Synthesis of Stereoblock Elastomeric Poly(propylene)s Using a (2-PhInd)₂ZrCl₂ Metallocene Catalyst in the Presence of Co-Catalyst Mixtures: Study of Activity and Molecular Weight

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The effect of adding various aluminum alkyls (R = Et, *i*-Bu) on the polymerization of propylene is studied using a (2-PhInd)₂ZrCl₂ pre-catalyst. A mild deactivating effect is found upon addition of TIBA, whereas TEA shows a sharp deactivating effect. Increasing amounts of AlR₃ results in a significant activity increase for TIBA, but an activity plateau for TEA. AlR₃ imposes remarkably different effects on the molecular weight and stereochemical microstructure of polymers. As the TIBA concentration increases, $\overline{M}_v$ increases at first, growing from 49 000 to 72 000, but subsequently drops to 40 000. For TEA, $\overline{M}_v$ decreases sharply, plummeting from 49 000 to 17 000. Both TIBA and TEA increase the *mmmm* pentad content from 7.9 to 23.5% and 17.6%, respectively.
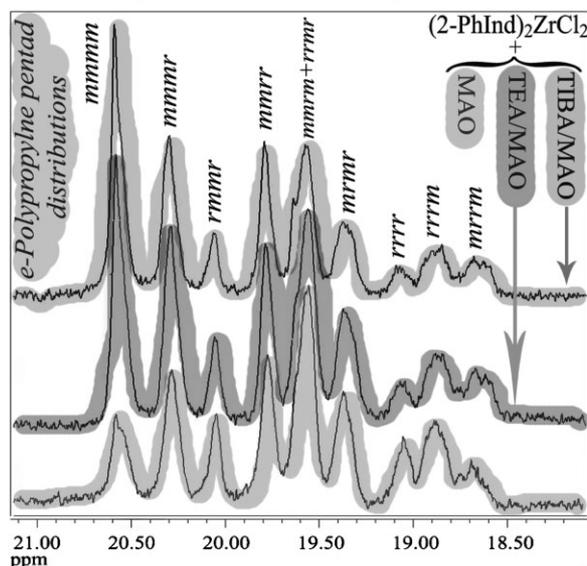
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1. Introduction

One of the main issues in the polymerization of α-olefins using catalyst alloys, hybrid catalysts, or multi-catalyst systems is the interaction of different species present in the reaction media. The interaction of co-catalysts, active species, and other side products present in the media are still rather vague, intensely studied, and under debate.[1] The topic of co-catalysts seems especially important because the co-catalyst agents can perform distinct

functions. For example, electron deficient methylaluminoxane (MAO) will accept an anion and activate a metallocene catalyst by producing metallocenium cations, and thereby function as the catalyst's counter-anion.[2] In contrast, TEA (triethylaluminum, AlEt₃) is used to activate classical Ziegler-Natta catalysts by transferring an alkyl group to the transition metal center, forming the required metal carbon bond of the active species.[3] TIBA [triisobutylaluminum, Al(*i*-Bu)₃] is another aluminum alkyl compound that can activate Ziegler-Natta catalysts through the same ligand exchange mechanism; however, its contained aluminum is less than that of TEA and its greater comparative cost prevents its widespread employment.[3] An additional important consideration is the trimethylaluminum (TMA, AlMe₃) present in MAO, which can certainly affect the activity and observed polymer characteristics such as molecular weight and microstructure. In short, while the primary catalyst structure clearly impacts the polymerization behavior, the co-catalysts, and activation method play a crucial role in controlling the polymer microstructure – for both metallocene systems and classical Ziegler-Natta catalysts.[4–11]

Previously, different effects have been reported for the presence of alkyl aluminums during olefin polymerization by metallocene catalysts and MAO. They may function as alkylating agents for the metallocene catalysts,[1] chain transfer agents,[1,3,12–15] scavengers of impurities present in the feed or reaction media,[1,3,16–18] metal site reactivating agents,[1] and finally, traps for TMA present in MAO through alkyl group exchange.[1,19] Moreover, multiple independent studies have shown that the efficiency of MAO as a co-catalyst is increased by the addition of TIBA[20–23] while additional amounts of other organometallic compounds such as AlEt₃ reduce the MAO efficiency.[20] The studies on molecular weight have revealed that TIBA can increase the molecular weight of the polymers obtained while TEA generally reduces it.[20,21] Different explanations are posited for the special advantage of TIBA and the main reasons include: (i) the replacement of Al–Me bonds in MAO with Al–*i*-Bu bonds; (ii) Al(*i*-Bu)₃ modifies Lewis acidic centers in MAO and augments their Lewis acidity; and (iii) the introduction of Al(*i*-Bu)₃ prevents metallocenium cations from forming complexes with AlMe₃ sourced from the MAO.[22]

The pre-catalyst (2-PhInd)₂ZrCl₂ is a well known metallocene introduced by Waymouth and Coates for the production of stereoblock poly(propylene); the obtained poly(propylene)s exhibit elastomeric behavior because of a non-statistical, blocky tacticity (Scheme 1).[24–28] Multiple
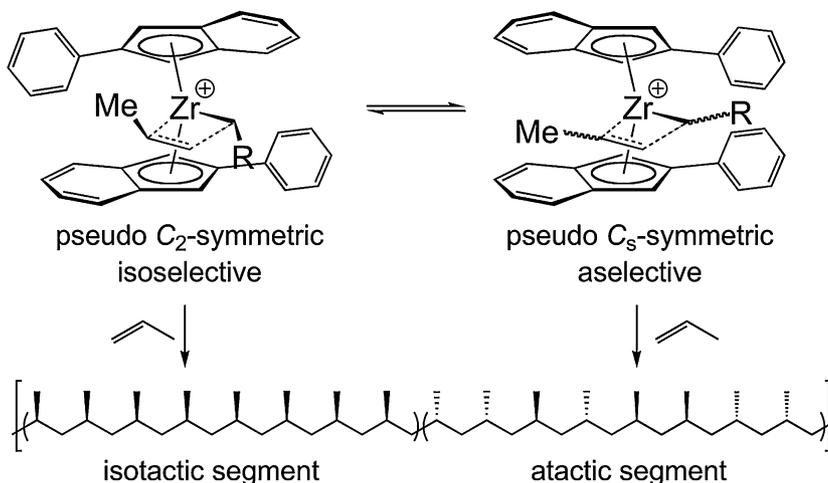
Scheme 1. Proposed mechanism for stereoblock isotactic/atactic poly(propylene) formation from (2-PhInd)₂ZrCl₂/MAO.

papers have been published on the mechanism of producing this class of stereoblock polymer. For example, the conformationally oscillating behavior of the catalyst was cited as the governing factor in the production of the stereoblocks.[24,25] Complementary mechanisms were suggested by different research groups in which separate factors such as reaction medium polarity and counter-ion effects were recognized as important factors.[29] It is noteworthy to point out that this general class of poly(propylene)s was first synthesized by Natta using conventional Ziegler-Natta catalysts and it was proposed that the formation of the polymer was governed by a kinetic factor equaling the quotient of the growth rate and a catalyst configurational inversion rate.[30]

In the present article, the effect of adding different aluminum alkyls to the polymerization medium is investigated regarding the polymerization of propylene by the metallocene catalyst (2-PhInd)₂ZrCl₂. The polymerization activities and viscometric molecular weights of all produced poly(propylene)s are measured as a function of the mole percent of added aluminum alkyls. The different poly(propylene) microstructures are investigated using ¹³C NMR analysis in order to confirm the stereochemical influence of the cocatalysts in the polymerization process.

2. Experimental Section

2.1. Materials

2-Phenylindene and MAO (10 wt% solution in toluene) were obtained from Aldrich Chemical Company (Munich, Germany). TEA was provided by Maroon Petrochemical Company (Mahshahr, Iran). Methyllithium and TIBA were purchased from Merck Chemical Company (Germany). Ethereal hydrochloric acid (2 N) was purchased from Acros Chemical Company (USA). Propylene

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and Toluene were provided by Bandar Imam Petrochemical Company (Mahshahr, Iran) and the latter was refluxed and distilled over sodium before use and kept over 4 Å/13X activated molecular sieves. All the manipulations involving air-sensitive compounds were performed under an atmosphere of dried nitrogen in a glove box.

2.2. Metallocene Synthesis

$(2\text{-PhInd})_2ZrCl_2$ was synthesized using a modified version of the literature method.[31–33] The final product was obtained by removing the solvent under reduced pressure. A fine yellow powder was obtained and characterized by ^1H NMR (CDCl$_3$, δ): 7.59 (d, 4H), 7.39 (m, 4H), 7.27 (m, 2H), 7.19 (dd, 4H), 7.02 (dd, 4H), 6.55 (s, 4H).

2.3. Polymerization

Polymerization reactions were performed in a 1 L Büchi reactor (Büchi Glas Uster bmd300) equipped with controlling systems for temperature, stirring speed, and reaction pressure. 500 mL of dried toluene were injected into the reactor. The desired amount of AlR$_3$ (R = Et or i-Bu) was injected and then MAO was introduced. The amounts were prescribed such that Al$_{MAO}$/Zr was constant at 500; the amount of AlR$_3$ varied so that its molar fraction was equal to 0.2, 0.4, 0.6, 0.8, 0.9, 0.95, and 0.97, relative to MAO. A measured amount of catalyst was injected (dissolved in a small volume of toluene) and then the polymerization reaction was conducted at 6 bar of propylene, 35 °C, and 800 rpm for 60 min. The obtained polymers were poured into acidified methanol, collected by filtration, dried, and weighed.

2.4. Characterization

The intrinsic viscosities were determined in decahydronaphthalene at 135 ± 1 °C using a SOFICA-CINEVISCO viscometer serial V04/1CE. For calculation of $\overline{M}_v$, the Mark-Houwink-Sakurada equation was used.[34] The requisite constants a and K were not available for elastomeric poly(propylene); hence, the constants for atactic poly(propylene) were employed ($a = 0.77$; $K = 15.8 \times 10^{-3}$ mL $\cdot$ g^{-1}). ^{13}C NMR analysis of the polymers was performed on an INOVA 500 NMR Instrument at 110 °C using C$_2$D$_2$Cl$_4$ as the solvent and ^{1}H NMR analysis of the catalyst was recorded using a Bruker 400 Avance NMR Instrument.

3. Results and Discussion

3.1. Activity and Molecular Weight

Figure 1 describes the polymerization activity as a function of the Al$_{MAO}$/Zr quotient for the catalyst (2-PhInd)$_2$ZrCl$_2$ in the polymerization of propylene. The obtained activity optimum of Al$_{MAO}$/Zr = 500 is somewhat low in comparison with other metallocenes.[19,35–40] No significant decline in activity is observed with increasing Al$_{MAO}$/Zr
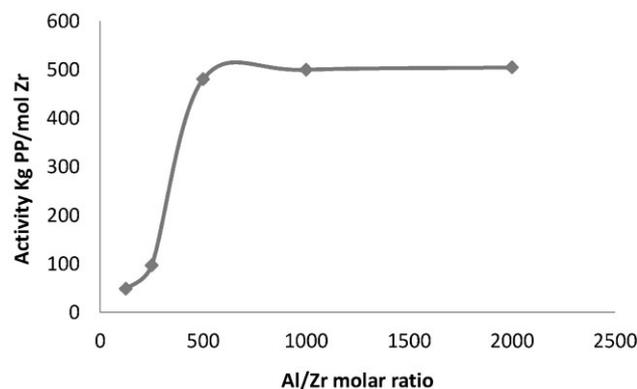
Figure 1. Propylene polymerization activity with (2-PhInd)₂ZrCl₂ versus the Al$_{MAO}$/Zr quotient. Polymerization conditions: 6 bar propylene, solvent = toluene, 35 °C, 1 h.

values, which is in accordance with a report by Waymouth and coworkers.[41] A possible explanation for this behavior is that the substantial steric hindrance of the ligands shields the cationic metal center and prevents bimolecular deactivation pathways.[19,42]

Figure 2 depicts the effects of increasing amounts of TEA and TIBA on the propylene polymerization activity in the presence of MAO, held at the constant molar quotient of Al$_{MAO}$/Zr = 500, a value that was chosen from the initial optimization stage. As can be concluded from Figure 2, the initial amounts of added TEA considerably diminished the catalyst activity, but as the mole fraction increased further, a slight increase in the activity occurred until Al$_{TEA}$/Al$_{MAO}$ = 0.8; for Al$_{TEA}$/Al$_{MAO}$ >0.9, the system became completely inactive. As shown in Figure 3, the molecular weights of the polymers also decreased steadily as Al$_{TEA}$/Al$_{MAO}$ increased from 49 000 to 17 000.

AlEt$_3$ disrupts the catalytic cycle and diminishes the activity – perhaps by modifying the MAO counteranion structure and decreasing its Lewis acidity, or through complexation of the metallocene active coordination site, which is apparently complete as Al$_{TEA}$/Al$_{MAO}$ nears unity. The slight increase in activity in the range of
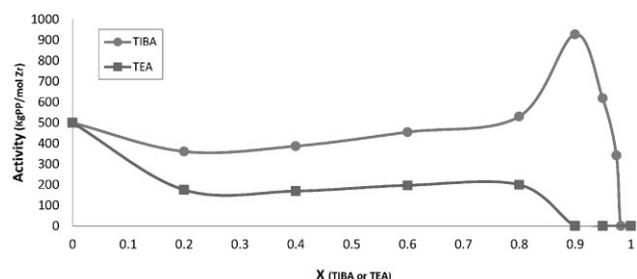
Figure 2. Effect of AlR$_3$ (R = Me or i-Bu) on the polymerization activity of (2-PhInd)₂ZrCl₂ in the presence of MAO; Al$_{(MAO)}$/Zr molar ratio is constant and equal to 500 in all the experiments. Polymerization Conditions: 6 bar propylene, 35 °C, 1 h.

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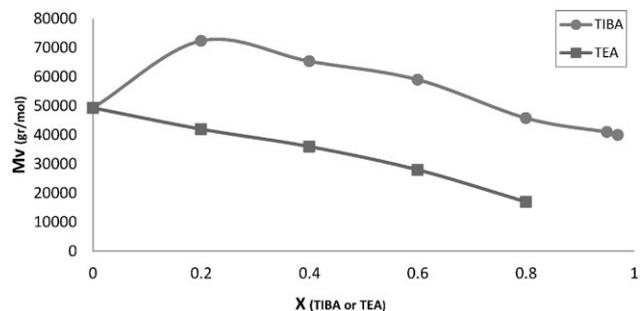
Figure 3. Effect of AlR$_3$ (R = Me or i-Bu) on the molecular weight of synthesized poly(propylene)s.

Figure 4. ^{13}C NMR spectra of the methyl region of poly(propylene) samples from (2-PhInd)$_2$ZrCl$_2$: (a) with MAO only; (b) with Al$_{TEA}$/Al$_{MAO}$ = 0.8; and (c) with Al$_{TIBA}$/Al$_{MAO}$ = 0.8.

Al$_{TEA}$/Al$_{MAO}$ = 0.2–0.8 could be rationalized by increased chain shuttling and catalyst site regeneration upon exchange of Zr-polymer for Zr-ethyl.[12] This polymer/alkyl transfer phenomenon is also a bi-molecular chain transfer reaction that readily explains the diminution of the molecular weight.

TIBA exhibited a somewhat different behavior. Upon addition of small molar fractions a slight decrease of the catalyst activity was observed (Figure 2). However, increasing amounts of TIBA allowed the activity of the system to fully recover (at Al$_{TIBA}$/Al$_{MAO}$ = 0.8) and even exceed the MAO-only polymerization activity when Al$_{TIBA}$/Al$_{MAO}$ = 0.9. Larger fractions of TIBA (Al$_{TIBA}$/Al$_{MAO}$ = 0.95) reversed this trend and when Al$_{TIBA}$/Al$_{MAO}$ reached 1.0, the activity dropped to zero. Added TIBA (Al$_{TIBA}$/Al$_{MAO}$ = 0.2) initially effected an increase in $\overline{M}_v$, but greater quantities caused a gradual decrease in polymer molecular weight (Figure 3). Above Al$_{TIBA}$/Al$_{MAO}$ = 0.8, $\overline{M}_v$ trended below the MAO-only value of 49 000.

The initial decrease in catalyst activity with small added amounts of TIBA is probably related to complexation of the metallocenium catalyst with the alkyl aluminums, some of which are smaller than TIBA because they now bear methyl groups obtained via alkyl exchange with MAO [e.g., MeAl(i-Bu)$_2$ and Me$_2$Al(i-Bu)]. Because of their decreased steric bulkiness, they can readily access the metal cation center

and deactivate it.[19] At higher concentrations, TIBA more effectively binds AlMe$_3$ and other Me$_n$Al(i-Bu)$_{3-n}$ by forming aggregates such as Al$_2$Me$_4$(i-Bu)$_2$, Al$_2$Me$_3$(i-Bu)$_3$, Al$_2$Me$_2$(i-Bu)$_4$, and Al$_2$Me(i-Bu)$_5$.[19] As the smaller alkyl aluminums are scavenged, their deleterious binding of the metallocene is minimized[15] and activity recovers. It is also
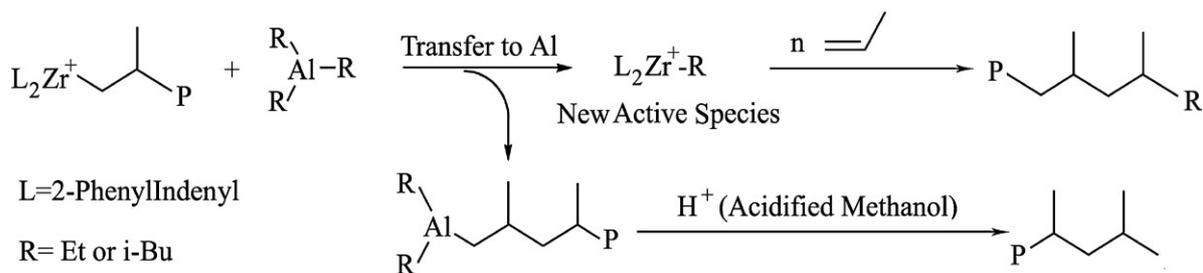
Scheme 2. A sample transmetallation reaction which results in regeneration of new active centers. As the concentration of AlR$_3$ increases the concentration of L$_2$Zr$^+$R increases in the reaction media.

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possible that alkyl exchange between TIBA and MAO results in bulkier, more Lewis acidic counteranions, as compared to the counteranions available solely from MAO,[22] giving rise to the appreciably enhanced activity found for $Al_{TIBA}/Al_{MAO} = 0.9$. Furthermore, the enhanced molecular weight observed could arise from the aforementioned scavenging effect of TIBA.

Regarding the nature of active centers in both of the cases, i.e., TIBA/MAO and TEA/MAO it can be said that the large abundance of MAO present in the reaction media generally means that most transmetallation reactions will result in L_2Zr^+-Me (L = 2-Phenylindenyl), which then continues with polymerization of propylene. Almost definitely, as AlR_3/MAO ratio increases, the likelihood of L_2Zr^+-R active centers after transmetallation increases and this will change the nature of the chain end increasingly from Me to R. This transmetallation phenomenon is continuously present during the polymerization period which results in lower $\overline{M}_v$ and regeneration of active centers (Scheme 2).

3.2. Polymer Stereochemistry

An interesting observation was made when the obtained polymers were analyzed by ^{13}C NMR analysis. The ^{13}C NMR spectra (showing the methyl region $\delta = 18$–21) of three

poly(propylene) samples are shown in Figure 4 and Table 1 catalogues the corresponding stereochemical pentad distributions. Sample (**a**) was obtained from the polymerization employing (2-PhInd)₂ZrCl₂ and MAO only (no TEA or TIBA) while sample (**b**) included TEA ($Al_{TEA}/Al_{MAO} = 0.8$) and sample (**c**) included TIBA ($Al_{TIBA}/Al_{MAO} = 0.8$).

Upon considering of the pentad composition of these polymers, it is clear that TEA and TIBA have an important effect on the catalyst's stereoregulation of the polymerization. Without added AlR_3, the obtained polymer is remarkably similar to atactic poly(propylene), for which the relative peak heights are 1:2:1:2:4:2:1:2:1. This comparison is shown numerically in Table 1 and the RMS error (calculated as $\{\Sigma(I_{obs} - I_{calc})^2]/9\}^{0.5}$) is calculated to be 2.68 versus perfectly atactic poly(propylene). An improved statistical fit is found for enantiomorphic-site control (RMS error = 2.38) and chain-end control (RMS error = 2.59).[43] These latter comparisons can be visualized in Figure 5 ($Al_{AlR3}/Al_{MAO} = 0$). The poly(propylene) is slightly isotactic with an enantiomorphic site control parameter of $\alpha = 0.560$.

When TEA or TIBA are added, a significant shift toward isoselectivity is observed. When $Al_{TEA}/Al_{MAO} = 0.8$, the *mmmm* pentad fraction increases from 7.9 to 17.6% and the enantiomorphic-site control parameter increases from $\alpha = 0.560$ to 0.680. TIBA has an even greater effect and

Table 1. The distribution of stereochemical pentads (%) in produced elastomeric poly(propylene)s from (2-PhInd)₂ZrCl₂: (a) with MAO only; (b) with $Al_{TEA}/Al_{MAO} = 0.8$; and (c) with $Al_{TIBA}/Al_{MAO} = 0.8$. In all cases Al_{MAO}/Zr is constant and equal to 500. The ^{13}C NMR peak assignments are in accord with ref.[29] Shown are the best fit calculated pentad distributions for enantiomorphic-site control and chain-end control, along with the corresponding calculated stereoselectivity parameters (α and σ).

Entry	Catalyst	RMS error[a]	Pentad content [%]								
			mmmm	*mmmr*	*rmmr*	*mmrr*	*mmrm + rmrr*	*mrmr*	*rrrr*	*rrrm*	*mrrm*
a	MAO		7.9	11.6	6.5	11.6	23.9	13.2	6.3	11.8	7.1
enantiomorphic		2.38	7.2	12.9	6.1	12.9	24.3	12.1	6.1	12.1	6.4
$\alpha = 0.560$											
chain-end $\sigma = 0.505$		2.59	6.6	12.8	6.2	12.5	25.0	12.5	5.9	12.2	6.2
atactic PP		2.68	6.25	12.5	6.25	12.5	25	12.5	6.25	12.5	6.25
$\alpha = \sigma = 0.500$											
b	TEA + MAO		17.6	14.9	4.9	11.6	21.4	11.4	3.3	8.8	6.2
enantiomorphic		5.80	14.9	15.1	4.7	15.1	18.9	9.5	4.7	9.5	7.6
$\alpha = 0.680$											
chain-end $\sigma = 0.620$		6.08	14.8	18.1	5.6	11.1	24.9	11.1	2.1	6.8	5.6
c	TIBA + MAO		23.5	15.8	5.1	13.1	18.7	8.9	3.0	6.9	5.3
enantiomorphic		6.16	21.1	16.1	3.9	16.1	15.4	7.7	3.9	7.7	8.1
$\alpha = 0.731$											
chain-end $\sigma = 0.679$		9.03	21.2	20.1	4.8	9.5	24.6	9.5	1.1	4.5	4.8

[a]The least-squares minimization was performed for the nine measured intensities (*mmrm* and *rrmr* were combined) according to RMS error = $[\Sigma(I_{obs} - I_{calc})^2]/9]^{0.5}$.
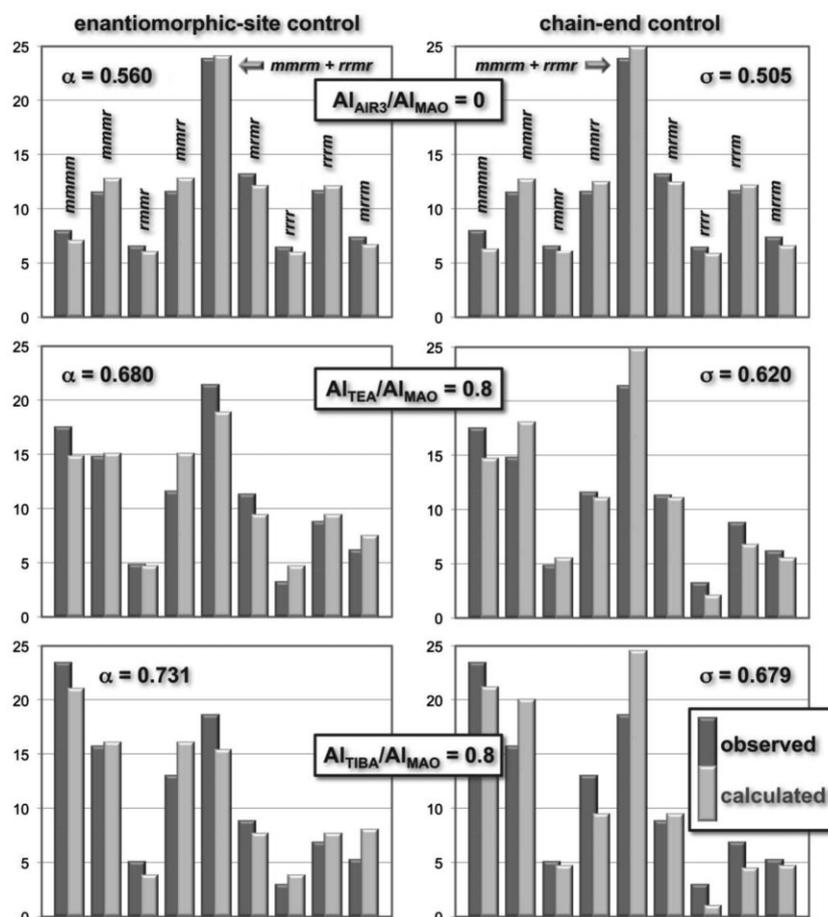
Figure 5. Comparative observed (dark gray) and calculated (light gray) pentad distributions (%) for isoselective enantiomorphic-site control and chain-end control models when $Al_{AlR3}/Al_{MAO} = 0$, $Al_{TEA}/Al_{MAO} = 0.8$, and $Al_{TIBA}/Al_{MAO} = 0.8$.

producing polymers with longer isotactic segments.[29,44,45] These results demonstrate that it is possible to mimic lower temperature polymerization conditions (slower catalyst oscillation, longer isotactic stereoblocks[28]) by introducing alkyl aluminums such as TEA and TIBA. Without these added agents, the catalyst oscillation at 35 °C is comparable to the rate of the insertion events and fairly atactic poly(propylene) is obtained. With these added agents, the catalyst oscillation is apparently slowed, relative to propagation, and stereoselectivity is enhanced.

4. Conclusion

These investigations demonstrated the effects of alkyl aluminums on the propylene polymerization behavior of the unbridged $(2\text{-PhInd})_2ZrCl_2/MAO$ catalyst system. The addition of both TEA ($AlEt_3$) and TIBA [$Al(i\text{-Bu})_3$] has a considerable effect on the polymerization activity, polymer molecular weight, and polymer tacticity. At low concentrations, TIBA functioned as a TMA ($AlMe_3$) scavenger and afforded higher polymer molecular weights; at higher concentrations, the effect of TIBA on molecular weight diminished, but it enhanced the polymerization activity. TEA generally decreased both the molecular weight

when $Al_{TIBA}/Al_{MAO} = 0.8$, the *mmmm* pentad fraction increases from 7.9 to 23.5% and the enantiomorphic-site control parameter increases from $\alpha = 0.560$ to 0.731. Note that the addition of AlR_3 also significantly increased the RMS error with the calculated models. For the enantiomorphic-site control model, added TEA increased the RMS error from 2.38 to 5.80 and added TIBA increased the RMS error from 2.38 to 6.16. Errors for the chain-end control model were higher still. The increased inconsistency between the observed and calculated pentad distributions can be visualized in Figure 5 (compare $Al_{AlR3}/Al_{MAO} = 0$ with $Al_{TEA}/Al_{MAO} = 0.8$ and $Al_{TIBA}/Al_{MAO} = 0.8$). The polymers formed in the presence of TEA and TIBA do not adhere to a simple, single-variable model – and this is evidence of a multi-site polymerization catalyst.

These findings implicate the effect of modified counterions (compared to MAO only polymerizations) on the behavior of the conformationally free, non-bridged catalyst–perhaps through locking the catalyst structure and

and the activity. Preliminary analysis of the poly(propylene) pentad distributions indicated that added TEA and TIBA significantly increased the isotactic block content of the polymers and TIBA excelled TEA in this regard. Additional ^{13}C NMR data and interpretation, thermal (DSC) analysis of the polymers produced at the various molar ratios of AlR_3:MAO, and ^1H NMR analysis of the catalyst/MAO/AlR_3 mixtures will be the subject of future reports.

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