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RESEARCH ARTICLE

Polar Isotactic and Syndiotactic Polypropylenes via Organo-zirconium-Catalyzed Masking-Reagent-Free Propylene + Amino-Olefin Copolymerization

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Abstract. Polar functionalized isotactic and syndiotactic polypropylenes (PPs) are synthesized by direct, masking reagent-free propylene + amino-olefin (AO, CH_2=$CH(CH_2)_xN^nPr_2$, x = 2, 3, 6) copolymerizations using the activated precatalysts *rac*-[$Me_2Si(indenyl)_2$]-$ZrMe_2$ and [$Me_2C(Cp)(fluorenyl)$]$ZrMe_2$, respectively. Polymerization activities at 25 °C are up to 4027 and 535 kg/(mol·h·atm) with AO incorporations up to 3.2 mol% and 1.9 mol%, respectively. Remarkably, introducing the amino-olefin comonomers significantly enhances stereoselection for both isotactic (*mmmm*: 59.5% → 91.9%) and syndiotactic (*rrrr*: 66.3% → 80.8%) products.

Polypropylenes (PPs) are among the most widely used polymeric materials, and their ever-growing applications scope has driven the demand for higher performance PP materials.[1] Introducing polar functional groups into PPs offers an attractive means to enhance properties such as adhesion, toughness, conductivity, dyeability, compatibility, rheology, etc., without compromising the parent polyolefin performance characteristics. Such modified/enhanced performance could greatly expand the range of PP applications.[2] For synthesizing polar polyolefins, post-polymerization functionalization is commonly used to derivatize commercial PPs. However such processes often require harsh conditions, lack selectivity, and induce side reactions such as chain scission and cross-linking.[2b, 3] If possible, direct alkene/polar monomer coordinative copolymerization would be far more expeditious and atom-economical, and is of both fundamental and technological interest.[4]

To date, most polar monomer copolymerization studies have focused on ethylene, with propylene receiving far less attention.[5] Note that d^8 metal (Ni, Pd) catalysts exhibit significant heteroatom tolerance and have been investigated for propylene + polar monomer copolymerizations (Figure 1a). However, these catalysts have modest activity and thermal stability,[5a, 6] with regio- and stereocontrol compromised by "chain walking".[7] While d^0 group 4 catalysts are efficient in olefin polymerizations, they are typically deactivated by polar comonomers,[5b, 5d] and stoichiometrically excess Lewis acidic "masking reagents" are typically used to tie up the polar groups.[8] Thus, Chung,[2a, 9] Hagihara and Shiono,[8d, 10] Li,[11] Schulze,[12] and Nasman[13] reported group 4-catalyzed propylene + polar monomer copolymerizations (Figure 1b). However, the masking reagents

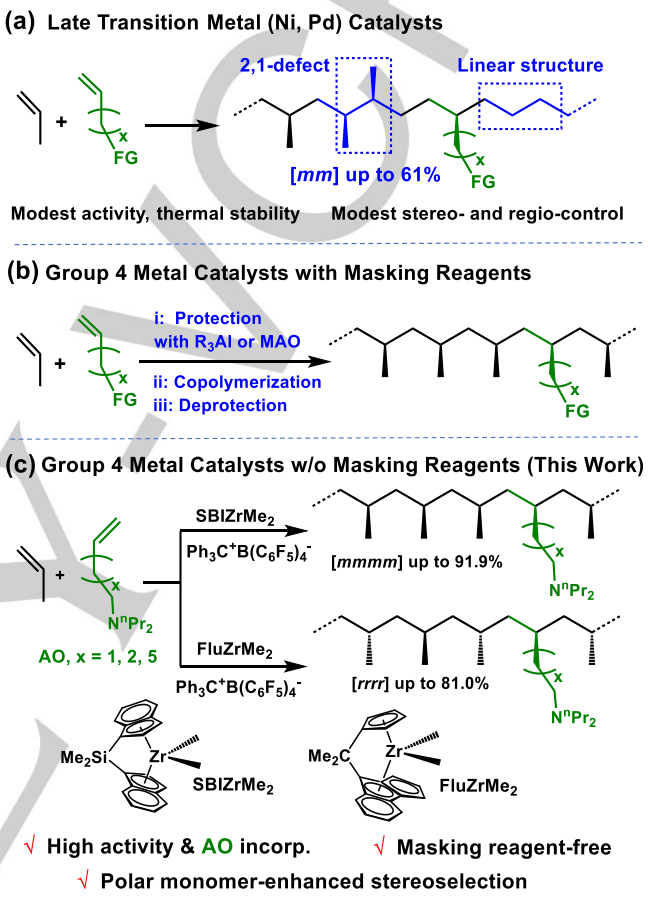

Figure 1. Functionalized isotactic and syndiotactic polypropylene synthesis via: (a) late transition metal (Pd, Ni) catalysts; (b) group 4 catalysts with masking reagents; (c) group 4-catalyzed direct copolymerization without masking reagents (this work).

and their removal from the product increase cost, compromise atom economy, and complicate rigorous mechanistic analysis. Note that some group 4 catalysts were reported active for masking reagent-free direct polar monomer homopolymerization and 1-hexene + polar monomer copolymerization,[14] but product stereochemistry and the monomer polar group role were not scrutinized.[15] Note that previous studies only showed the "negative" poisoning effects of introducing polar monomers, and focused catalyst development on mitigating such effects to obtain polar polyolefins.[16]

Recently, this Laboratory reported organo-Zr-catalyzed direct ethylene + amino-olefin (AO) copolymerizations and revealed heretofore unknown facets of cationic Zr center - amine and olefin competitive interactions, which, through careful catalyst and monomer design, provide efficient and selective catalytic systems.[17] Here we probe the generality of these findings for propylene and report organo-Zr catalyzed masking reagent-free direct amino-olefin copolymerizations for the syntheses of both functionalized isotactic and syndiotactic PPs with substantial

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activity, comonomer incorporation, and surprisingly, *comonomer-enhanced stereocontrol* (Figure 1c).

Polymerizations were carried out at 25 °C under constant 1.0 atm propylene pressure and rigorously anhydrous/anaerobic conditions with attention to exotherm and mass transfer effects.[18] Precatalysts *rac*-[$Me_2Si(indenyl)_2$]$ZrMe_2$ (**SBIZrMe$_2$**)[19] and [$Me_2C(Cp)(fluorenyl)$]$ZrMe_2$ (**FluZrMe$_2$**),[20] were activated with $Ph_3C^+B(C_6F_5)_4^-$ (**BT**) for isotactic (Table 1) and syndiotactic (Table 2) propylene + amino-olefin (AO) copolymerizations, respectively. The copolymer polar monomer contents and number average molecular mass ($M_{n,\ NMR}$) were analyzed by ^{1}H NMR,[14a, 14b, 17] and tacticity by established ^{13}C NMR assays (see SI).[8d, 10a, 21] Products were repeatedly washed with MeOH to remove unreacted AO monomer, confirmed by the absence of vinyl olefinic ^{1}H NMR signals (see SI).

Using **SBIZrMe$_2$** + **BT** for isotactic propylene copolymerizations affords poly(propylene-*co*-AO) with high activity, significant AO incorporation, and surprisingly *enhanced* isoselection (Table 1). For example, versus propylene homopolymerization, propylene + N(octenyl)^{n}Pr$_2$ copolymerization ([AO] = 0.012 M) activity falls slightly from 6535 to 4027 kg/(mol·h·atm) with 0.7 mol% comonomer incorporation; surprisingly, however, the product pentad isotacticity *mmmm* increases remarkably from 59.5% to 83.8% (Table 1, entry 1 vs. 2). Furthermore, N(octenyl)^{n}Pr$_2$ concentration effects are substantial (Figure 2a). Increasing [AO] from 0.012 M to 0.10 M dramatically increases comonomer enchainment from 0.7 to 3.2 mol% with a 7.7x decline in activity. Simultaneously, there is negligible change in product *mmmm*, from 83.8% to 81.3% (Table 1, entry 2 vs. 5). Furthermore, when [N(octenyl)^{n}Pr$_2$] reaches 0.20 M, only trace copolymer is produced (Table 1, entry 6), suggesting significant deactivation effects.[17, 22] These polar monomer stereocontrol effects contrast with catalysts using masking reagents which exhibit essentially unchanged *mmmm*[2a, 12]

Table 1. Data for propylene + AO isotactic copolymerizations mediated by **SBIZrMe$_2$** + **BT** [a]

entry	comonomer	conc., M	time, min	yield (g)	act. [b]	inc., mol%[c]	*mmmm*, %[d]	Mn, NMR[e]	T_m (°C) [f]	contact angle, ° [g]
1	None	-	4.0	4.36	6535	-	59.5	20	131.3[h]	108
2	N(octenyl)^{n}Pr$_2$	0.012	4.0	2.69	4027	0.7	83.8	46	135.2	106
3	N(octenyl)^{n}Pr$_2$	0.025	2.0	1.28	3832	1.4	87.4	35	141.8	106
4	N(octenyl)^{n}Pr$_2$	0.05	2.0	0.77	2297	2.2	85.4	36	121.4	100
5	N(octenyl)^{n}Pr$_2$	0.10	2.0	0.17	520	3.2	81.3	54	n.d.	-
6	N(octenyl)^{n}Pr$_2$	0.20	20.0	trace	-	-	-	-	-	-
7	N(pentenyl)^{n}Pr$_2$	0.012	20.0	0.08	25	0.5	90.4	99	140.9	106
8	N(butenyl)^{n}Pr$_2$	0.012	20.0	0.03	9	0.5	91.9	32	141.9	104
9	N(octenyl)^{n}Pr$_2$	0.05	6.0	1.32	1323	2.6	85.3	83	124.0	102
10[i]	N(octenyl)^{n}Pr$_2$	0.012	1.0	0.89	5354	1.2	89.1	62	134.5	102
11	N(octenyl)^{i}Pr$_2$	0.012	2	1.49	4468	0.3	81.5	66	128.7	100

[a] Conditions: 10 μmol **SBIZrMe$_2$**, 10 μmol **BT**, 1 atm propylene, 20 mL toluene, 25 °C; each entry performed in duplicate. [b] kg/(mol ·h·atm). [c] mol% incorporation by ^{1}H NMR.[17] [d] ^{13}C NMR by literature procedure .[8d, 10a] [e] kg/mol, see SI. [f] By DSC. [g] At least 6 advancing aqueous contact measurements for each sample, uncertainty range ±2°. [h] Additional melting peak at 141.2 °C. [i] 0 °C.

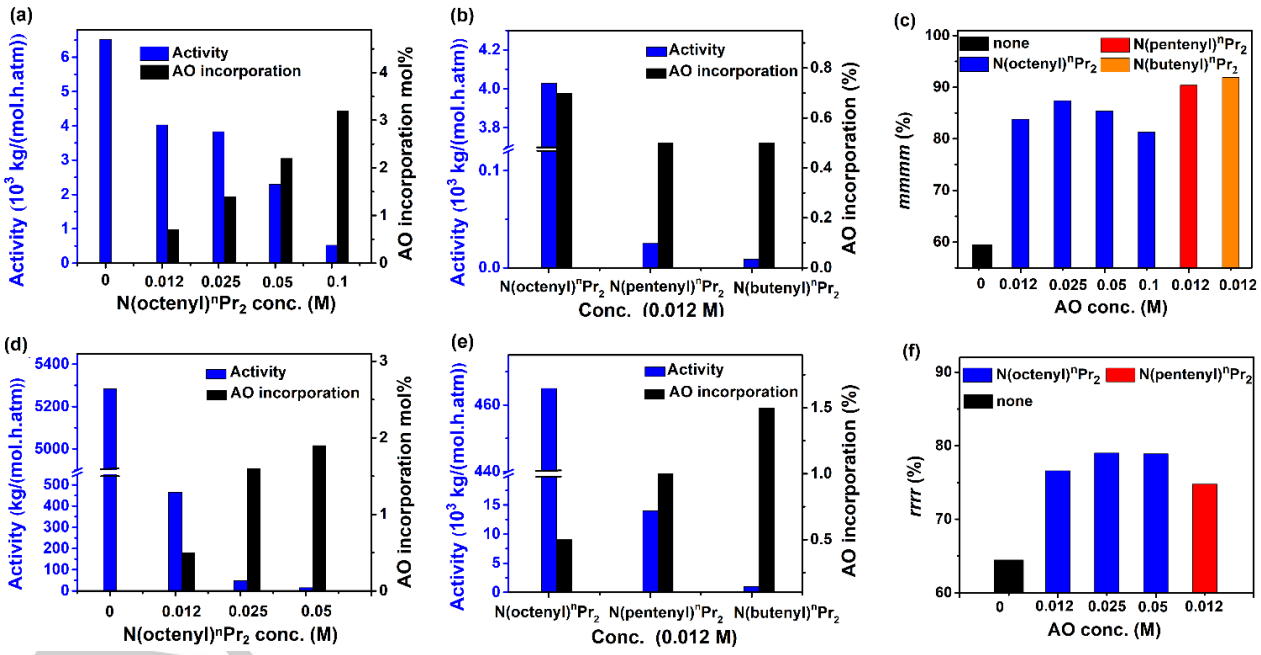

Figure 2. SBIZrMe$_2$-catalyzed isotactic propylene copolymerization with the indicated amino-olefins (AOs). (**a**) Effects of [N(octenyl)^{n}Pr$_2$] and (**b**) AO linker length on activity and AO incorporation. (**c**) [AO] effects on pentad isotacticity. **FluZrMe$_2$**-catalyzed isotactic propylene copolymerization with the indicated amino-olefins (AOs): (**d**) Effects of [N(octenyl)^{n}Pr$_2$] and (**e**) AO linker length on activity and AO incorporation. (**f**) [AO] effects on pentad syndiotacticity.

By varying the AO linker length (x, Figure 1c), distinctive x-dependent selectivity and activity patterns are noted (Figure 2b). Contracting the linker from N(octenyl)^{n}Pr$_2$ → N(pentenyl)^{n}Pr$_2$ → N(butenyl)^{n}Pr$_2$ while keeping [AO] = 0.012 M leads to essentially constant AO incorporation, from 0.7 → 0.5 → 0.5 mol%, respectively, while significantly depressing the activity, from 4027 → 25 → 9 kg/(mol·h·atm), respectively, and slightly increasing *mmmm* from 83.8% → 90.4% → 91.9%, respectively (Table 1, entry 2 vs.7 and 8). Such comonomer and linker length-stereoregulation effects are to our knowledge unprecedented.[23]

FluZrMe$_2$ + BT mediated propylene copolymerizations afford poly(propylene-*co*-AO) products with modest polar comonomer incorporation and substantial syndiotacticity, albeit at reduced activity (Table 2). Compared with propylene homopolymerization, propylene + N(octenyl)^{n}Pr$_2$ copolymerization ([AO] = 0.012 M) exhibits 11.4x reduced activity with 0.6 mol% comonomer incorporation; remarkably and similar to the above isotactic case, the product pentad syndiotacticity *rrrr* increases significantly, from 66.3% to 76.6% (Table 2, entry 1 vs. 2). Substantial [N(octenyl)^{n}Pr$_2$] effects are also observed (Figure 2d): increasing [AO] from 0.012 M to 0.05 M increases comonomer incorporation by 3.2x (0.6 mol% → 1.9 mol%) with a 31x fall in activity. In contrast to the **SBIZrMe$^+$**-catalyzed isotactic polymerizations (Figure 2c), *rrrr* is kept essentially unchanged, from 76.6% → 78.9% (Table 2, entry 2 vs. 4). Note that when [N(octenyl)^{n}Pr$_2$] reaches 0.10 M, only trace polymer is obtained (Table 1, entry 5), suggesting greater deactivation than in the isotactic system.

Contracting the AO linker length from N(octenyl)^{n}Pr$_2$ → N(pentenyl)^{n}Pr$_2$ → N(butenyl)^{n}Pr$_2$ with [AO] at 0.012 M slightly increases AO incorporation, from 0.6 mol% → 1.0 mol% → 1.5 mol%, while significantly depressing activity, from 465 → 14 → 1 kg/(mol·h·atm), respectively (Table 2, entry 2 vs. 6 and 7). In contrast to the isoselection trends (Figure 2c), the corresponding *rrrr* is largely insensitive to AO linker length, 76.6% and 80.8% for copolymerization with N(octenyl)^{n}Pr$_2$ and N(pentenyl)^{n}Pr$_2$, respectively, while propylene + N(butenyl)^{n}Pr$_2$ copolymerizations (Table 2, entry 7) yield insufficient polymer for ^{13}C NMR analysis. The greater activity drop again argues that **FluZrMe$^+$** is more readily deactivated than **SBIZrMe$^+$** in propylene + AO copolymerizations.

Table 2. Data for propylene + AO syndiotactic copolymerizations mediated by **FluZrMe$_2$ + BT** [a]

entry	comonomer	conc., M	time, min	yield (g)	act. [b]	inc., mol%[c]	*rrrr*, %[d]	Mn, NMR[e]	T_m (°C) [f]	contact angle, ° [g]
1	None	-	2.0	1.76	5284	0	66.3	80	103.9	108
2	N(octenyl) ^{n}Pr$_2$	0.012	10.0	0.78	465	0.6	76.6	52	116.4	104
3	N(octenyl) ^{n}Pr$_2$	0.025	25.0	0.20	48	1.6	79.0	56	117.3	103
4	N(octenyl) ^{n}Pr$_2$	0.05	25.0	0.06	15	1.9	78.9	72	111.4	104
5	N(octenyl) ^{n}Pr$_2$	0.10	25.0	trace	-	-	-	-	-	-
6	N(pentenyl)^{n}Pr$_2$	0.012	25.0	0.06	14	1.0	80.8	27	119.7	104
7	N(butenyl)^{n}Pr$_2$	0.012	25.0	0.01	1	1.5	-	n.d.	n.d.	107
8	N(octenyl) ^{n}Pr$_2$	0.012	5.0	0.45	535	0.9	79.0	30	120.7	103
9	N(octenyl) ^{n}Pr$_2$	0.012	20.0	1.33	400	0.6	78.7	21	111.3	105
10[h]	N(octenyl) ^{n}Pr$_2$	0.012	10.0	1.76	1055	0.6	85.3	59	132.6	99
11	N(octenyl) ^{i}Pr$_2$	0.012	10.0	1.56	939	0.2	72.0	59	n.d.	102

[a] Conditions: 10 μmol **FluZrMe$_2$**, 10 μmol **BT**, 1 atm propylene, 20 mL toluene, 25 °C; each entry performed in duplicate. [b] units of kg/(mol·h·atm). [c] Incorporation, mol%, by ^{1}H NMR.[17] [d] By ^{13}C NMR by literature procedure.[21] [e] kg/mol, see SI. [f] By DSC. [g] At least 6 measurements per sample, uncertainty, ±2°. [h] 0 °C.

Terminal unsaturations such as vinylidene and allyl end groups, are common in metallocene-catalyzed propylene polymerizations and are assigned to β-hydride and β-methyl transfer, processes, respectively.[24] All PP and poly(propylene-*co*-AO) products here were analyzed by ^{1}H NMR. Vinylidene (δ 4.80-4.95 ppm), vinylene (*cis* and *trans*, δ 5.38–5.56 ppm) and isobutenyl (^{i}But: δ5.00–5.20 ppm) signatures are observed in all samples, suggesting β-H elimination is the major chain transfer pathway.[24] The $M_{n,NMR}$s of the **SBIZrMe$_2$ + BT** and **FluZrMe$_2$ + BT** derived PPs are 20 kg/mol and 80 kg/mol, respectively, and are overall consistent with the homopolymer GPC data (Figure S56, 17 kg/mol and 39 kg/mol, respectively), and the literature,[20a, 20c, 25] arguing that NMR is reliable for M_n estimation. Note that GPC analysis of polar PP samples is intrinsically inaccurate, reflecting known artifacts in ethylene + AO copolymer analyses.[17, 26] While the $M_{n,NMR}$ of isotactic polar PP is slightly higher than that of the isotactic homopolymer, the $M_{n,NMR}$ of the syndiotactic polar PP is similar to or slightly lower than that of the syndiotactic homopolymer (Table 2), both indicating high M_n polymer.

All samples were characterized by advancing aqueous contact angle[27] and melting point (T_m) determination to assess any polar comonomer effects. AO incorporation into the PPs depresses the advancing aqueous contact angles by as much as 8° and 9° for the isotactic and syndiotactic PPs, respectively, reflecting increased surface energy. Most PP samples exhibit a single DSC T_m (Figures S57 and S58). The isotactic PP and polar PP samples in Table 1 exhibit similar high T_ms, while the syndiotactic analogues of Table 2, exhibit higher T_ms than the homopolymer, presumably reflecting the enhanced syndiotacticity. Thus, AO monomer introduction clearly enhances PP film hydrophilicity without significantly depressing the PP melting point.

To decouple α-olefin and tertiary amine effects, polymerizations were next carried out with these catalysts in the presence of 1-octene and/or free N^{n}Pr$_3$. We find that **SBIZrMe$_2$**-catalyzed 1-octene copolymerization enchains ~0.6 mol% comonomer with minimal effect on *mmmm* (60.1% vs. 59.5%. Table 3, entry 3 vs. 1), suggesting little enchained alkene effects on enantiomorphic site control.[1e, 18b, 20c, 28] Regarding free and tethered amino group effects on tacticity, N^{n}Pr$_3$ addition increases *mmmm* ~16% to ~69% for both propylene homo-polymerization and 1-octene copolymerization (Table 3, entries 2 and 4). As noted above, propylene + N(octenyl)^{n}Pr$_2$ copolymerization yields greater isotacticity (*mmmm* = 83.8%, Table 1, entry 2). Thus, both N^{n}Pr$_3$ and AOs enhance isotacticity with the latter somewhat more effectively (Figure 3a). In contrast, **FluZrMe$_2$**-catalyzed copolymerization enchains ~0.4 mol% 1-octene, to depress *rrrr* from 66.3% to 58.4% (Table 4, entry 3 vs. 1), likely reflecting small chain-end control effects and the length of 1-octene vs. propylene.[1e, 20a, 28-29] Next, introducing N^{n}Pr$_3$ increases *rrrr* by 15% and 26% for propylene homopolymerization and

Table 3. Tertiary amine effects on SBIZrMe$_2$c-atalyzed propylene homo-polymerization and copolymerization with 1-octene[a]

entry	monomer	t, min	yield, g	act. [b]	incorp, mol%[c]	*mmmm*, %[d]	Mn, NMR[e]
1	P	4	4.36	6535	-	59.5	20
2	P[f]	2	1.96	5892	-	69.1	30
3	P + O	2	2.32	6967	0.6	60.1	24
4	P + O[f]	2	1.36	4103	1.0	69.4	41

[a] Conditions: 10 μmol **SBIZrMe$_2$**, 10 μmol **BT**, 1 atm propylene (P), 1-octene (O), 0.012 M, 20 mL toluene, 25 °C; each entry performed in duplicate. [b] kg/(mol ·h·atm). [c] mol% incorporation by ^{1}H NMR.[17] [d] By ^{13}C NMR, analyzed by literature procedure.[8d, 10a] [e] kg/mol, see SI. [f] added N^{n}Pr$_3$, 0.012 M.

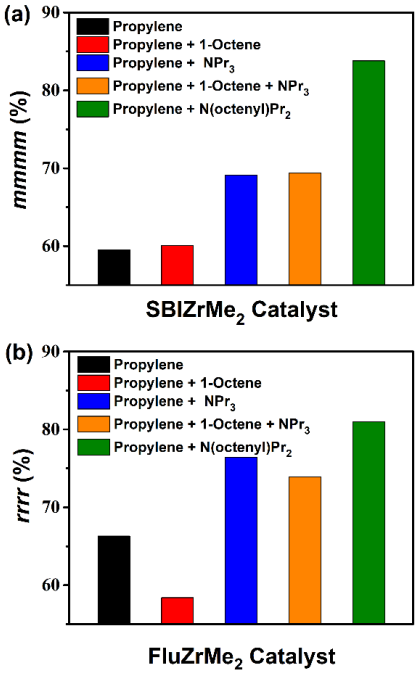

Figure 3. Decoupled effects of comonomer and tertiary amine group on stereocontrol in (**a**) isotactic and (**b**) syndiotactic propylene polymerization.

copolymerization with 1-octene, respectively (Table 4, entries 2 and 4). In contrast to the above isotactic propylene polymerization experiments, **FluZrMe$_2$**-mediated propylene + N(octenyl)^{n}Pr$_2$ copolymerization does not further enhance *rrrr* (76.6%, Table 2, entry 2) vs. propylene polymerization in the presence of N^{n}Pr$_3$ (76.4, Table 4, entries 2). Interestingly, introducing 1-octene doesn't change syndiotacticity in the presence of (73.9 mol%, Table 4, entry 4). Thus, N^{n}Pr$_3$ and AO promote similar syndiotacticity (Figure 3b).

Table 4. Tertiary amine effects on **FluZrMe$_2$**-catalyzed propylene homo-polymerization and copolymerization with 1-octene[a]

entry	monomer	t, min	yield, g	act. [b]	incorp, mol%[c]	*rrrr*, %[d]	Mn, NMR[e]
1	P	2	1.76	5283	-	66.3	80
2	P[f]	10	1.49	895	-	76.4	65
3	P + O	10	1.90	1142	0.4	58.4	46
4	P + O[f]	10	0.51	305	0.9	73.9	59

[a] Conditions: 10 μmol **FluZrMe$_2$**, 10 μmol **BT**, 1 atm propylene (P), 1-octene (O), 0.012 M, 20 mL toluene, 25 °C; each entry performed in duplicate. [b] kg/(mol ·h·atm). [c] mol% incorporation by ^{1}H NMR.[17] [d] By ^{13}C NMR, analyzed by literature procedure.[8d, 10a] [e] kg/mol, see SI. [f] added N^{n}Pr$_3$, 0.012 M.

Stereoselection mechanisms for propylene polymerization are well-established.[1e, 29b, 30] For C_2-symmetric catalysts such as **SBIZrMe$_2$**, enantiomorphic site control promotes isotacticity; for C_s-symmetric catalysts such as **FluZrMe$_2$**, regularly alternating propylene insertions at enantiotopic sites via chain-end control promote syndiotacticity (Figures 4a,b). Regarding the present amine effects, in addition to reducing polymerization activity, reasonably attributable to AO $R_3N\rightarrow Zr^+$ coordination,[17, 31] the AO presence significantly enhances both isotacticity and syndiotacticity (Figure 3), and in a way that is relatively insensitive to added 1-octene, and whether the amine is exogeneous or tethered to an α-olefin. Indeed, the above control experiments argue that amine base coordination, either N^{n}Pr$_3$ or AO, to the acidic Zr^+ center enhances both isotactic and syndiotactic stereoselection, regardless of the exact stereocontrol mechanism.[1e, 29b] Regarding the processes in Figure 4, it is known that in both scenarios stereoerrors can be suppressed/enhanced by the interplay of sterically incumbered substituents,[21, 32] donor solvents,[20a, 28] basic R_2Al-H species,[30a] and/or tightly ion-paired counteranions with basic groups,[20c, 28]) which interact with the electrophilic catalytic center so as to enhance/disrupt the chain-swinging-olefin insertion synchrony and switch on diverse alternative enchainment pathways. [20a, 21 28, 31, 23] Here the added polar comonomer amino-olefins fill such a role most effectively.

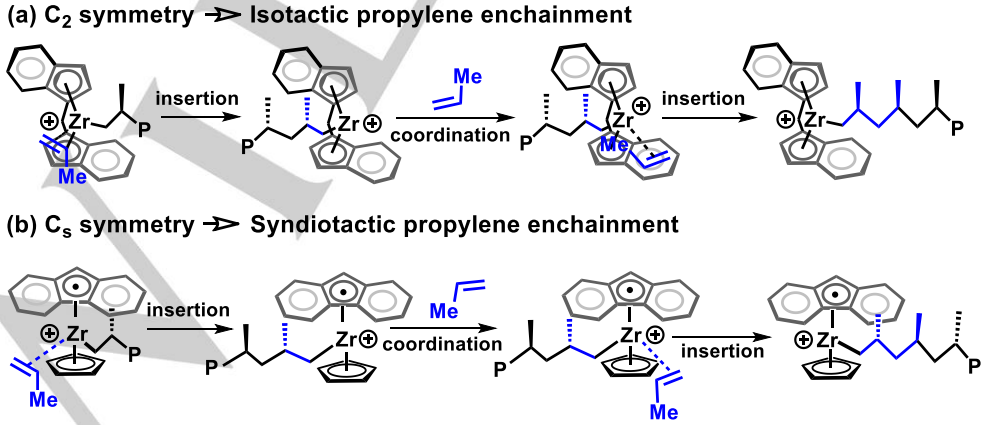

Figure 4. Mechanisms of (**a**) isotactic propylene enchainment by C_2-symmetric **SBIZrMe$_2$** + **BT**; (**b**) syndiotactic propylene enchainment by C_s-symmetric **FluZrMe$_2$** + **BT**.

In summary, these results present new and efficient d^0 group 4 catalyst-mediated direct, masking reagent-free isotactic and syndiotactic PP + AO polar comonomer copolymerization systems, which exhibit several intriguing trends: *i*. Significant amounts of AO polar comonomer are enchained with substantial activities in the absence of masking reagents; *ii*. Substantial tacticities (up to 91.9% *mmmm* and 80.8% *rrrr*, respectively) are achieved, frequently exceeding those of the corresponding homopolymerizations; *iii*. AO incorporation levels increase but are ultimately suppressed at higher [AO]; *iv*. AO deactivation is more severe for the **FluZrMe$_2$**-derived catalysts than for the **SBIZrMe$_2$**-derived ones. Detailed mechanistic studies are underway.

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Keywords: propylene polymerization • copolymerization • polar monomer • organo-zirconium catalyst

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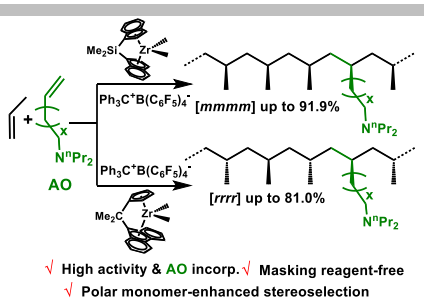

*Minglu Huang, Jiazhen Chen, Binghao Wang, Wei Huang, Haibo Chen, Yanshan Gao, * and Tobin J. Marks **

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Polar Isotactic and Syndiotactic Polypropylenes via Organo-zirconium-Catalyzed Masking-Reagent-Free Propylene + Amino-Olefin Copolymerization

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RESEARCH ARTICLE

Polar Isotactic and Syndiotactic Polypropylenes via Organo-zirconium-Catalyzed Masking-Reagent-Free Propylene + Amino-Olefin Copolymerization

Minglu Huang,[a][b] Jiazhen Chen,[a] Binghao Wang,[a] Wei Huang,[a] Haibo Chen,[b] Yanshan Gao,*[a] and Tobin J. Marks*[a]

Abstract. Polar functionalized isotactic and syndiotactic polypropylenes (PPs) are synthesized by direct, masking reagent-free propylene + amino-olefin (AO, CH_2=$CH(CH_2)_xN^nPr_2$, x = 2, 3, 6) copolymerizations using the activated precatalysts *rac*-[$Me_2Si(indenyl)_2$]-$ZrMe_2$ and [$Me_2C(Cp)(fluorenyl)$]$ZrMe_2$, respectively. Polymerization activities at 25 °C are up to 4027 and 535 kg/(mol·h·atm) with AO incorporations up to 3.2 mol% and 1.9 mol%, respectively. Remarkably, introducing the amino-olefin comonomers significantly enhances stereoselection for both isotactic (*mmmm*: 59.5% → 91.9%) and syndiotactic (*rrrr*: 66.3% → 80.8%) products.

Polypropylenes (PPs) are among the most widely used polymeric materials, and their ever-growing applications scope has driven the demand for higher performance PP materials.[1] Introducing polar functional groups into PPs offers an attractive means to enhance properties such as adhesion, toughness, conductivity, dyeability, compatibility, rheology, etc., without compromising the parent polyolefin performance characteristics. Such modified/enhanced performance could greatly expand the range of PP applications.[2] For synthesizing polar polyolefins, post-polymerization functionalization is commonly used to derivatize commercial PPs. However such processes often require harsh conditions, lack selectivity, and induce side reactions such as chain scission and cross-linking.[2b, 3] If possible, direct alkene/polar monomer coordinative copolymerization would be far more expeditious and atom-economical, and is of both fundamental and technological interest.[4]

To date, most polar monomer copolymerization studies have focused on ethylene, with propylene receiving far less attention.[5] Note that d^8 metal (Ni, Pd) catalysts exhibit significant heteroatom tolerance and have been investigated for propylene + polar monomer copolymerizations (Figure 1a). However, these catalysts have modest activity and thermal stability,[5a, 6] with regio- and stereocontrol compromised by "chain walking".[7] While d^0 group 4 catalysts are efficient in olefin polymerizations, they are typically deactivated by polar comonomers,[5b, 5d] and stoichiometrically excess Lewis acidic "masking reagents" are typically used to tie up the polar groups.[8] Thus, Chung,[2a, 9] Hagihara and Shiono,[8d, 10] Li,[11] Schulze,[12] and Nasman[13] reported group 4-catalyzed propylene + polar monomer copolymerizations (Figure 1b). However, the masking reagents

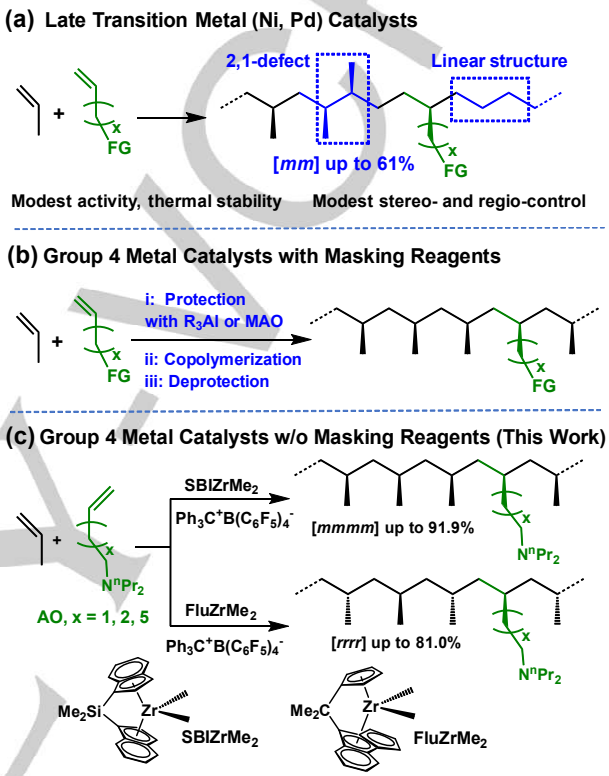

Figure 1. Functionalized isotactic and syndiotactic polypropylene synthesis via: (a) late transition metal (Pd, Ni) catalysts; (b) group 4 catalysts with masking reagents; (c) group 4-catalyzed direct copolymerization without masking reagents (this work).

and their removal from the product increase cost, compromise atom economy, and complicate rigorous mechanistic analysis. Note that some group 4 catalysts were reported active for masking reagent-free direct polar monomer homopolymerization and 1-hexene + polar monomer copolymerization,[14] but product stereochemistry and the monomer polar group role were not scrutinized.[15] Note that previous studies only showed the "negative" poisoning effects of introducing polar monomers, and focused catalyst development on mitigating such effects to obtain polar polyolefins.[16]

Recently, this Laboratory reported organo-Zr-catalyzed direct ethylene + amino-olefin (AO) copolymerizations and revealed heretofore unknown facets of cationic Zr center - amine and olefin competitive interactions, which, through careful catalyst and monomer design, provide efficient and selective catalytic systems.[17] Here we probe the generality of these findings for propylene and report organo-Zr catalyzed masking reagent-free direct amino-olefin copolymerizations for the syntheses of both functionalized isotactic and syndiotactic PPs with substantial

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activity, comonomer incorporation, and surprisingly, *comonomer-enhanced stereocontrol* (Figure 1c).

Polymerizations were carried out at 25 °C under constant 1.0 atm propylene pressure and rigorously anhydrous/anaerobic conditions with attention to exotherm and mass transfer effects.[18] Precatalysts *rac*-[$Me_2Si(indenyl)_2$]$ZrMe_2$ (**SBIZrMe$_2$**)[19] and [$Me_2C(Cp)(fluorenyl)$]$ZrMe_2$ (**FluZrMe$_2$**),[20] were activated with $Ph_3C^+B(C_6F_5)_4^-$ (**BT**) for isotactic (Table 1) and syndiotactic (Table 2) propylene + amino-olefin (AO) copolymerizations, respectively. The copolymer polar monomer contents and number average molecular mass ($M_{n,\ NMR}$) were analyzed by ^{1}H NMR,[14a, 14b, 17] and tacticity by established ^{13}C NMR assays (see SI).[8d, 10a, 21] Products were repeatedly washed with MeOH to remove unreacted AO monomer, confirmed by the absence of vinyl olefinic ^{1}H NMR signals (see SI).

Using **SBIZrMe$_2$** + **BT** for isotactic propylene copolymerizations affords poly(propylene-*co*-AO) with high activity, significant AO incorporation, and surprisingly *enhanced* isoselection (Table 1). For example, versus propylene homopolymerization, propylene + N(octenyl)^{n}Pr$_2$ copolymerization ([AO] = 0.012 M) activity falls slightly from 6535 to 4027 kg/(mol·h·atm) with 0.7 mol% comonomer incorporation; surprisingly, however, the product pentad isotacticity *mmmm* increases remarkably from 59.5% to 83.8% (Table 1, entry 1 vs. 2). Furthermore, N(octenyl)^{n}Pr$_2$ concentration effects are substantial (Figure 2a). Increasing [AO] from 0.012 M to 0.10 M dramatically increases comonomer enchainment from 0.7 to 3.2 mol% with a 7.7x decline in activity. Simultaneously, there is negligible change in product *mmmm*, from 83.8% to 81.3% (Table 1, entry 2 vs. 5). Furthermore, when [N(octenyl)^{n}Pr$_2$] reaches 0.20 M, only trace copolymer is produced (Table 1, entry 6), suggesting significant deactivation effects.[17, 22] These polar monomer stereocontrol effects contrast with catalysts using masking reagents which exhibit essentially unchanged *mmmm*[2a, 12]

Table 1. Data for propylene + AO isotactic copolymerizations mediated by **SBIZrMe$_2$** + **BT** [a]

entry	comonomer	conc., M	time, min	yield (g)	act. [b]	inc., mol%[c]	*mmmm*, %[d]	Mn, NMR[e]	T_m (°C) [f]	contact angle, ° [g]
1	None	-	4.0	4.36	6535	-	59.5	20	131.3[h]	108
2	N(octenyl) ^{n}Pr$_2$	0.012	4.0	2.69	4027	0.7	83.8	46	135.2	106
3	N(octenyl) ^{n}Pr$_2$	0.025	2.0	1.28	3832	1.4	87.4	35	141.8	106
4	N(octenyl) ^{n}Pr$_2$	0.05	2.0	0.77	2297	2.2	85.4	36	121.4	100
5	N(octenyl) ^{n}Pr$_2$	0.10	2.0	0.17	520	3.2	81.3	54	n.d.	-
6	N(octenyl) ^{n}Pr$_2$	0.20	20.0	trace	-	-	-	-	-	-
7	N(pentenyl)^{n}Pr$_2$	0.012	20.0	0.08	25	0.5	90.4	99	140.9	106
8	N(butenyl)^{n}Pr$_2$	0.012	20.0	0.03	9	0.5	91.9	32	141.9	104
9	N(octenyl) ^{n}Pr$_2$	0.05	6.0	1.32	1323	2.6	85.3	83	124.0	102
10[i]	N(octenyl) ^{n}Pr$_2$	0.012	1.0	0.89	5354	1.2	89.1	62	134.5	102
11	N(octenyl) ^{i}Pr$_2$	0.012	2	1.49	4468	0.3	81.5	66	128.7	100

[a] Conditions: 10 μmol **SBIZrMe$_2$**, 10 μmol **BT**, 1 atm propylene, 20 mL toluene, 25 °C; each entry performed in duplicate. [b] kg/(mol ·h·atm). [c] mol% incorporation by ^{1}H NMR.[17] [d] ^{13}C NMR by literature procedure .[8d, 10a] [e] kg/mol, see SI. [f] By DSC. [g] At least 6 advancing aqueous contact measurements for each sample, uncertainty range ±2°. [h] Additional melting peak at 141.2 °C. [i] 0 °C.

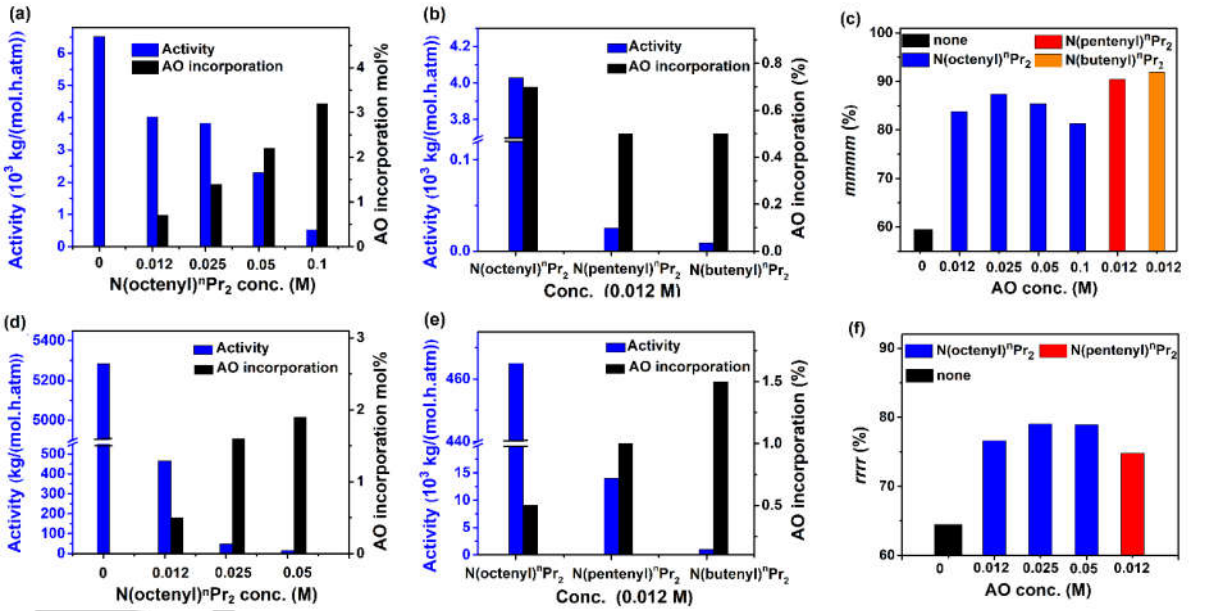

Figure 2. **SBIZrMe$_2$**-catalyzed isotactic propylene copolymerization with the indicated amino-olefins (AOs). (**a**) Effects of [N(octenyl)^{n}Pr$_2$] and (**b**) AO linker length on activity and AO incorporation. (**c**) [AO] effects on pentad isotacticity. **FluZrMe$_2$**-catalyzed isotactic propylene copolymerization with the indicated amino-olefins (AOs): (**d**) Effects of [N(octenyl)^{n}Pr$_2$] and (**e**) AO linker length on activity and AO incorporation. (**f**) [AO] effects on pentad syndiotacticity.

By varying the AO linker length (x, Figure 1c), distinctive x-dependent selectivity and activity patterns are noted (Figure 2b). Contracting the linker from N(octenyl)^{n}Pr$_2$ → N(pentenyl)^{n}Pr$_2$ → N(butenyl)^{n}Pr$_2$ while keeping [AO] = 0.012 M leads to essentially constant AO incorporation, from 0.7 → 0.5 → 0.5 mol%, respectively, while significantly depressing the activity, from 4027 → 25 → 9 kg/(mol·h·atm), respectively, and slightly increasing *mmmm* from 83.8% → 90.4% → 91.9%, respectively (Table 1, entry 2 vs.7 and 8). Such comonomer and linker length-stereoregulation effects are to our knowledge unprecedented.[23]

FluZrMe$_2$ + BT mediated propylene copolymerizations afford poly(propylene-*co*-AO) products with modest polar comonomer incorporation and substantial syndiotacticity, albeit at reduced activity (Table 2). Compared with propylene homopolymerization, propylene + N(octenyl)^{n}Pr$_2$ copolymerization ([AO] = 0.012 M) exhibits 11.4x reduced activity with 0.6 mol% comonomer incorporation; remarkably and similar to the above isotactic case, the product pentad syndiotacticity *rrrr* increases significantly, from 66.3% to 76.6% (Table 2, entry 1 vs. 2). Substantial [N(octenyl)^{n}Pr$_2$] effects are also observed (Figure 2d): increasing [AO] from 0.012 M to 0.05 M increases comonomer incorporation by 3.2x (0.6 mol% → 1.9 mol%) with a 31x fall in activity. In contrast to the **SBIZrMe$^+$**-catalyzed isotactic polymerizations (Figure 2c), *rrrr* is kept essentially unchanged, from 76.6% → 78.9% (Table 2, entry 2 vs. 4). Note that when [N(octenyl)^{n}Pr$_2$] reaches 0.10 M, only trace polymer is obtained (Table 1, entry 5), suggesting greater deactivation than in the isotactic system.

Contracting the AO linker length from N(octenyl)^{n}Pr$_2$ → N(pentenyl)^{n}Pr$_2$ → N(butenyl)^{n}Pr$_2$ with [AO] at 0.012 M slightly increases AO incorporation, from 0.6 mol% → 1.0 mol% → 1.5 mol%, while significantly depressing activity, from 465 → 14 → 1 kg/(mol·h·atm), respectively (Table 2, entry 2 vs. 6 and 7). In contrast to the isoselection trends (Figure 2c), the corresponding *rrrr* is largely insensitive to AO linker length, 76.6% and 80.8% for copolymerization with N(octenyl)^{n}Pr$_2$ and N(pentenyl)^{n}Pr$_2$, respectively, while propylene + N(butenyl)^{n}Pr$_2$ copolymerizations (Table 2, entry 7) yield insufficient polymer for ^{13}C NMR analysis. The greater activity drop again argues that **FluZrMe$^+$** is more readily deactivated than **SBIZrMe$^+$** in propylene + AO copolymerizations.

Table 2. Data for propylene + AO syndiotactic copolymerizations mediated by **FluZrMe$_2$ + BT** [a]

entry	comonomer	conc., M	time, min	yield (g)	act. [b]	inc., mol%[c]	*rrrr*, %[d]	Mn, NMR[e]	T_m (°C) [f]	contact angle, ° [g]
1	None	-	2.0	1.76	5284	0	66.3	80	103.9	108
2	N(octenyl)^{n}Pr$_2$	0.012	10.0	0.78	465	0.6	76.6	52	116.4	104
3	N(octenyl)^{n}Pr$_2$	0.025	25.0	0.20	48	1.6	79.0	56	117.3	103
4	N(octenyl)^{n}Pr$_2$	0.05	25.0	0.06	15	1.9	78.9	72	111.4	104
5	N(octenyl)^{n}Pr$_2$	0.10	25.0	trace	-	-	-	-	-	-
6	N(pentenyl)^{n}Pr$_2$	0.012	25.0	0.06	14	1.0	80.8	27	119.7	104
7	N(butenyl)^{n}Pr$_2$	0.012	25.0	0.01	1	1.5	-	n.d.	n.d.	107
8	N(octenyl)^{n}Pr$_2$	0.012	5.0	0.45	535	0.9	79.0	30	120.7	103
9	N(octenyl)^{n}Pr$_2$	0.012	20.0	1.33	400	0.6	78.7	21	111.3	105
10[h]	N(octenyl)^{n}Pr$_2$	0.012	10.0	1.76	1055	0.6	85.3	59	132.6	99
11	N(octenyl)^{i}Pr$_2$	0.012	10.0	1.56	939	0.2	72.0	59	n.d.	102

[a] Conditions: 10 μmol **FluZrMe$_2$**, 10 μmol **BT**, 1 atm propylene, 20 mL toluene, 25 °C; each entry performed in duplicate. [b] units of kg/(mol·h·atm). [c] Incorporation, mol%, by ^{1}H NMR.[17] [d] By ^{13}C NMR by literature procedure.[21] [e] kg/mol, see SI. [f] By DSC. [g] At least 6 measurements per sample, uncertainty, ±2°. [h] 0 °C.

Terminal unsaturations such as vinylidene and allyl end groups, are common in metallocene-catalyzed propylene polymerizations and are assigned to β-hydride and β-methyl transfer, processes, respectively.[24] All PP and poly(propylene-*co*-AO) products here were analyzed by ^{1}H NMR. Vinylidene (δ 4.80-4.95 ppm), vinylene (*cis* and *trans*, δ 5.38–5.56 ppm) and isobutenyl (^{i}But: δ5.00–5.20 ppm) signatures are observed in all samples, suggesting β-H elimination is the major chain transfer pathway.[24] The $M_{n,NMR}$s of the **SBIZrMe$_2$ + BT** and **FluZrMe$_2$ + BT** derived PPs are 20 kg/mol and 80 kg/mol, respectively, and are overall consistent with the homopolymer GPC data (Figure S56, 17 kg/mol and 39 kg/mol, respectively), and the literature,[20a, 20c, 25] arguing that NMR is reliable for M_n estimation. Note that GPC analysis of polar PP samples is intrinsically inaccurate, reflecting known artifacts in ethylene + AO copolymer analyses.[17, 26] While the $M_{n,NMR}$ of isotactic polar PP is slightly higher than that of the isotactic homopolymer, the $M_{n,NMR}$ of the syndiotactic polar PP is similar to or slightly lower than that of the syndiotactic homopolymer (Table 2), both indicating high M_n polymer.

All samples were characterized by advancing aqueous contact angle[27] and melting point (T_m) determination to assess any polar comonomer effects. AO incorporation into the PPs depresses the advancing aqueous contact angles by as much as 8° and 9° for the isotactic and syndiotactic PPs, respectively, reflecting increased surface energy. Most PP samples exhibit a single DSC T_m (Figures S57 and S58). The isotactic PP and polar PP samples in Table 1 exhibit similar high T_ms, while the syndiotactic analogues of Table 2, exhibit higher T_ms than the homopolymer, presumably reflecting the enhanced syndiotacticity. Thus, AO monomer introduction clearly enhances PP film hydrophilicity without significantly depressing the PP melting point.

To decouple α-olefin and tertiary amine effects, polymerizations were next carried out with these catalysts in the presence of 1-octene and/or free N^{n}Pr$_3$. We find that **SBIZrMe$_2$**-catalyzed 1-octene copolymerization enchains ~0.6 mol% comonomer with minimal effect on *mmmm* (60.1% vs. 59.5%. Table 3, entry 3 vs. 1), suggesting little enchained alkene effects on enantiomorphic site control.[1e, 18b, 20c, 28] Regarding free and tethered amino group effects on tacticity, N^{n}Pr$_3$ addition increases *mmmm* ~16% to ~69% for both propylene homo-polymerization and 1-octene copolymerization (Table 3, entries 2 and 4). As noted above, propylene + N(octenyl)^{n}Pr$_2$ copolymerization yields greater isotacticity (*mmmm* = 83.8%, Table 1, entry 2). Thus, both N^{n}Pr$_3$ and AOs enhance isotacticity with the latter somewhat more effectively (Figure 3a). In contrast, **FluZrMe$_2$**-catalyzed copolymerization enchains ~0.4 mol% 1-octene, to depress *rrrr* from 66.3% to 58.4% (Table 4, entry 3 vs. 1), likely reflecting small chain-end control effects and the length of 1-octene vs. propylene.[1e, 20a, 28-29] Next, introducing N^{n}Pr$_3$ increases *rrrr* by 15% and 26% for propylene homopolymerization and

Table 3. Tertiary amine effects on SBIZrMe$_2$c-atalyzed propylene homo-polymerization and copolymerization with 1-octene[a]

entry	monomer	t, min	yield, g	act. [b]	incorp, mol%[c]	*mmmm*, %[d]	Mn, NMR[e]
1	P	4	4.36	6535	-	59.5	20
2	P[f]	2	1.96	5892	-	69.1	30
3	P + O	2	2.32	6967	0.6	60.1	24
4	P + O[f]	2	1.36	4103	1.0	69.4	41

[a] Conditions: 10 μmol **SBIZrMe$_2$**, 10 μmol **BT**, 1 atm propylene (P), 1-octene (O), 0.012 M, 20 mL toluene, 25 °C; each entry performed in duplicate. [b] kg/(mol ·h·atm). [c] mol% incorporation by ^{1}H NMR.[17] [d] By ^{13}C NMR, analyzed by literature procedure.[8d, 10a] [e] kg/mol, see SI. [f] added N^{n}Pr$_3$, 0.012 M.

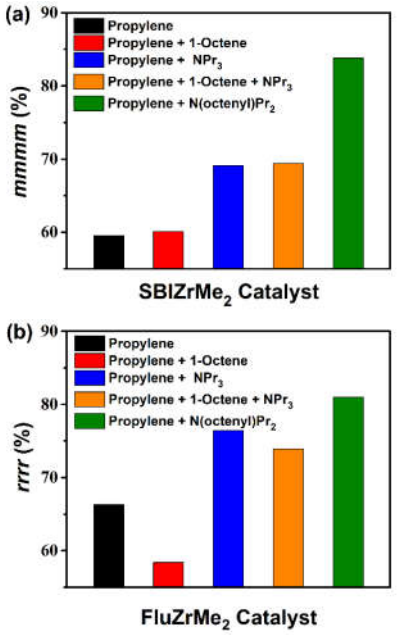

Figure 3. Decoupled effects of comonomer and tertiary amine group on stereocontrol in (**a**) isotactic and (**b**) syndiotactic propylene polymerization.

copolymerization with 1-octene, respectively (Table 4, entries 2 and 4). In contrast to the above isotactic propylene polymerization experiments, **FluZrMe$_2$**-mediated propylene + N(octenyl)^{n}Pr$_2$ copolymerization does not further enhance *rrrr* (76.6%, Table 2, entry 2) vs. propylene polymerization in the presence of N^{n}Pr$_3$ (76.4, Table 4, entries 2). Interestingly, introducing 1-octene doesn't change syndiotacticity in the presence of (73.9 mol%, Table 4, entry 4). Thus, N^{n}Pr$_3$ and AO promote similar syndiotacticity (Figure 3b).

Table 4. Tertiary amine effects on **FluZrMe$_2$**-catalyzed propylene homo-polymerization and copolymerization with 1-octene[a]

entry	monomer	t, min	yield, g	act. [b]	incorp, mol%[c]	*rrrr*, %[d]	Mn, NMR[e]
1	P	2	1.76	5283	-	66.3	80
2	P[f]	10	1.49	895	-	76.4	65
3	P + O	10	1.90	1142	0.4	58.4	46
4	P + O[f]	10	0.51	305	0.9	73.9	59

[a] Conditions: 10 μmol **FluZrMe$_2$**, 10 μmol **BT**, 1 atm propylene (P), 1-octene (O), 0.012 M, 20 mL toluene, 25 °C; each entry performed in duplicate. [b] kg/(mol ·h·atm). [c] mol% incorporation by ^{1}H NMR.[17] [d] By ^{13}C NMR, analyzed by literature procedure.[8d, 10a] [e] kg/mol, see SI. [f] added N^{n}Pr$_3$, 0.012 M.

Stereoselection mechanisms for propylene polymerization are well-established.[1e, 29b, 30] For C_2-symmetric catalysts such as **SBIZrMe$_2$**, enantiomorphic site control promotes isotacticity; for C_s-symmetric catalysts such as **FluZrMe$_2$**, regularly alternating propylene insertions at enantiotopic sites via chain-end control promote syndiotacticity (Figures 4a,b). Regarding the present amine effects, in addition to reducing polymerization activity, reasonably attributable to AO R$_3$N→Zr$^+$ coordination,[17, 31] the AO presence significantly enhances both isotacticity and syndio-tacticity (Figure 3), and in a way that is relatively insensitive to added 1-octene, and whether the amine is exogeneous or tethered to an α-olefin. Indeed, the above control experiments argue that amine base coordination, either N^{n}Pr$_3$ or AO, to the acidic Zr$^+$ center enhances both isotactic and syndiotactic stereo-selection, regardless of the exact stereocontrol mechanism.[1e, 29b] Regarding the processes in Figure 4, it is known that in both scenarios stereoerrors can be suppressed/enhanced by the interplay of sterically incumbered substituents,[21, 32] donor solvents,[20a, 28] basic R$_2$Al-H species,[30a] and/or tightly ion-paired counteranions with basic groups,[20c, 28]) which interact with the electrophilic catalytic center so as to enhance/disrupt the chain-swinging-olefin insertion synchrony and switch on diverse alternative enchainment pathways. [20a, 21 28, 31, 23] Here the added polar comonomer amino-olefins fill such a role most effectively.

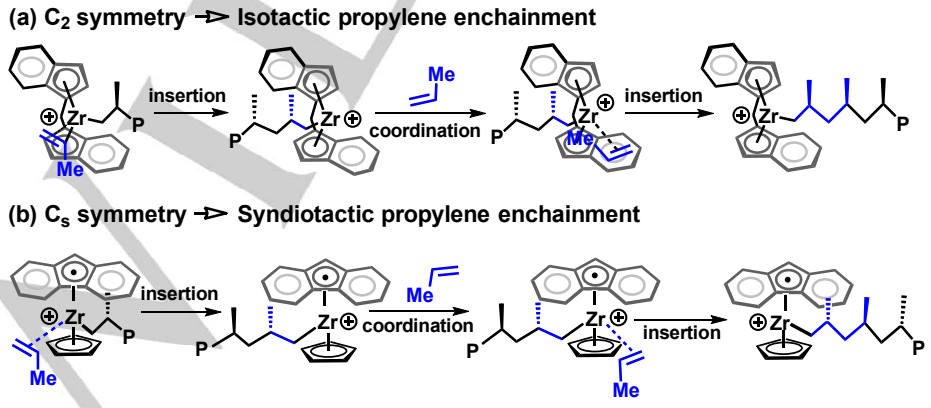

Figure 4. Mechanisms of (**a**) isotactic propylene enchainment by C_2-symmetric **SBIZrMe$_2$** + **BT**; (**b**) syndiotactic propylene enchainment by C_s-symmetric **FluZrMe$_2$** + **BT**.

In summary, these results present new and efficient d^0 group 4 catalyst-mediated direct, masking reagent-free isotactic and syndiotactic PP + AO polar comonomer copolymerization systems, which exhibit several intriguing trends: *i*. Significant amounts of AO polar comonomer are enchained with substantial activities in the absence of masking reagents; *ii*. Substantial tacticities (up to 91.9% *mmmm* and 80.8% *rrrr*, respectively) are achieved, frequently exceeding those of the corresponding homopolymerizations; *iii*. AO incorporation levels increase but are ultimately suppressed at higher [AO]; *iv*. AO deactivation is more severe for the **FluZrMe$_2$**-derived catalysts than for the **SBIZrMe$_2$**-derived ones. Detailed mechanistic studies are underway.

Acknowledgements

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Keywords: propylene polymerization • copolymerization • polar monomer • organo-zirconium catalyst

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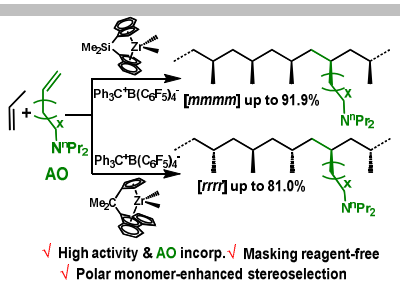

*Minglu Huang, Jiazhen Chen, Binghao Wang, Wei Huang, Haibo Chen, Yanshan Gao, * and Tobin J. Marks **

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Polar Isotactic and Syndiotactic Polypropylenes via Organo-zirconium-Catalyzed Masking-Reagent-Free Propylene + Amino-Olefin Copolymerization