that monomer uptake goes along with the release of the latter, which offsets the olefin entropic loss (eq 2).<sup>13</sup>

We do not know how general this finding is, but we are tempted to hypothesize that a key difference between fast and slow olefin polymerizations can be whether or not the entropic penalty for monomer capture is neutralized. The latter would typically be the case for inner-sphere ion pairs (like **1**/MAO; eq 3)<sup>13</sup> or may follow from some specific feature(s) of the catalyst (as in the case we have just discussed in detail). Of course, situations intermediate between the above two extremes are conceivable.



It may appear counterintuitive that the activation enthalpy for 1-hexene insertion at an inner-sphere metallocene ion pair is *lower* than that for ethene insertion at an outer-sphere metallocene ion pair (compare entries 1 and 7 of Table 1). On this, however, we note that DFT calculations on models of inner-sphere ion pairs indicated that it is not necessary to fully displace the anion for the monomer to slip in,<sup>14</sup> and that part of the ‘cost’ can be paid with the monomer binding energy. On the other hand, for typical outer-sphere ion pairs the growing polymeryl has a strong  $\beta$ -H-agostic interaction with the transition metal, which must be broken before the monomer can insert; this represents an ‘extra cost’ on top of that for solvent displacement.

We are currently testing this interpretation by carrying out quenched-flow studies on a variety of olefin polymerization catalysts with different activators and solvents. The results will be reported in due course.

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**Supporting Information Available:** Details on the polymerization runs and polymer characterizations, and computational studies. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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