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Steric and Solvation Effects on Polymerization Kinetics, Dormancy, and Tacticity of Zr-Salan Catalysts

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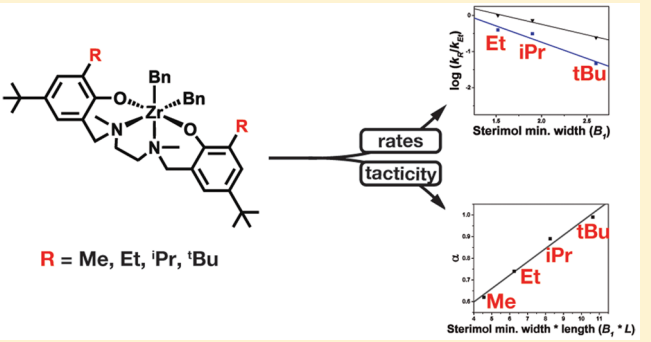
Supporting Information

ABSTRACT: 1-Hexene polymerization using four zirconium-based amine bis(phenolate) catalysts, Zr[2-R-4-*t*Bu-ONNO]-Bn_2 (where R = methyl (**1**), ethyl (**2**), isopropyl (**3**), and *tert*-butyl (**4**)), was examined to establish the effect of ligand sterics on kinetics and stereocontrol of olefin polymerization. For each catalyst, a rich data set was obtained including monomer consumption, molecular weight evolution, end-group analysis, and active site counts. A set of reaction specific rate constants was determined for catalysts **2**−**4**. In addition to the standard elementary reaction steps of initiation, propagation, mis-insertion, and chain transfer, these catalysts undergo isomerization leading to dormancy. This isomerization is particularly prominent in bromobenzene and for less sterically hindered complexes. Across the series **2**−**4**, ligand steric properties have a systematic effect on both insertion and chain transfer rate constants. This relationship was rationalized using the Sterimol steric parameters. The rates of propagation and mis-insertion were found to be similarly sensitive to steric effects with sensitivities of 0.9 and 0.76 $Å^{-1}$, respectively, while initiation was found to be slightly more sensitive (0.99 $Å^{-1}$) and chain transfer to be considerably less sensitive (0.58 $Å^{-1}$) owing to the reduced steric demand for monomer independent chain termination compared to bimolecular insertion. The rates of propagation and mis-insertion in bromobenzene were found to be more sensitive to sterics (1.24 and 0.98 $Å^{-1}$, respectively). In addition, ligand sterics play a significant role in the tacticity of the resulting polymer, the difference in polymers resulting from catalysts **1**−**4** was also systematic and could be compared to the Sterimol steric parameters. All kinetic data were critical in the determination of the full mechanism for this series; thus, this study illustrates the importance of obtaining a complete kinetic data in order to confidently establish quantitative structure−activity relationships (QSARs).



INTRODUCTION

The production of plastics and elastomers based on polyolefins is an important industry that continues to grow.[1] Catalysts have been extensively studied by varying ligand architectures, transition metals, and cocatalysts.[2] In particular, group 4 amine bis(phenolate) complexes are interesting because of their high activity,[3] and their potential to produce polymers with controlled, narrow molecular weight distributions[4] with either isotactic[4b,5] or syndiotactic[6] microstructures. Because of these features, careful kinetic examination of these catalysts provides valuable insight into the factors controlling different reaction steps in α-olefin polymerization.

Traditionally, the effect of catalyst structure was investigated through activity measurements and polymer product characterization. While this approach is useful in catalyst screening, this type of analysis does not allow determination of the individual rate constants for the elementary reaction steps involved in polymerization.[7] Additionally, unique reaction steps beyond the standard mechanism might be missed.

Landis and co-workers,[7b,8] as well as our group,[9] have shown that a comprehensive kinetic data set is necessary for proper deciphering of the elementary reaction steps of polymerization. Specifically, a multiresponse data set including monomer consumption, vinyl end-group analysis, active site counts, and, most critically, molecular weight distributions (MWDs) at several time points throughout the reaction is necessary to establish the reaction mechanism and obtain the rate constants of the elementary reaction steps.

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Ligand design is a powerful tool to control reactivity in homogeneous catalysis. To this end, amine bis(phenolate) based catalysts are particularly useful, as they allow both steric and electronic variations. Electronic changes have been shown to affect propagation as well as chain transfer rate constants.[5a,10] Steric changes, on the other hand, result in far less substantial changes to propagation or chain transfer rates but are very effective at controlling stereoselectivity.[11] Notably, steric effects are capable of altering polymer microstructure from being fully atactic to being greater than 95% isotactic by means of enantiomorphic-site control,[4b] wherein tacticity is induced through the structure of the catalyst. This is in comparison to chain-end control where the orientation of the last inserted monomer controls the tacticity of the polymer. This is the typical mechanism to produce syndiotactic architecture,[6,12] though metallocenes can produce isotactic polyolefins by this mechanism as well.[13] More recently, chain-end control has also been utilized in the isotactic polymerization of γ-lactones with both metallocene[14] and amine bis(phenolate) catalysts.[15]

The presence of dormant catalyst sites, i.e., sites that are not fully deactivated but spend some significant time period without activity, is another factor that must be considered to fully understand the catalytic mechanism. There are multiple potential causes for catalyst dormancy, where for the salan-type catalysts the most common origin of dormancy is a 2,1-insertion of a monomer (i.e., "misinsertion") resulting in a stable species (often called a secondary site) that undergoes insertion at a greatly reduced rate.[16] However, dormancy is not always a result of misinsertion, as illustrated with both zirconocene[17] and ONNO-type postmetallocene catalysts,[18] where secondary sites were observed to be either similarly or even more active than their primary counterparts. Also of note are the theoretical observations and NMR studies by Macchioni and co-workers of a dynamic behavior of ONNO-type catalysts involving an isomerization from the inactive form that is incapable of monomer insertion into the active form (denoted herein as the *cis* active polymerization site, or CAPS).[19] The inactive form is thought to be due to the docked monomer and growing polymeryl being *trans* to one another (this form is denoted herein as the *trans* inactive polymerization site, or TIPS). If the energy required to isomerize from TIPS to CAPS is substantial, the *trans* form will act as a dormant catalytic site. Through a combination of reaction kinetics, time-evolved MWDs and active site and vinyl end-group counts, we argue in this paper that the dynamic catalyst behavior proposed by Macchioni and co-workers is consistent with our analysis, and present the first kinetic examination of this mechanism and its effects on the polymerization reaction.

In this study, we present our results for a series of four catalysts **1**−**4**, chosen as structurally similar salan ONNO-type catalysts with targeted steric changes in the ortho position (Figure 1). For catalysts **2**−**4**, a full set of data was obtained and a kinetic analysis for 1-hexene polymerization was carried out in two solvents, toluene (ε = 2.38) and bromobenzene (ε = 5.17); their respective rate constants are summarized in Table 1. The rate constants for each case (i.e., catalyst and solvent) are for the minimal number of reaction steps necessary to describe each data set. This minimal reaction set is determined for each catalyst/solvent system independently. The kinetic rate constants have enabled for the first time a quantitative relationship to be established for initiation, propagation, misinsertion, and chain transfer with Verloop (Sterimol) steric parameters.

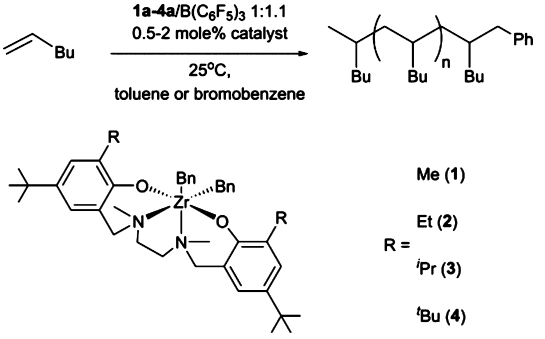

Figure 1. Polymerization of 1-hexene with a series of Zr-based catalyst systems **1**−**4**.

EXPERIMENTAL PROCEDURES

General Procedure. All manipulations involving air sensitive materials were performed under a dry, inert nitrogen atmosphere using either a glovebox or standard Schlenk techniques. Solvents were distilled over activated alumina and a copper catalyst using a solvent purification system (PPT- Pure Process Technology) and stored over activated molecular sieves. 1-Hexene was purchased from Aldrich, purified by distillation over Cp_2ZrMe_2, and stored over sieves. $B(C_6F_5)_3$ was purchased from STREM and purified by sublimation. Diphenylmethane (CPh_2H_2), toluene-d_8, and bromobenzene-d_5 were distilled over CaH_2 or $CaCl_2$, degassed, and stored over sieves before use. CD_3OD was purchased from Aldrich and used as received. Starting materials for the synthesis of ligand precursors for complexes **1**−**4** were purchased from Sigma and used as received. ^{1}H NMR array experiments were performed on a Varian INOVA 600 MHz instrument. Other ^{1}H and ^{2}H experiments were performed on a Bruker DRX 500 MHz or Bruker ARX 800 MHz spectrometer. Precatalysts (**1**−**4**) were prepared following modified literature procedures.[4b] Procedures and characterization are provided in the Supporting Information.

NMR Scale Polymerization of 1-Hexene. The procedure for NMR scale polymerization is based on the literature.[9b,20] In a typical reaction, Zr[2-tBu-ONNO]Bn_2(**4**) (17.9 mg, 0.0225 mmol) was dissolved in 0.75 mL of d_8-toluene and sealed in a vial with a screw-cap septum. The vial containing the precatalyst solution was pierced with a 1 mL syringe, placed in a N_2 bag, and equilibrated to 25 °C. To a 5 mL volumetric flask, 1-hexene (0.9470 g, 11.3 mmol) and CPh_2H_2 (37.9 mg 0.225 mmol) were added and diluted with d_8-toluene. $B(C_6F_5)_3$ (12.7 mg, 0.0248 mmol) in 0.75 mL of d_8-toluene was combined with 1 mL of this solution in an NMR tube and sealed with a septum. This combined solution was placed in the spectrometer and allowed to equilibrate to 25 °C with a VT controller. A spectrum was collected to determine the initial concentration of monomer relative to the internal standard, CPh_2H_2. The NMR tube was removed, and the catalyst solution was added to the solution by piercing the NMR tube's septum while the syringe remained in the N_2 bag. The reaction mixture was shaken for approximately 30 s and placed back in the spectrometer. Spectra were acquired at regular time intervals until the reaction reached at least 90% completion. Each sample was prepared for GPC analysis by evaporation and then dissolution in hexane followed by filtration through an alumina plug to remove the dead catalyst. Evaporation of volatiles yielded clear, colorless poly(1-hexene).

Batch Polymerization of 1-Hexene. The procedure for manual quench is based on the literature[21] and modified to be similar to NMR scale experiments, except reaction temperature was maintained by a constant temperature bath rather than a VT controller. After the reaction was initiated, the sample was quenched with methanol-d_4 at a predetermined time correspondent to a chosen % conversion. The quenched reaction was analyzed by ^{1}H NMR to verify monomer conversion. Each sample was prepared for analysis by evaporation, dissolution in hexanes, and filtration through alumina to remove the quenched catalyst. Evaporation of solvent yielded clear, colorless poly(1-hexene).

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Table 1. Summary of Kinetic Data for Catalysts 2−4 in Toluene and Bromobenzene

solvent	toluene			bromobenzene		
2-X, 4-^{t}Bu ONNO[a]	Et (**2**)	^{i}Pr (**3**)	^{t}Bu (**4**)	Et (**2**)	^{i}Pr (**3**)	^{t}Bu (**4**)
Sterimol[b] (B_1)/Å	1.52	1.90	2.60	1.52	1.90	2.60
k_i[c](10^{-4})/M^{-1} s^{-1}	230	110	20	≈k_p	≈k_p	≈k_p
$k_p(10^{-4})$/M^{-1} s^{-1}	2300	1800	270	13600	8600	1000
$k_{mis}(10^{-4})$/M^{-1} s^{-1}	2.7	1	0.41	22.5	10	2
$k_{dene}(10^{-4})$/s^{-1}	4.1	3	1			1.2
$k_{dene}(10^{-4})$[d]/M^{-1} s^{-1}				120	70	
$k_{ene}(10^{-4})$[e]/s^{-1}	fast	fast	fast	fast	fast	5.0
$k_{rec}(10^{-4})$[f]/s^{-1}						1.0
$k_{dorm}(10^{-4})$/s^{-1}	N/A	N/A	N/A	1500	900	20
k_{-dorm} (10^{-4})/s^{-1}	N/A	N/A	N/A	1200	400	50
[CAPS]/[total sites]	N/A	N/A	N/A	0.45	0.30	0.72

[a]Precatalyst synthesis in the Supporting Information. [b]From literature.[24] [c]k_i was indistinguishable from propagation due to accelerated rate constants in bromobenzene, and approximated as equal to k_p. [d]First order $k_{vinylidene}$ is monomer independent, and second order is monomer dependent. [e]Fast is defined as much faster than recovery, resulting in no detection of secondary sites. [f]Recovery not observed in cases where chain transfer was much faster.

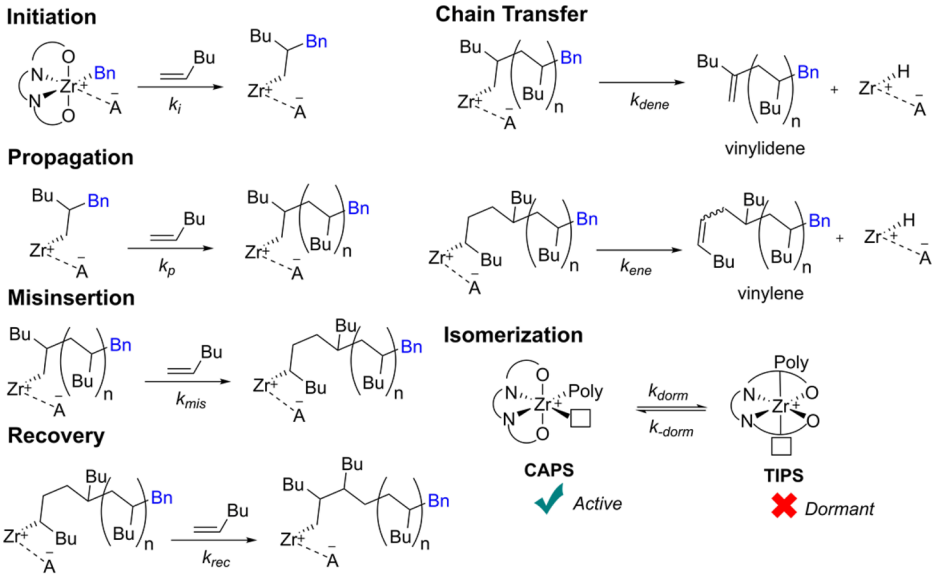

Figure 2. Elementary steps for the polymerization of 1-hexene with **2**−**4**/B$(C_6F_5)_3$. Bn = benzyl and A$^-$ = [BnB$(C_6F_5)_3$]$^-$.

For vinyl end group analysis, the resulting polymer was dissolved in $CDCl_3$ and analyzed by ^{1}H NMR using CPh_2H_2 as an internal standard. The method of standard additions was used for quantification of vinyl end groups.

For analysis of active sites, the polymer was dissolved in CH_2Cl_2 and analyzed by ^{2}H NMR. Benzene-d_6 was used as an internal standard.

Measurement of Polymer Tacticity by Quantitative ^{13}C NMR. The method of quantification of poly(1-hexene) tacticity was based on the literature[22] and accomplished by integration of the total *m* character (for **1**), *mm* peak (for **2** and **3**), or *mmmm* peak (for **4**) of the C_3 carbon signal compared to total C_3 peak integration (see the Supporting Information) using the technique of inverse-gated proton decoupling and a relaxation delay of ∼24 s.[23]

Gel Permeation Chromatography (GPC) Analysis. Poly(1-hexene) was dissolved in THF to concentrations between 5 and 10 mg/mL. The samples were filtered and injected at 35 °C into a Viscotek TDAmax GPC equipped with refractive index, viscosity, and two light scattering detectors (7 and 90°). Instrument calibration was performed against a known, narrow polystyrene standard. The data analysis was performed on the proprietary OmniSEC software with triple detection methodology.

Kinetic Modeling. The polymer MWDs and concentration data collected by NMR were fit to chemical mechanisms unique to each catalyst. Rate constants were optimized using a Levenberg−Marquardt algorithm, with each data type weighted by the error in its measurement. The methodology has been previously described.[9b]

RESULTS

Herein is presented the experimental data and kinetic analysis of 1-hexene polymerization by the Zr-based catalysts **2**−**4**. Catalyst **1** was also synthesized (see the Supporting Information), and a kinetic analysis of the full data set was attempted. However, attempts to predict the entirety of the kinetic data for catalyst **1** were not successful, and it was concluded that the mechanism for this catalyst must be complicated by additional mechanistic step(s) which remain to be identified. Consequently, analytical methods independent of the kinetic model (tacticity measurements by ^{13}C NMR and activity measurements based on monomer consumption) will be presented for catalysts **1**−**4**, while a full kinetic analysis will only be presented for **2**−**4**. It should be noted that any additional mechanistic steps possible with **1** can be presumed to

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be possible with **2**–**4**; however, these are seemingly minor contributors to the mechanism, as they were not required to fit all kinetic data acceptably. The full kinetic analysis was performed separately for each of the catalysts **2**–**4** in both toluene and bromobenzene. Each catalyst and solvent system was analyzed independently, and no *a priori* assumptions were made with respect to mechanistic steps. The procedure used to determine the simplest mechanism able to satisfy all data has been described previously by our group and is detailed in the Supporting Information. In what follows, we will only describe the simplest kinetic mechanism consistent with the data.

For each of the catalysts studied, the mechanism can be described by activation, initiation, 1,2-insertion (propagation), 2,1-insertion (mis-insertion), and monomer independent and monomer dependent chain transfer reactions to form vinylidene and vinylene end groups, respectively (Figure 2). For catalyst **4** in bromobenzene, a recovery from mis-insertion step was also needed to describe the data. For reactions using catalysts **2**–**4** in bromobenzene, additional steps of catalyst isomerization from an inactive *trans* form (*trans* inactive polymerization site, or TIPS) to the active *cis* form (*cis* active polymerization site, or CAPS) and the reverse isomerization from CAPS to TIPS had to be included. A summary of all of the elementary steps is presented in Figure 2. For each catalyst/solvent system, a previously developed method was utilized that involves analysis of monomer consumption, time-evolved MWDs, active site concentrations, vinyl end group concentrations, and product tacticity (analyzed by ^{13}C NMR). A representative kinetic modeling fit for catalyst **4** is shown in Figure 3. Similar kinetic fits and data for catalysts **2**–**4** are provided in the Supporting Information.

Examination of the full set of rate constants in Table 1 allows for several relevant comparisons to be made between catalyst systems and individual elementary reaction steps. The rate of initiation is only slightly slower than that of propagation for each catalyst, resulting in the absence of a visible induction period in the monomer consumption kinetic profiles, and active site counts that are essentially unchanged throughout the reaction. In bromobenzene, it is difficult to robustly determine initiation rate constants. This is because the experiment is incapable of capturing the very early portion of the reaction. As a result, initiation was assumed to be comparable to propagation. The rates of mis-insertion for all three catalysts are 3 orders of magnitude slower than propagation ($k_{mis} \approx k_p/1000$). Recovery from mis-insertion had to be included only for catalyst **4** in bromobenzene, as this is the only system where secondary active sites were observed. Chain termination (vinylidene and vinylene formation) was monomer independent in toluene and monomer dependent in bromobenzene, with catalyst **4** being the exception, where in both solvents chain transfer was monomer independent.

Comparison of the same catalyst in each solvent shows several common features. Most notably, polar solvent results in an increase in propagation rate by approximately an order of magnitude, with the extent of the increase following the order of **2** > **3** > **4**, while chain transfer experienced a notable apparent mechanism change from monomer independent to monomer dependent chain transfer.

For catalysts **2**–**4**, we examined the mechanism both including CAPS/TIPS isomerization and excluding isomerization. This was done for reactions performed in both toluene and bromobenzene. We considered two scenarios: without dormancy and with sites becoming dormant at the rate k_{dorm} and recovering from dormancy at the rate k_{-dorm}. For each of these scenarios, a full optimization was performed to obtain the best possible fit to all data. If the inclusion of dormancy did not result in a qualitatively improved fit, we did not include it in the mechanism. It is important to note that the decision to include or exclude dormancy in the mechanism results in a change to all other rate constants.

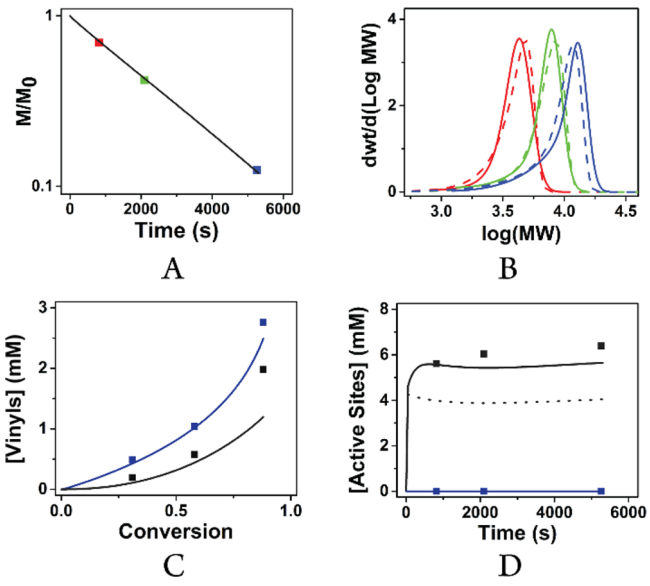

Figure 3. Data and modeling fits for the **4**/B(C_6F_5)$_3$ system in bromobenzene at 25 °C. (A) Monomer consumption, red, green, and blue dots are data under conditions of [**4**]:[1-hexene] of 9:900 mM, at approximately 30% (red), 60% (green), and 90% (blue) conversion. The solid line is the modeling fit. (B) MWDs of polymers resulting from reactions shown in part A. (C) Vinyl end-group analyses of NMR scale reactions quenched using MeOD at different reaction times. Blue symbols are vinylidene; black symbols are vinylene. Curves are modeling fits. (D) Active site counts from NMR scale reactions quenched using MeOD at different reaction times. Black symbols are primary active sites, and blue symbols are secondary active sites. Solid curves are model fits of total primary/secondary active sites; the dashed curve is the model fit of primary CAPS sites only.

In toluene, the amount of dormant sites evaluated was less than 20% of the total catalyst sites for **2** and **3**, and was very low (less than 1%) for **4**. For these systems with toluene as the solvent, the inclusion of CAPS/TIPS isomerization leading to dormancy did not improve the fit, and the simpler mechanism without isomerization was preferred. Since the amount of dormant sites was not significant, the other rate constants did not change substantially (a comparison of the two mechanisms is reported in the Supporting Information). In bromobenzene, the amount of dormant sites was found to be as much as 20–40%, and thus, inclusion of CAPS/TIPS isomerization in the kinetic mechanism results in a qualitative improvement of the fit. As the amount of dormancy is higher in these systems, the effect on the other rate constants was substantial (see the Supporting Information for comparison). The concentration of CAPS and TIPS quickly forms an equilibrium,[19a,c] which tended to favor the dormant TIPS form more in catalysts **2** and **3**, and least in the case of **4**.

Examination of ^{13}C NMR for catalyst systems **1**–**4** revealed that the microstructure of the polymer in each system changes in tacticity from being essentially atactic when using catalyst **1** (with the smallest ortho substituent) to being >95% isotactic

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with catalyst **4**. Polymer microstructure was unaffected by solvent choice.

DISCUSSION

For this series of catalysts, it is important to note that multiple factors can contribute to any single mechanistic step. For instance, for any monomer addition event to occur, four separate barriers must be overcome:

(1) The counteranion $[B(C_6F_5)_3Bn]^-$ must be displaced from the catalyst.
(2) The catalyst must isomerize from the lower energy TIPS form to the active CAPS form, if it is not already.
(3) A monomer must dock in the available coordination site with the right orientation.
(4) A monomer must insert into the growing polymer.

Note that barrier 4 cannot be rate determining for systems **1**−**4**, since if it was the rate-determining step the propagation would not have been first order in monomer, as shown by the linear logarithm (monomer concentration) vs time curves in Figure 3a and similar figures in the Supporting Information. It is important to emphasize that depending on the exact monomer addition event in question (initiation, propagation, or mis-insertion) each barrier may have a different contribution to the overall rate of this event, where altering reaction conditions can affect one or more barriers. Our objective is to understand how catalyst structure and reaction conditions can affect each of these barriers and determine descriptors and structure−activity relationships.

The ease of displacement of the counteranion has a significant effect on catalyst activity and can be affected by both catalyst structure and solvent polarity. A sufficiently polar solvent will more readily solvate the individual ions, enabling an easier displacement of the counteranion. In the case of bromobenzene, the solvent polarity is presumed sufficient to completely separate the catalyst/counteranion pair. By examining the difference in rate using the same catalyst but changing from nonpolar (toluene, ε = 2.38) to polar (bromobenzene, ε = 5.17) solvent, we observe a 5−10-fold increase in rate, where the increase in rate is ordered as **1** > **2** > **3** > **4** based on relative observed monomer consumption rate (k_{obs}) ratios. This specific ordering is likely due to the inherent ability of larger substituents to displace the counteranion; specifically, for **4**, the bulky ^{t}Bu groups are more effective at displacing the anion than catalysts **1** and **2** with smaller methyl or ethyl groups. As a result, the rate increase from changing solvent is less pronounced for larger substituents.

Catalyst dormancy is an important part of the mechanism for these salan ONNO-type catalysts, and sensitive to both solvent polarity and catalyst structure for **2**−**4**. Decreased ligand bulkiness leads to an increase in the fraction of dormant sites. The TIPS form has been shown to be the lower energy resting state of the catalyst, and the one most sensitive to steric changes on the ligand.[19a,b] In the TIPS form, the ortho substituents point almost directly at one another, while in the CAPS form there is little interaction between the ortho substituents and the rest of the catalyst structure. Thus, the CAPS form remains unchanged in stability with respect to changes in sterics. The TIPS form is less stable; consequently, the energy required to isomerize to CAPS becomes smaller with greater steric bulk, and an increase in rate is expected as a result. When a smaller olefin such as ethylene or propylene is used, barriers 1 and 2 are expected to become more important. In this case, these effects dominate and an increase in the observed rate with increased steric bulk is observed.[19d]

Additionally, it should be noted that we report herein an increase in apparent dormancy resulting in CAPS/TIPS isomerization as a result of changing to a polar solvent. The most obvious explanation is that catalyst isomerization is solvent dependent; however, it has previously been reported by Macchioni and co-workers that the activation parameters for the isomerization reaction have very little to no dependence on solvent or cocatalyst.[19c] Therefore, we propose that this behavior is likely due to a subtle difference between effect 1 (counteranion displacement) and effect 2 (isomerization). If in a nonpolar solvent a sufficiently "sticky" counteranion caused dormancy, one would expect to observe a characteristic symmetrical broadening of the MWD. This is not observed, and instead, simply shorter chains and a longer tail on the low end of the distribution appear presumably due to an increase in the amount of chain transfer. Thus, we propose that for CAPS/TIPS isomerization the catalyst is not only dormant while in the TIPS form, but it also is much less able to undergo chain transfer. In short, we speculate that the increased time spent displacing the counteranion is essentially masking much of the effects of dormancy. This may also account for the apparent changes in mechanism from monomer independent to monomer dependent chain transfer (see Table 1), as the effectiveness of one reaction over the other may be dependent on CAPS/TIPS isomerization. For higher α-olefins such as 1-hexene, monomer docking (barrier number 3) has the most prevalent effect in terms of monomer addition rates (especially for the bulkiest case with catalyst **4**) and we observe an overall decrease in rate with increased sterics, approximately equal to an order of magnitude between catalysts **2** and **4**.

For this series of catalysts in toluene, initiation is approximately 10 times slower than propagation. The difference between these rates is controlled primarily by the steric bulk presented by the ligand, the Zr-alkyl, and the monomer. The difference in the steric hindrance of inserting into the initial Zr-alkyl versus inserting into the monomer-Zr bond at the end of the growing chain generally results in a decreased rate of initiation versus propagation when the Zr-alkyl is a benzyl group. As an example, previous work by our group on both Zr and Hf based ON^{X}O-type catalysts showed an approximately 100-fold increase in rate for propagation versus initiation.[10a,20] In the case of **2**−**4**, since initiation involves insertion into a benzyl as well, and 1-hexene is the monomer used in both cases, it stands to reason that the difference in these results is a consequence of a more open catalytic site in ONNO-type catalysts than ON^{X}O ligands. This behavior has been studied computationally,[19] and is also responsible for the dynamic isomerization of activated catalysts between CAPS and TIPS present in ONNO-type catalysts but not in other more rigid frameworks.

With this catalyst series, we report 2,1-insertion (mis-insertion) is approximately 1000 times slower than normal 1,2-insertion. Often amine bis(phenolate) catalysts of the ONNO type are reported to produce polymers with no evidence of regioerrors,[25] as evidenced by a lack of distinct ^{13}C NMR resonances at ca. 30.2−30.7 ppm and ca. 34.9−35.9 ppm.[26] For catalysts **1**−**4**, we do not observe regioerrors by NMR. The rate of mis-insertion can be accurately established by a combination of measuring the concentration of regioerrors, vinylene terminated polymers, and secondary active sites throughout the reaction. In this series of catalysts, we

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observed vinylene terminated products but did not observe any secondary active sites with ^{2}H labeled quench experiments. This was a surprising result, as often 2,1-mis-inserted sites act as dormant sites (albeit different from TIPS dormant sites), and are often not only present but actually accumulate throughout the reaction.[17,18b] The presence of vinylenes implies that mis-insertion must be occurring, but the absence of secondary sites implies that they are short-lived. There are two conceivable ways to achieve this outcome: (i) these sites very quickly recover by completing a normal 1,2-insertion to convert back to a primary site, or (ii) rapid chain transfer occurs after each mis-insertion. If recovery from mis-insertion were fast, one would expect a substantial amount of regioerrors to be present in the polymer (greater than the amount of vinylene). However, the absence of appropriate ^{13}C NMR peaks in the polymer spectra for each system implies that, for this family of catalysts, rapid chain transfer must occur after a mis-insertion event. This mechanism allows for a highly regioregular polymer to be formed, since internal regioerrors are exceedingly rare compared to vinylenes, which themselves are also relatively uncommon.

Several steric descriptors have been proposed. One often utilized in organometallic catalysis is the ligand cone angle which is determined by either using known parameters (Tolman method for phosphines[27]) or more accurately (and universally) by calculating the cone angle by means of crystallography[28] or DFT.[29] Subsequently, one attempts a QSAR between the cone angles and the reaction rate constants for this set of systems. However, the Tolman cone angles are limited to phosphine ligands and using crystallographic data requires the growth of X-ray quality crystals for each individual catalyst of interest. Furthermore, information obtained from precatalyst structures may not necessarily translate to the activated species, and obtaining crystals of activated catalyst is often very challenging due to the relative instability of many active polymerization catalysts, particularly in the absence of substrate.

Alternatively, steric sensitivity can be measured by use of standardized steric parameters. We employed the Sterimol set of steric parameters developed by Verloop[24] to evaluate the effect of sterics on insertion and chain termination rates and the regioselectivity of the resulting polymer. Compared to experimentally obtained parameters such as Taft[30] or the Winstein–Holness A-values,[31] the computationally developed Sterimol parameters avoid many of the limitations inherent to the experimental data upon which the Taft and Winstein–Holness parameters are based, in particular for larger and less symmetric substituents. The Sterimol set of steric parameters includes the length of the substituent along the axis of the ligand–substituent bond (L) and the widths (B_1–B_5) perpendicular to L, where the minimum width is B_1, the widths B_2–B_4 are at sequential 90° rotations from B_1, and finally the maximum width is B_5.

QSARs for the rates of initiation, propagation, mis-insertion, and chain transfer with the Sterimol minimum width (B_1) are shown in Figure 4. For each rate constant, the slope of a plot of the logarithm of the rate constants versus B_1 was examined. In toluene, propagation had a steric sensitivity factor of 0.90 ± 0.22/Å, while mis-insertion had a slightly lower factor of 0.73 ± 0.14/Å, indicating that the geometry of mis-insertion may be less affected by steric influence than proper propagation. Initiation was similarly sensitive to steric effects (0.99 ± 0.05/Å) as propagation, with a small increase in sensitivity being

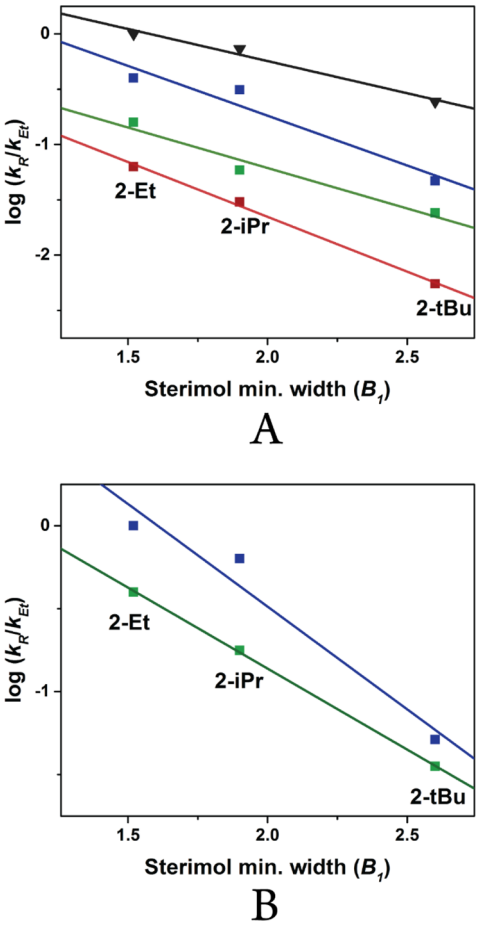

Figure 4. Sterimol steric factor B_1 compared to the log of rate constants: propagation (blue), misinsertion (green), initiation (red), and monomer independent chain transfer (black). (A) Rate constant comparisons for **2**–**4** in toluene. (B) Rate constant comparisons for **2**–**4** in bromobenzene.

consistent with the increased steric repulsion resulting from the larger benzyl group. Comparing the sensitivity of propagation to that of chain termination (0.58 ± 0.08/Å) suggests that, under similar conditions, reducing the steric bulk of the ligand will increase the average molecular weight of the polymer produced by a factor of 2 from **4** to **2**, consistent with MWDs reported herein as well as previously observed for similar ONNO-type catalysts.[5a,32] This is also consistent with the difference in the addition of monomer (i.e., bimolecular reaction) and a monomer independent chain termination (i.e., a unimolecular reaction). In bromobenzene, the sensitivity of propagation (1.24 ± 0.26/Å) and mis-insertion (0.98 ± 0.02/Å) were higher than in toluene, likely due to the increased importance of docking in monomer addition rates, with the displacement of counteranion as a less significant factor.

In addition to affecting propagation rates, steric control is an effective strategy for controlling polymer microstructure. Originally, phenolate sterics were reported to be able to control the tacticity of the synthesized polymer based on the C3 signal in the ^{13}C NMR. On the basis of the relative concentrations of *mrrm* and *mmrm* pentads of the C3 signal, it was concluded that stereoselectivity was a result of an enantiomorphic site control mechanism, rather than chain-end control.[5a] Similarly, the series of catalysts **1**–**4** studied herein show varying levels of isotacticity, with a similar site-

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controlled mechanism for each. Further, when examining the tacticity across catalyst systems under identical concentration and temperature conditions, a direct relationship with the size of the ortho substituent and the degree of stereocontrol emerges. Calculating the enantioselectivity factor α, which was defined by Busico[33] for site-controlled mechanisms as the probability of inserting a monomer meso as calculated from the relative concentration of the *mm* triad or *mmmm* pentad, we compared this value of α for each catalyst system to the Sterimol steric parameter combination L^*B_1 (Figure 5). This

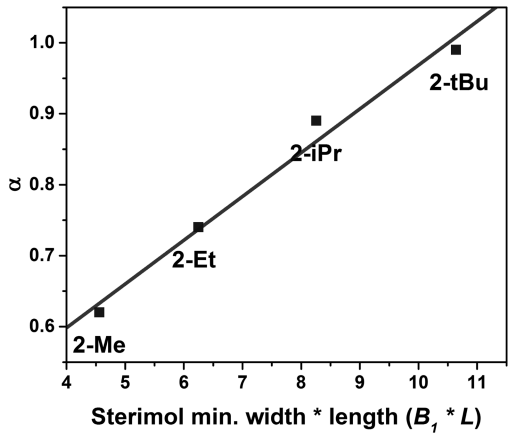

Figure 5. Comparison of the enantioselectivity factor (α) for site-controlled tacticity compared to Sterimol steric factor combination for minimum width (B_1) and length (L).

combination was chosen, as changing the substituent from methyl to ethyl changes L (length of the substituent) only and changing from ethyl to isopropyl or *tert*-butyl changes B_1 (width of the substituent) only. For this series of catalysts, the evaluation of the effects of length (L) on tacticity was not robust, so we made the assumption that the sensitivities to width and length of the substituent are approximately equal. It might be possible to differentiate between the effects of length vs width by using a properly designed series of catalysts.

CONCLUSIONS

A diverse set of multiresponse kinetic data was collected, and quantitative kinetic analysis was carried out for a series of four Zr-salan ONNO-type catalysts. Rate constants were determined for each elementary step for 1-hexene polymerization in two solvents—toluene and bromobenzene. The reaction mechanism for each catalyst was found to consist of initiation, which was only moderately slower than propagation due to the flexibility of this catalyst series compared to those of the ON^XO-type; mis-insertion that was very slow compared to propagation, leading to very few regioerrors in the polymer; and both monomer independent chain transfer (in toluene) and monomer dependent chain transfer (in bromobenzene) to form, respectively, vinylidene and vinylene terminated polymers. Chain termination following mis-insertion was found to be quite fast, as evidenced by the appearance of vinylene, but where secondary active sites could not be detected. Furthermore, catalyst isomerization between a lower-energy dormant site (TIPS) and the active polymerization site (CAPS) was proposed, as both dormancy formation and recovery steps were found to be required to explain kinetic data for reactions done in bromobenzene. Most notably, the steric effect on initiation, propagation, mis-insertion, and chain termination rate constants in both solvents could be expressed in QSARs utilizing Sterimol steric parameters. Differences in these rate constants as a result of steric changes were shown to be related to the ability of sterics to affect counteranion displacement, CAPS/TIPS isomerization, and the ability for 1-hexene to dock the active site of the catalyst. Similarly, a relationship between substituent size and the isotacticity of the resulting polymer was also presented, as demonstrated by a comparison of the enantioselectivity factor α and the Sterimol steric parameters.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00295.

The synthesis, characterization, and experimental procedures for each ligand/catalyst system as well as kinetic modeling (PDF)

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All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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