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Metallocene/Borate-Catalyzed Polymerization of Amino-Functionalized α-Olefins

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ABSTRACT: Cationic metallocene/borate catalysts, generated from zirconocene dimethyl compounds, L_nZrMe_2, and anilinium borate, $[HNMe_2Ph]^+[B(C_6F_5)_4]^-$, were used to polymerize 5-amino-1-pentenes and one 4-amino-1-butene with dimethyl, diethyl, diisopropyl, or diphenyl substitution patterns on nitrogen. The monomer 5-(*N*,*N*-diisopropylamino)-1-pentene showed the highest activity with $Cp^*_2ZrMe_2$/borate and was used for all further investigations. The catalytic system $Cp^*_2ZrMe_2$/borate was 4 times more active than the corresponding methylaluminoxane-based system and 180 times more active than the heterogeneous system, $TiCl_3/Al(i\text{-}Bu)_3$. 1-Hexene and 5-(*N*,*N*-diisopropylamino)-1-pentene were polymerized with $Cp^*_2ZrMe_2$ and *rac*-ethylenebis(tetrahydroindenyl) zirconium dimethyl, *rac*-EB(THI)-$ZrMe_2$. Polymerization of both monomers with $Cp^*_2ZrMe_2$ displayed similar activities. Hexene polymerizations with *rac*-EB(THI)$ZrMe_2$ were 30 times more active than those with aminopentene. 5-(*N*,*N*-Diisopropylamino)-1-pentene polymerizations gave rise to isotactic poly(aminopentene) with C_2 symmetric catalysts, syndiotactic polymer with a C_s symmetric catalyst, and atactic polymer with achiral catalyst precursors.

Introduction

Functionalized polyolefins are a class of polymers which have new properties due to the presence of functional polar groups attached to the backbone but also maintain, to a large extent, the original properties of the polyolefins.[1] Functionalization can, for example, result in improved adhesion between polar and unpolar phases and thus better mechanical characteristics of fibrous or laminate reinforcements and anticorrosive coatings. Polymers bearing polar groups can function as materials with a low permeability to gases (oxygen, steam) which are demanded in the food and chemical packing sector. Functionalized polyolefins can also serve as compatibilizing agents in polymer alloys. Attaching antioxidants to polymer chains increases the lifetime of polymer articles because this avoids the physical loss of admixed stabilizers by migration.[2,3]

There are, in principle, two different ways to obtain functionalized polyolefins: chemical modification or free-radical graft polymerization of preformed polyolefins and block polymerizations and copolymerizations of olefins with suitable polar monomers.[1] The advantage of the second approach is direct access to the desired polymer under mild and controlled conditions. Promising catalysts containing group 8 transition metals have recently been described by Brookhart et al.[4] Copolymerization of ethylene and propylene with alkyl acrylates using palladium(II) catalysts gave high molar mass copolymers. Yasuda described organolanthanide-(III)-initiated block copolymerizations of ethylene with alkyl methacrylates and lactones.[5,6] Although Ziegler−Natta catalysts are known for their intolerance to Lewis bases due to their highly oxophilic nature,[7−16] zirconocene/methylaluminoxane (MAO) catalysts were successful in copolymerizing ethylene and propylene with 1-hydroxy-10-undecene,[17,18] 1-chloro-10-undecene,[19] *N*,*N*-bis(trimethylsilyl)-1-amino-10-undecene,[20] and an *o*-heptenylphenol derivative.[3] However, the interaction between MAO and polar Lewis basic monomers is unclear, and to some extent, the polymerization activity rose with an increasing MAO concentration. Copolymerization of α-olefins and Lewis acidic borane monomers via Ziegler−Natta catalysis is an approach extensively investigated by Chung and co-workers.[21−25] The borane groups in the copolymer are versatile synthetic intermediates, which can be transformed to a variety of functionalities in a post polymerization step.[25]

The development of cationic, group 4 metallocene catalysts made possible the polymerization of olefins in the absence of alkylaluminum cocatalysts in solvents

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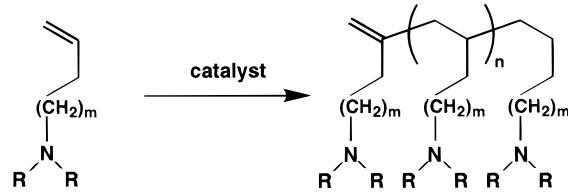
Scheme 1. Homopolymerization of Amino Olefins



R = Me, Et, ^{i}Pr, Ph; m = 1, 2

such as anisole, *N*,*N*-dimethylaniline, and chlorobenzene.[26,27] This prompted our study of the homopolymerization of α-olefins containing silyl-protected alcohols and tertiary amines.[28] In a continuation of our efforts to investigate the scope of homopolymerizations with cationic metallocene catalysts, we discuss in the present paper the effect of different amine structures and catalyst/cocatalyst systems on polymerization activity. The influence of catalyst symmetries on the stereoselectivity of 5-(*N*,*N*-diisopropylamino)-1-pentene homopolymerizations will also be described.

Results

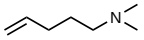
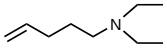
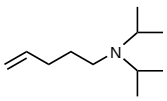
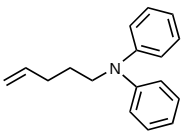
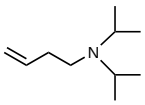
Five different aminoolefins were synthesized and used as monomers (Table 1 and Scheme 1). These monomers included substituted 5-amino-1-pentenes and one 4-amino-1-butene with dimethyl, diethyl, diisopropyl, or diphenyl substitution patterns on nitrogen. Bis(pentamethylcyclopentadienyl) zirconium(IV) dimethyl, $Cp^*_2ZrMe_2$, was reacted with *N*,*N*-dimethylanilinium tetrakis(pentafluorophenyl)borate, $[HNMe_2Ph]^+[B(C_6F_5)_4]^-$, to generate the active catalyst $[Cp^*_2ZrMe]^+[B(C_6F_5)_4]^-$. As revealed in Table 1, only low molecular weight oils were produced with this catalyst system under these conditions. The conversion of monomers were determined by gas chromatography (GC) after the indicated polymerization time. Progression from dimethyl- to diethyl- to diisopropyl-substituted 5-amino-1-pentenes yielded an increasing activity. Diphenyl substitution or shortening of the methylene spacer length by one carbon [4-(*N*,*N*-diisopropylamino)-1-butene] caused a decrease in activity. 5-(*N*,*N*-Diisopropylamino)-1-pentene gave the highest polymerization activity and was therefore used for all further investigations.

Three different systems were investigated to compare catalyst effectiveness for the polymerization of 5-(*N*,*N*-diisopropylamino)-1-pentene (Table 2). The heterogeneous catalyst $TiCl_3/Al(i\text{-}Bu)_3$ produced very high molecular weight polymers but exhibited low activity. Activities up to 40 times higher were observed for the MAO-based homogeneous catalysts $Cp^*_2ZrCl_2$ and $Cp^*_2ZrMe_2$. The most active catalyst investigated was a homogeneous system generated from $Cp^*_2ZrMe_2$ with the borate cocatalyst $[HNMe_2Ph]^+[B(C_6F_5)_4]^-$.

An improved and standardized polymerization method was chosen (method B) to determine the maximum velocity of monomer conversion. The zirconocenes $Cp^*_2ZrMe_2$ and *rac*-ethylenebis(4,5,6,7-tetrahydroindenyl)zirconium(IV) dimethyl, *rac*-EB(THI)$ZrMe_2$, were activated with the borate cocatalyst $[HNMe_2Ph]^+[B(C_6F_5)_4]^-$ to polymerize 5-(*N*,*N*-diisopropylamino)-1-pentene (Table 3). 1-Hexene was polymerized with the same catalysts under the same conditions for comparison. As shown in Table 3, aminopentene polymerizations with $Cp^*_2ZrMe_2$ and *rac*-EB(THI)$ZrMe_2$ yielded similar activities; hexene polymerizations with $Cp^*_2ZrMe_2$ gave results of the same magnitude. In contrast, monomer conversion was 30 times higher for hexene polymerization with *rac*-EB(THI)$ZrMe_2$.

Polymerizations of 5-(*N*,*N*-diisopropylamino)-1-pentene with six different dimethylzirconocenes and one isospecific heterogeneous Ziegler−Natta catalyst system, $TiCl_3/Al(i\text{-}Bu)_3$, were investigated to study how the amine functionality might influence the stereospecificity (Table 4). For reference, the results of a series of 1-hexene polymerizations are included in this table. All catalysts, except the heterogeneous system, were activated with the borate cocatalyst. The ^{13}C NMR chemical shifts of poly(1-hexene) have been identified through the literature.[29,30] Figure 1 contains the full ^{13}C NMR spectrum of isotactic poly[5-(*N*,*N*-diisopropylamino)-1-pentene] from *rac*-ethylenebis(indenyl)zirconium dimethyl, *rac*-EBI$ZrMe_2$, whose chemical shifts have been identified through the use of model compounds [29] and a ^{13}C NMR with DEPT pulse sequence. Figure 2 con-

Table 1. Amine Monomers Polymerized with the $Cp^*_2ZrMe_2$/Borate System[a]

monomer	[catalyst] (mM)	[monomer] (M)	conversion[b](%) [time (min)]	activity[c] (h·c[M])$^{-1}$	M_n[d]
	9.8	1.9	8.5 (60)	9	NA
	9.7	1.7	75.2 (30)	155	920
	3.2	3.0	99.0 (30)	619	1278
	10.9	0.5	90.7 (45)	111	826
	7.1	2.1	71.3 (40)	151	3046

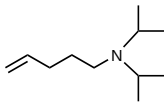
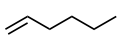
[a] Conditions: 6-mL toluene solutions, $T = 22$ °C, N_2 atmosphere in a drybox. [b] Percent conversion of monomer, determined by GC after indicated time. [c] Activity in amount of monomer consumed per amount of catalyst, concentration of monomer, and hour. These numbers are comparable if we assume that activities are linear in catalyst and also monomer concentrations under the chosen conditions. [d] Determined from ^1H NMR vinylidene end group analysis.

Table 2. Comparison of Ziegler−Natta Initiators for the Polymerization of 5-(*N*,*N*-Diisopropylamino)-1-pentene[a]

catalyst + cocatalyst (ratio: cocat/cat)	[catalyst] (mM)	[monomer] (M)	conversion[b] (%) [time (h)]	activity[c] (h·c[M])$^{-1}$
$TiCl_3$ + Al(*i*-Bu)$_3$[d] (3.7)	72.3	0.83	89 (3.5)	3.5
$Cp^*_2ZrCl_2$ + MAO[e] (92)	4.6	0.83	13 (6)	4.7
$Cp^*_2ZrMe_2$ + MAO[e] (664)	0.76	0.84	12 (1)	152
$Cp^*_2ZrMe_2$ + MAO[e] (89)	4.6	0.83	72 (1)	157
$Cp^*_2ZrMe_2$ + MAO[e] (9)	4.4	0.85	5 (6)	1.9
$Cp^*_2ZrMe_2$ + $[HNMe_2Ph]^+[B(C_6F_5)_4]^-$ [e] (1)	3.2	3.0	99 (0.5)	619

[a] The average M_n of polymers produced with $Cp^*_2ZrX_2$ was 1016, determined from ^{1}H NMR vinylidene end group analysis; the ^{1}H NMR spectrum of the polymer produced with the heterogeneous catalyst showed no end group signals. [b] Percent conversion of monomer, determined by GC after indicated time. [c] Activity in amount of monomer consumed per amount of catalyst, concentration of monomer and hour. [d] Polymerization at 60 °C in benzene.[43] [e] Polymerization at 22 °C in toluene.

Table 3. Maximum Velocity and Activity of 5-(*N*,*N*-Diisopropylamino)-1-pentene and 1-Hexene Polymerizations[a]

monomer	catalyst	maximum velocity ($mol_{monomer}$/L·s)	activity[b] (h·c[M])$^{-1}$	M_n[c]
	$Cp^*_2ZrMe_2$	3.96×10^{-5}	569	914
	rac-EB(THI)$ZrMe_2$	3.87×10^{-5}	546	8500
	$Cp^*_2ZrMe_2$	3.80×10^{-5}	520	412
	rac-EB(THI)$ZrMe_2$	1.16×10^{-3}	15570	1672

[a] Conditions: c(Zr) = 0.5−0.53 mmol/L, ratio [Zr]:[borate] = 1:1.07 (±0.05), c(monomer)$_{initial}$ = 0.5 mol/L, T = 22.5 °C, toluene solutions, calculation of velocity and activity: Experimental Section (polymerization method B). [b] Activity = mol of monomer/mol of Zr·c[monomer]·h. [c] Determined from ^{1}H NMR vinylidene end-group analysis.

Table 4. Polymer Data Obtained from Polymerizations with Catalysts of Different Symmetries[a]

5-(*N*,*N*-Diisopropylamino)-1-pentene Polymerization

metallocene[b]	M_n[c]	$[\eta]_{inh}$[d] (dL/g)	mmm[e] (%)	rrr[e] (%)	T_m[f] (°C) [H_{fus}[f] (J/g)]
i-Pr(*tert*-BuCp)-(Flu)$ZrMe_2$	>14 000	4.548	99.1		109 (11.2)
rac-EBI$ZrMe_2$	>14 000	0.286	96.1		115 (12.4)
rac-EB(THI)$ZrMe_2$	9 590		94.1		85 (1.2)
$TiCl_3$/Al(*i*-Bu)$_3$ (1:3.7)[g]	>14 000	24.74	76.3	9.7	115 (1.4)
Ind_2ZrMe_2	8 600		2.0	3.8	
i-Pr(Cp)(Flu)$ZrMe_2$	9 670		1.9	86.0	110 (0.8)

1-Hexene Polymerization

metallocene[b]	M_n[c]	mmmm[i] (%)	rrrr[i] (%)
rac-EBI$ZrMe_2$	5 600	85.1	
$TiCl_3$/Al(*i*-Bu)$_3$ (1:3.9)	83 000[h]	64.3	2.4
Ind_2ZrMe_2	2 710	14.7	6.3
i-Pr(Cp)(Flu)$ZrMe_2$	3 060	3.8	68.3

[a] Conditions: c(monomer) = 1.9−2.5 M, c(catalyst) = 3−4 mM, [Zr]:[borate] = 1:1, toluene, T(polym.) = 22 °C. [b] *i*-Pr(*tert*-BuCp)-(Flu)$ZrMe_2$ = isopropyl(3-*tert*-butylcyclopentadienyl)(1-fluorenyl), EBI = ethylene-1,2-bis(1-indenyl), EB(THI) = ethylene-1,2-bis(4,5,6,7-tetrahydro-1-indenyl), Ind = indenyl, Cp* = pentamethylcyclopentadienyl, *i*-Pr(Cp)(Flu)$ZrMe_2$ = isopropyl(cyclopentadienyl)(1-fluorenyl). [c] M_n from ^{1}H NMR vinylidene end-group analysis. [d] Inherent viscosity, $[\eta]_{inh}$, determined in toluene at 50 °C. [e] Data reported are for the C_1 carbon at tetrad resolution. [f] Data are peak melting transitions for the second heating cycle. [g] Data for acetone-insoluble fraction. [h] M_n was determined by GPC in 1,2,4-trichlorobenzene (PDI = 7.5), PDI's were between 2.2 and 2.8 for homogeneous catalyst systems. [i] Tacticity from ^{13}C NMR spectra at pentad resolution (C_3 carbon).

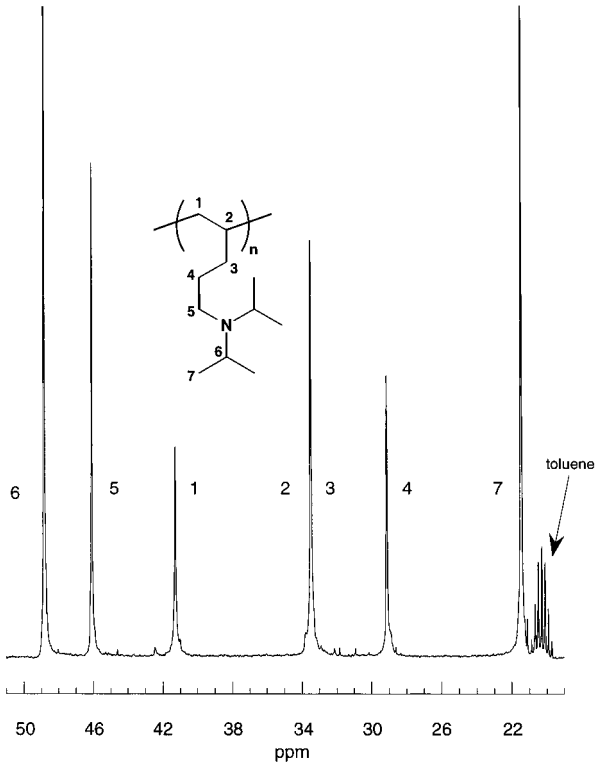


Figure 1. ^{13}C NMR spectrum of isotactic poly[5-(*N*,*N*-diisopropylamino)-1-pentene] from *rac*-EBI$ZrMe_2$/borate.

tains the ^{13}C NMR spectra of poly[5-(*N*,*N*-diisopropylamino)-1-pentene] synthesized with aspecific bis(indenyl)-zirconium dimethyl, Ind_2ZrMe_2, syndiospecific isopropyl-(cyclopentadienyl)(1-fluorenyl)zirconium dimethyl, *i*-Pr-(Cp)(Flu)$ZrMe_2$, and *rac*-EBI$ZrMe_2$ catalyst precursors. Due to the overlap of the peaks associated with carbons C_2 and C_3, the more sensitive carbon, C_3, cannot be used to probe the stereoregularity of the polymers. However, carbon C_1 is moderately sensitive to the microstructure of the polymer and was used to interpret the stereospecificity of the polymerization. Figure 2 indicates that the achiral catalyst precursor, Ind_2ZrMe_2, produced an atactic poly[5-(*N*,*N*-diisopropylamino)-1-pentene], the chiral, C_2 symmetric catalyst precursor, *rac*-EBI$ZrMe_2$, produced a highly isotactic polyamine, and the C_s symmetric catalyst precursor, *i*-Pr(Cp)(Flu)$ZrMe_2$, produced a highly syndiotactic polyamine.

Melting transitions of the various crystalline polyamine materials were measured by differential scanning calorimetry (DSC) (Table 4). The amorphous polymers from the aspecific catalyst precursors displayed no melting transitions. The isotactic poly[5-(*N*,*N*-diisopropylamino)-1-pentenes] display peak melting points from

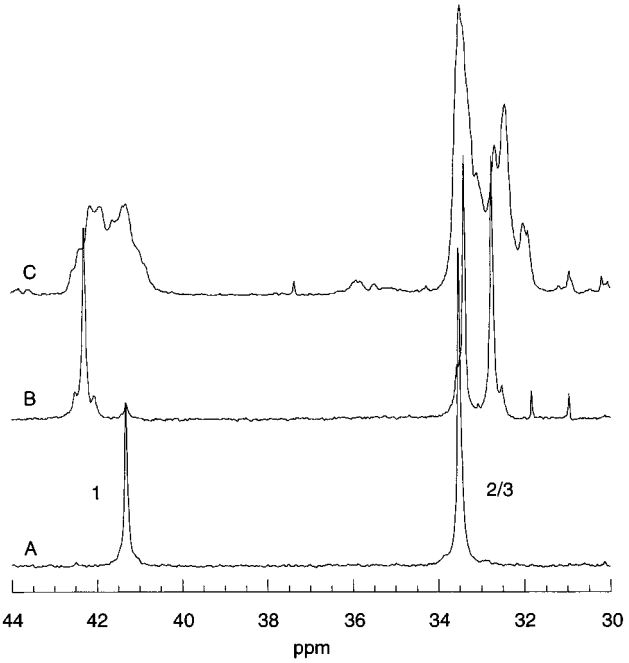


Figure 2. ^{13}C NMR spectra of poly[5-(*N*,*N*-diisopropylamino)-1-pentene]: (A) isotactic from *rac*-EBIZrMe$_2$/borate, (B) syndiotactic from *i*-Pr(Cp)(Flu)ZrMe$_2$/borate, and (C) atactic from Ind$_2$ZrMe$_2$/borate.

109 to 115 °C. Poly[5-(*N*,*N*-diisopropylamino)-1-pentene] produced with *rac*-EBIZrMe$_2$ displayed the highest ΔH_{fus} (12.4 J/g). This was followed closely by material produced with *i*-Pr(*tert*-BuCp)(Flu)ZrMe$_2$ (ΔH_{fus} = 11.2 J/g). The ΔH_{fus} for the polyamine synthesized by *rac*-EB(THI)ZrMe$_2$ was much lower (1.2 J/g). The melting points of these isotactic polymers follow a similar pattern. Isotactic material produced with the heterogeneous catalyst system did not follow the trend established for the homogeneous catalyst systems. It displayed a melting point similar to that observed for *rac*-EBIZrMe$_2$ but a smaller ΔH_{fus}. The syndiotactic polyamine displayed a melting point 5 °C lower than that of the most isotactic polymer. However, although the syndiotactic polyamine has a high relative degree of stereoregularity, it has the lowest observed ΔH_{fus} and is therefore the least crystalline of the materials which display a melting transition.

Discussion

The polymerization of functionalized monomers represents a significant challenge in Ziegler−Natta catalysis. The development of cationic metallocene systems affords the opportunity to combine the unique stereoselectivities and other advantages observed with defined metallocene single-site catalysts with the incorporation of functional groups into polyolefins. Our previous research with a number of O-, N-, and P-functionalized monomers[28,31,32] indicated that the amine family of substituted α-olefins was the most compatible for polymerization with cationic group 4 metallocenes. Therefore, a series of tertiary amino functionalized α-olefins was synthesized to investigate the scope and limitations of this catalyst system (Scheme 1).

The polymerization activity of functionalized monomers is dependent on a number of factors such as the functionality itself, the steric nature of the functional group, metallocene, and cocatalyst, and the length of the methylene spacer between the double bond and the functional group. Electronic and steric effects must be taken into account when discussing the basicity of a functional group. A typical way to describe the strength of bases is to compare them in terms of the dissociation constants, K_a, of the conjugate acids.[33] Because the pK_a for an amine cation slightly increases on changing the substituents from methyl to ethyl to isopropyl, we expected a decrease in activity due to an increase of the base strength. However, the isopropyl-substituted aminopentene was the monomer which showed the highest polymerization activity by far (Table 1) and was 70 times more productive than (dimethylamino)pentene. These results suggest that steric effects are critical in preventing the Lewis basic amine from binding to the metal in preference to the olefin. Phenyl substitution on nitrogen gives smaller pK_a values, indicating weaker basicity. The electronic and also the steric effects of phenyl groups led us to expect an even higher polymerization activity than that for the isopropyl-substituted aminopentene. Instead, the conversion of this monomer was 6-fold smaller. It is known that the phenyl groups of tetraphenylborate[34−38] or of attached benzyl ligands[39−42] can coordinate to the cationic d^0 metal center and compete with the olefin substrate for the coordination site. Thus, coordination of the aminophenyls might account for the lower productivity for this monomer.

The removal of one methylene spacer unit led to a 4-fold decrease of the activity when comparing (diisopropylamino)butene with its aminopentene congener. The lower activity of the substituted butene might be rationalized on the basis of the higher stability of a six-membered rather than seven-membered pseudo-metallacycle of the last inserted monomer unit. The data seem to support an intramolecular inhibition between the amine and the active metal center.

We investigated three different catalytic systems to compare their effectiveness for the polymerization of diisopropyl-substituted aminopentene (Table 2). Consistent with previous studies by Giannini and co-workers,[43] we found that polymerization with TiCl$_3$/Al(*i*-Bu)$_3$ produced very high molecular weight polymers but with extremely low activity. We observed an activity of 3.5, which is only slightly higher than the number reported by Giannini with a TiCl$_3$/AlCl$_3$/AlR$_2$Cl catalyst (activity = 0.9 mol of monomer/mol of Zr·h·c[monomer]). We observed up to 40 times higher activities for a MAO-based homogeneous catalyst system. It is generally accepted that, for each catalyst precursor utilized, a different amount of MAO is required to generate cations of all of the metal centers in solution (often >1000 Al:Zr is required).[44−47] The lower productivities for polymerizations with zirconocene dichloride relative to the dimethyl precursors suggest that at an [Al]:[Zr] ratio of 90 the dimethyl compound is more efficiently converted to the active catalyst, resulting in the highest activity with MAO as cocatalyst. The protonolysis reaction of dimethylzirconocenes with the aluminum-free initiator, anilinium borate, produced the most active catalyst system we investigated. This homogeneous system does not require a large excess of a Lewis acidic cocatalyst to ensure optimal catalytic activity. The anionic borate is unlikely to coordinate to the Lewis basic functional monomers; such interactions could be the reason for the lower activity of MAO-based systems.

Cyclopentadienyl ligand modification has an important effect on the polymerization activity of α-olefins. We chose two zirconocenes, the sterically hindered bis(pentamethyl)cyclopentadienyl complex and the ethylene-bridged bis(tetrahydroindenyl) complex, to investigate aminopentene versus hexene polymerizations. The tetrahydroindenyl ligand is unsubstituted in one of its α- and β-positions of the cyclopentadienyl ring. This allows α-olefins easier access to the cationic zirconium center. Unfortunately, also Lewis basic functionalities can more easily coordinate and inhibit the polymerization. We observed almost identical numbers of monomer conversions and oligomers with an average number of 5 monomer units for hexene and aminopentene polymerizations using the pentamethylcyclopentadienyl (Cp*) substituted complex. This means the polymerization activity is dominated by the accessibility of the coordination site of the metal and not decreased by inhibitive interactions of diisopropyl-substituted amino groups with the metal. The less sterically constrained ethylenebis(tetrahydroindenyl)zirconocene displayed a 30 times higher activity for hexene than for aminopentene. It produced polymers with an average number of 20 monomer units for polyhexene and 50 for the polyamine. The decrease in activity of the aminopentene polymerization with this catalyst precursor could arise from either an intermolecular inhibitive interaction or an intramolecular inhibition of the last inserted monomer in a "back-biting" manner.

It has been exhaustively shown that, through ligand modifications, one can direct which enantioface of a prochiral olefin will coordinate during homogeneous Ziegler−Natta catalysis. Such control allows the synthesis of a complete range of microstructures simply by manipulating the ligands of metallocenes.[44] Comparing the results of the analysis of NMR spectra from hexene and (diisopropylamino)pentene polymerizations with catalysts of different symmetries showed us that amine interaction does not affect the stereoselectivity of these reactions (Table 4). We calculated a higher degree of iso- and syndiotacticity for poly(aminopentenes) compared to polyhexenes. This might be partially explained by the selection of different carbon atoms for NMR spectral analysis and the lower resolution of tetrads compared to pentads. Aside from this difference, the data indicate that achiral catalyst precursors produce atactic poly[(diisopropylamino)pentene], chiral C_2 and C_1 symmetric precursors produce isotactic polyamine, and C_s symmetric catalyst precursors give syndiotactic polyamine. It is interesting that the C_1 symmetric zirconocene *i*-Pr(*tert*-BuCp)(Flu)$ZrMe_2$ generated a polymer with the highest relative percentage of mmm tetrads. The heterogeneous polymerization of (diisopropylamino)pentene, with $TiCl_3$/Al(*i*-Bu)$_3$, produces a stereoregular polymer which can be further fractionate with refluxing acetone. The acetone-soluble fraction (20% of raw polymer) is a low molecular weight, amorphous material which is minimally isotactic. The acetone-insoluble fraction (80% of raw polymer) is a high molecular weight, crystalline material which is stereoregular. However, much like polyhexene produced with this heterogeneous catalyst system, the acetone-insoluble poly(aminopentene) has the lowest mmm percentage of any isospecific catalyst system investigated.

Analysis of the melting transitions of poly(aminopentenes) indicates that ΔH_{fus} and the melting temperature are relatively insensitive to molecular weight and to some extent of the degree of isotacticity. The melting points of the polyamines are in the range of 109 − 115 °C for both the isotactic and syndiotactic microstructures. Comparing the ^{13}C NMR spectra of poly(aminopentenes) produced with metallocenes having EB(THI), EBI, and *i*-Pr(*tert*-BuCp)(Flu) ligands, we detected in addition to the main peaks a number of further much smaller ^{13}C NMR signals, particularly for *rac*-EB(THI)-$ZrMe_2$ and *rac*-*i*-Pr(*tert*-BuCp)(Flu)$ZrMe_2$. These signals may be indicative of regioirregularities in the polymers, which might explain the lower melting points. Because viscosity measurements indicated a higher polymer molecular weight using the *rac*-*i*-Pr(*tert*-BuCp)-(Flu)$ZrMe_2$ catalyst compared to the *rac*-EBI$ZrMe_2$ system, the different molecular weights would not appear to account for the lower melting point of polymers obtained with the *i*-Pr(*tert*-BuCp)(Flu)$ZrMe_2$-derived catalyst. The observation of lower melting points for syndiotactic polymers is well documented for other α-olefins (except styrene).[48]

Conclusion

We have shown that cationic metallocene catalysts are capable of polymerizing olefins containing tertiary amines to a range of polymer microstructures. We have also demonstrated the merit of homogeneous Ziegler−Natta catalysts compared to one particular heterogeneous system for the polymerization of functionalized α-olefins. The activities of the homogeneous catalyst systems appear to be sensitive to the nature of the ligands at the transition metal and the substitution pattern at the amine. Optimum activities were achieved with the diisopropyl-substituted amine with an olefin tether length of three carbons. While the polymerization activities are influenced by the functional group, the stereospecificity of these catalyst systems is insensitive to the presence of the amine functionality. The high stereospecificity of these homogeneous Ziegler−Natta catalysts, coupled with the ability to polymerize functionalized monomers, should provide access to a range of new materials with novel physical and chemical properties.

Experimental Section

General Considerations. All reactions were carried out under an inert atmosphere of argon using standard Schlenk techniques or under nitrogen in a glovebox. Toluene was purified by passing through a column of activated alumina to remove impurities (purchased from Kaiser; type A9 alumina, 20 mesh; activated by heating to 250 °C under flowing nitrogen) followed by a column of Q5 reactant to remove oxygen (purchased from Engelhard, 13 wt % Cu(I)O on alumina; regenerated by heating to 300 °C under 5% H_2 forming gas). All other solvents were dried under a nitrogen atmosphere and distilled from sodium/benzophenone ketyl (tetrahydrofuran (THF), diethyl ether (Et_2O), benzene), from CaH_2 (methylene chloride, chloroform), or from $LiAlH_4$ (pentane). All solvents were stored in individual "Straus flasks" and degassed via ultrasound and three freeze−pump−thaw cycles prior to each use. Deuterated NMR solvents were used as received or were vacuum-transferred from a sodium/benzophenone ketyl (C_6D_6, toluene-d_8) or CaH_2 ($CDCl_3$, CD_2Cl_2) for organometallic specimens. All monomers utilized were >99% pure and were dried prior to use by vacuum transfer/distillation from CaH_2.

Characterization. Gas chromatography (GC) was performed on a Hewlett-Packard 5890 chromatograph equipped with a SE-30 column (100% dimethylpolysiloxane, 30 m × 0.32 mm × 0.25 μm); monomer conversion was monitored via GC

analysis on timed reaction aliquots utilizing decane as an internal standard. Gel permeation chromatography (GPC) was performed in 1,2,4-trichlorobenzene at 135 °C. Viscosity measurements were performed in toluene on a Schott AVS/G instrument with a Micro-Ubbelohde viscometer at 50 °C. Nuclear magnetic resonance spectroscopy (NMR) was performed on Varian XL-400 and Gemini 200 spectrometers. Data on polymer samples were obtained at 75 °C in toluene-d_8. Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer DSC/TGA 7 thermal analyzer. DSC data were collected in a nitrogen atmosphere at 10 °C/min over the appropriate temperature ranges. Elemental analyses were performed by E&R Microanalytical Laboratory, Inc., Corona, NY.

Monomer Synthesis. 5-(*N*,*N*-Dimethylamino)-1-pentene. From a modified literature procedure,[43] NaOH (123 g, 3.075 mol) was carefully dissolved in 100 mL of deionized water and placed in a 500-mL separatory funnel. 2-(Dimethylamino)ethyl chloride hydrochloride salt (86 g, 0.597 mol) was dissolved in a minimum amount of deionized water (50 mL) and added to the separatory funnel. A yellow organic layer formed immediately and was separated. The aqueous layer was extracted three times with 100 mL each of Et_2O and then discarded. The Et_2O washings and the yellow organic layer were combined and dried with a minimum amount of anhydrous magnesium sulfate overnight. Distillation from CaH_2 yielded the 2-(dimethylamino)ethyl chloride (23.56 g, 37% yield) as a clear, pungent, and highly toxic liquid. The amine was then placed in a three-neck 1000-mL flask equipped with an addition funnel, a reflux condenser, a vacuum/inert gas adapter, and a mechanical stirring apparatus and under argon was diluted with 150 mL of dry THF. Under constant stirring allylmagnesium chloride was added as a 2.0 M solution in THF (115 mL, 0.23 mol, 5% excess) at 0 °C. The addition of the Grignard reagent was complete after 1 h, at which time the flask was allowed to warm to room temperature and stir overnight. The next morning, the green/black solution was heated with constant stirring at reflux. After 2 h, a white precipitate began to form (magnesium salts), and after 12 h, the reaction was cooled to room temperature. The excess Grignard reagent was carefully quenched with water. When the quenching reaction had subsided, more water was added to bring the total amount added to 500 mL. The organic layer was separated, and the water layer was extracted with 100 mL of THF/Et_2O three times. The combined yellow organics were dried over anhydrous $MgSO_4$ and distilled from CaH_2. This yielded 16 g (25% yield) of a pungent, clear liquid, which was characterized by GC and ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.8 (m, 1H), 4.9 (m, 2H), 2.35 (t, 2H), 2.2 (s, 6H), 2.0 (m, 2H), 1.45 (m, 2H).

5-(*N*,*N*-Diethylamino)-1-pentene. From a modified literature procedure,[43] KOH (90.6 g, 1.615 mol) was carefully dissolved in 100 mL of deionized water and placed in a 500-mL separatory funnel. 2-(Diethylamino)ethyl chloride hydrochloride salt (63.127 g, 0.3668 mol) was dissolved in a minimum amount of deionized water (50 mL) and added to the separatory funnel. Workup of the immediately formed, slightly yellow organic layer was done as in the case of 5-(*N*,*N*-dimethylamino)-1-pentene. Distillation from CaH_2 yielded the 2-(diethylamino)-ethylchloride (40.92 g, 82% yield) as a clear, pungent, and highly toxic liquid. Allylmagnesium bromide was then added as a 1.0 M solution in Et_2O (305 mL, 0.305 mol, 1% excess) to a three-neck 2000-mL flask equipped with an addition funnel, a reflux condenser, a vacuum/inert gas adapter, and a mechanical stirring apparatus. The amine was added as a solution in 50 mL of Et_2O under constant stirring at 0 °C. Addition of the amine was complete after 1 h, at which time the flask was allowed to warm to room temperature and stir overnight. A gray/white precipitate was formed and worked up without further heating as described above for 5-(*N*,*N*-dimethylamino)-1-pentene. Distillation from CaH_2 yielded 36 g (70% yield) of a pungent, clear liquid, which was characterized by GC and ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.8 (m, 1H), 4.9 (m, 2H), 2.8 (m, 4H), 2.3 (t, 2H), 2.0 (m, 2H), 1.45 (m, 2H), 1.2 (s, 6H).

5-(*N*,*N*-Diisopropylamino)-1-pentene. From a modified literature procedure,[43] KOH (250 g, 4.46 mol) was carefully dissolved in 250 mL of deionized water and placed in a 1000-mL separatory funnel. 2-(Diisopropylamino)ethyl chloride hydrochloride salt (300 g, 1.5 mol) was dissolved in a minimum amount of deionized water (250 mL) and added to the separatory funnel. Workup of the immediately formed, yellow organic layer was as described above for 5-(*N*,*N*-dimethylamino)-1-pentene. Distillation from CaH_2 yielded the 2-diisopropylamino)ethyl chloride (239.5 g, 97.6% yield) as a clear, pungent, and highly toxic liquid. The amine was then placed in a three-neck 3000-mL flask equipped with an addition funnel, a reflux condenser, a vacuum/inert gas adapter, and a mechanical stirring apparatus. A total of 250 mL of dry THF was added under argon. To this solution, with constant stirring, was added the allylmagnesium chloride as a 2.0 M solution in THF (800 mL, 1.6 mol, 9% excess). The addition of the Grignard reagent was complete after 5 h, at which time the flask was allowed to warm to room temperature and stir overnight. The next morning, the turbid solution was heated to reflux. After 12 h the reaction was cooled to room temperature. The excess Grignard reagent was carefully quenched with water. When the quenching reaction had subsided, more water was added to bring the total amount added to 1000 mL. The organic layer was separated, and the water layer was extracted with 100 mL of Et_2O three times. The combined yellow organics were dried over anhydrous $MgSO_4$ and distilled from CaH_2. This yielded 230 g (91% yield) of a pungent, clear liquid, which was characterized by GC, ^{1}H NMR and ^{13}C NMR. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.8 (m, 1H), 4.9 (m, 2H), 2.95 (m, 2H), 2.35 (m, 2H), 2.0 (m, 2H), 1.45 (m, 2H), 0.95 (d, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.05, 114.11, 48.43, 44.78, 31.58, 30.56, 20.65.

5-(*N*,*N*-Diphenylamino)-1-pentene. Diphenylamine (24.9 g, 0.147 mol) was added as a white crystalline solid to a three-neck 1000-mL flask under argon. To the flask was added 250 mL of dry Et_2O and the solution was cooled to −78 °C. One equivalent of *n*-BuLi was added as a 2.5 M solution in hexanes (59 mL, 0.1475 mol) under constant stirring. A white precipitate was formed instantly, and the reaction was allowed to stir for 15 min at −78 °C before warming to room temperature and stirring for 1.5 h. At this point the 5-bromo-1-pentene (22.6 g, 0.152 mol, 3.4% excess) was added, and the resultant yellowish solution was allowed to stir overnight. The reaction was quenched by the addition of 200 mL of water, and the Et_2O layer was separated from the resultant slurry. The water layer was extracted with 100 mL of Et_2O two times. The organic layers were combined and washed two times each with a 5% HCl solution, a 10% NaOH solution, and a saturated NaCl solution. The organics were dried over anhydrous $MgSO_4$ and distilled from CaH_2. To further purify the material, the distilled fraction was placed on a silica column and eluted with an ethyl acetate/hexane (5:95) solution. The isolated material is redistilled from CaH_2 to yield 10 g (30% yield) of a clear, pungent liquid. The material was characterized by GC and ^{1}H NMR. ^{1}H NMR (400 MHz, toluene-d_8): δ 7.1 (m, 4H), 6.95 (m, 4H), 6.85 (m, 2H), 5.65 (m, 1H), 4.94 (m, 2H), 3.4 (t, 2H), 1.87 (m, 2H), 1.61 (m, 2H).

4-(*N*,*N*-Diisopropylamino)-1-butene. See the synthesis of 5-(*N*,*N*-diisopropylamino)-1-pentene. The Grignard reagent utilized for this synthesis was vinylmagnesium bromide, utilized as a 1.0 M solution in THF. This yielded 19.87 g (96.3% yield) of a pungent, clear liquid, which was characterized by GC, ^{1}H NMR and ^{13}C NMR. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.8 (m, 1H), 4.9 (m, 2H), 2.95 (m, 2H), 2.45 (m, 2H), 2.1 (m, 2H), 0.95 (d, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.9, 114, 48.3, 44.5, 36.2, 20.5.

Catalyst Synthesis. Synthesis of Bis(pentamethyl)-cyclopentadienylzirconium(IV) Dimethyl, $Cp^*_2ZrMe_2$. $Cp^*_2ZrCl_2$ was purchased from Strem Chemical and used as received or synthesized from a published procedure.[49] In the drybox, $Cp^*_2ZrCl_2$ (0.852 g, 1.97 mmol) was added to a 100-mL Schlenk tube (equipped with a stir bar and a septum) along with 30 mL of dry toluene. The Schlenk tube was removed from the drybox and placed in a −50 °C bath (*n*-octane/dry

ice) and allowed to stir for 10 min. Two equivalents of MeLi were added as a 1.4 M solution in Et_2O (3.0 mL, 4.2 mmol, 6.6% excess). The resultant off-white solution was allowed to stir at this reduced temperature for 30 min before it was warmed to room temperature and allowed to stir for 3 h. At this point the mixture, a white suspension, was filtered over a medium glass frit packed with Celite to remove the LiCl salt. The filtrate was concentrated to 15 mL and placed in a −15 °C freezer to crystallize overnight. This produced 0.75 g (97% yield) of colorless, needlelike crystals which were pure by ^{1}H NMR. ^{1}H NMR (400 MHz, C_6D_6): δ 1.77 (s, 30H), −0.56 (s, 6H).

Synthesis of Bis(indenyl)zirconium(IV) dimethyl, Ind_2ZrMe_2. From a modified literature procedure,[50] indene (10.95 mL, 93.8 mmol), which was freshly distilled from CaH_2, was combined with 300 mL of dry THF in a three-neck 500-mL flask and cooled to −78 °C. One equivalent of *n*-BuLi was added as a 2.5 M solution in hexanes (37.6 mL, 94 mmol) under constant stirring. The addition of the lithium alkyl was performed over 30 min, and the resultant orange solution was allowed to warm to room temperature and stir for 3 h. Previously, pure $ZrCl_4$ (purchased from Fluka) was added to a 500-mL Schlenk tube in the drybox. The Schlenk tube was removed from the drybox and cooled to −78 °C, and 150 mL of THF were added dropwise over 2 h *(very exothermic reaction).* After addition of the solvent was complete, the flask was warmed to room temperature and allowed to stir overnight. The resultant off-white suspension of $ZrCl_4(THF)_2$ was further cooled to 0 °C, and with rapid stirring the previously prepared lithium salt of indene (a red solution) was added over 15 min. The resultant orange/red mixture was allowed to warm to room temperature and stir for 12 h. The THF was removed under vacuum, and the product was sublimed at 220 °C under vacuum with a dry ice/acetone coldfinger. This produced 9.9 g (54% yield) of a lemon yellow powder which was pure by ^{1}H NMR. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.61 (m, 4H), 7.28 (m, 4H), 6.47 (t, 2H), 6.14 (d, 4H).

The previously synthesized Ind_2ZrCl_2 (1.8 g, 4,59 mmol) was combined with 50 mL of toluene in a 100-mL Schlenk tube in the drybox. The flask, equipped with a septum and a stir bar, was removed from the drybox, cooled to −50 °C, and allowed to stir for 10 min. Two equivalents of MeLi was added as a 1.4 M solution in Et_2O (7.0 mL, 9.8 mmol, 6.7% excess). The resultant yellow solution was allowed to stir at this reduced temperature for 30 min before it was warmed to room temperature and allowed to stir for 3 h. At this point the mixture, a dark suspension, was filtered over a medium glass frit packed with Celite to remove the LiCl salt. The filtrate was concentrated to 15 mL and placed in a −15 °C freezer to crystallize overnight. This produced 0.34 g (21% yield) of off-white/tan, needlelike crystals which were pure by ^{1}H NMR. ^{1}H NMR (400 MHz, C_6D_6): δ 7.21 (m, 4H), 6.89 (m, 4H), 5.79 (d, 3.2 Hz, 4H), 5.61 (t, 3.3 Hz, 2H), −0.78 (s, 6H).

Synthesis of *rac*-Ethylene-1,2-bis(1-indenyl)zirconium-(IV) Dimethyl, *rac*-EBIZrMe$_2$. *rac*-$EBIZrCl_2$ was purchased from Aldrich and used as received or synthesized from a published procedure.[51] In the drybox, *rac*-$EBIZrCl_2$ (2.304 g, 5.506 mmol) was added to a 300-mL Schlenk tube (equipped with a stir bar and a septum). The Schlenk tube was removed from the drybox, 200 mL of dry Et_2O was added, and the flask was placed in a −78 °C bath and allowed to stir for 10 min. Two equivalents of MeLi were added as a 1.4 M solution in Et_2O (8.0 mL, 11.2 mmol, 1.7% excess). The resultant bright yellow solution was allowed to stir at this reduced temperature for 30 min before it was warmed to room temperature and allowed to stir for 3 h. At this point the mixture, a cream/yellow colored solution, was pumped to dryness, redissolved in toluene, and filtered over a medium glass frit packed with Celite to remove the LiCl salt. The filtrate was concentrated to 15 mL and placed in a −15 °C freezer to crystallize overnight. This produced 1.45 g (70% yield) of light lemon/yellow cubic crystals which were pure by ^{1}H NMR. ^{1}H NMR (200 MHz, C_6D_6): δ 7.30 (m, 2H), 7.04 (m, 4H), 6.89 (m, 2H), 6.41 (d, 2H), 5.64 (d, 2H), 2.73 (m, 4H), −0.98 (s, 6H).

Synthesis of *rac*-Ethylene-1,2-bis(4,5,6,7-tetrahydro-1-indenyl) zirconium(IV) Dimethyl, *rac*-EB(THI)ZrMe$_2$. *rac*-$EB(THI)ZrCl_2$ was synthesized from a published procedure.[51] The dimethyl compound was prepared from *rac*-EB-$(THI)ZrCl_2$ (1.058 g, 2.48 mmol) following the method given for *rac*-$EBIZrMe_2$. Addition of MeLi yielded a yellow solution, and stirring at room temperature for 3 h, a white suspension. Crystallization produced 0.81 g (85% yield) of colorless, rectangular crystals which were pure by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.18 (d, 3.1 Hz, 2H), 5.33 (d, 3.1 Hz, 2H), 2.78 (m, 4H), 2.71 (s, 4H), 2.56 (m, 2H), 2.21 (m, 2H), 1.75 (m, 2H + 4H), 1.64 (m, 2H), −0.48 (s, 6H).

Synthesis of Isopropyl(cyclopentadienyl)(1-fluorenyl)-zirconium(IV) Dimethyl, *i*-Pr(Cp)(Flu)ZrMe$_2$. *i*-Pr(Cp)-$(Flu)ZrCl_2$ was synthesized from a published procedure.[52] The dimethyl compound was prepared from *i*-$Pr(Cp)(Flu)ZrCl_2$ (2.7 g, 6.243 mmol) following the method given for *rac*-$EBIZrMe_2$. Instead of MeLi 2 equiv of MeMgCl was added as a 3.0 M solution in THF (4.5 mL, 13.5 mmol, 8.0% excess). The resultant red/orange solution turned yellow after stirring at room temperature for 3 h. Crystallization produced 1.2 g (49% yield) of a yellow powder which was pure by ^{1}H NMR. ^{1}H NMR (400 MHz, C_6D_6): δ 7.80 (d, 2H), 7.39 (d, 2H), 7.32 (t, 2H), 6.97 (t, 2H), 6.07 (t, 2H), 5.26 (t, 2H), 1.74 (s, 6H), −1.13 (s, 6H).

Synthesis of Isopropyl(3-*tert*-butylcyclopentadienyl)-(1-fluorenyl)zirconium(IV) Dimethyl, *i*-Pr(*tert*-BuCp)-(Flu)ZrMe$_2$. *i*-Pr(*tert*-BuCp)$(Flu)ZrCl_2$ was synthesized from literature procedures.[52,53] The dimethyl compound was prepared from *i*-Pr(*tert*-BuCp)$(Flu)ZrCl_2$ (0.9 g, 1.844 mmol) following the method given for *rac*-$EBIZrMe_2$. Addition of MeLi turned the red/orange suspension to golden yellow upon warming. Crystallization produced 0.45 g (55% yield) of an orange powder which was pure by ^{1}H NMR. ^{1}H NMR (200 MHz, toluene-d_8): δ 7.87 (m, 2H), 7.43 (m, 2H), 7.22 (t, 2H), 6.97 (m, 2H), 6.05 (t, 1H), 5.39 (t, 1H), 5.33 (t, 1H), 1.81 (s, 3H), 1.80 (s, 3H), 1.18 (s, 9H), −1.12 (s, 3H), −1.14 (s, 3H).

Cocatalyst Synthesis. Synthesis of $B(C_6F_5)_3$. From a modified literature procedure,[54,55] bromopentafluorobenzene (8.4 g, 34.01 mmol) was added to a 300-mL Schlenk tube equipped with an addition funnel and a stir bar. The starting material was diluted with 75 mL of dry pentane, and the resultant solution was cooled to −78 °C. Over 20 min, *n*-BuLi was added as a 2.5 M solution in hexanes (13.6 mL, 34 mmol). *Caution! $Li(C_6F_5)$ is explosive! Handle with care and do not allow it to warm to room temperature!!* A white solid formed quickly, and the reaction was allowed to stir an additional 10 min before the BCl_3 was added as a 1.0 M solution in hexanes (11.4 mL, 11.4 mmol). The resulting white slurry was allowed to stir for several minutes at −78 °C before it was gradually warmed to room temperature and permitted to stir for an additional 1 h. The resultant off-white slurry was filtered through Celite over a medium frit to remove the lithium salts and was washed several times with dry pentane. The clear liquid was concentrated to 50 mL and placed in a −15 °C freezer to crystallize overnight. The white crystalline powder was further purified by sublimation at 150 °C. This produced 2.41 g of white needle crystals.

Synthesis of $[HNMe_2(C_6H_5)]^+[B(C_6F_5)_4]^-$. Bromopentafluorobenzene (3.79 g, 15.35 mmol) was added to a 300-mL Schlenk tube equipped with an addition funnel and a stir bar. The starting material was diluted with 150 mL of dry pentane, and the resultant solution was cooled to −78 °C. Over 20 min, *n*-BuLi was added as a 2.5 M solution in hexanes (6.2 mL, 15.5 mmol). A white solid formed quickly, and the reaction was allowed to stir an additional 10 min before being added to the $B(C_6F_5)_3$ solution (7.85 g) in 150 mL of dry pentane also at −78 °C. The resultant off-white suspension was allowed to stir for 1.5 h at this depressed temperature, before slowly warming it to room temperature and stirring it for 12 h. The supernatant pentane was decanted from the suspension, and the off-white solid was dried in vacuo. This produced 6 g (57% yield) of $LiB(C_6F_5)_4$ as a slightly off-white powder which was pure by elemental analysis. Anal. Calcd for $C_{24}F_{20}BLi$: C, 42.022; B, 1.58; H, 0. Found: C, 41.76; B, 1.67; H, 0.

The previously synthesized $LiB(C_6F_5)_4$ (4.09 g, 5.96 mmol) was placed in a 500-mL Schlenk tube equipped with a stir bar and a septum and removed from the drybox. $[Me_2HN(C_6H_5)]^+Cl^-$ (0.95 g, 6.03 mmol) was placed in a 50-mL Schlenk tube equipped with a stir bar and a septum and removed from the drybox. The anilinium salt was dissolved in 20 mL of dry CH_2Cl_2, and $Li(C_6F_5)_4$ was suspended in 100 mL of dry CH_2Cl_2. After a few minutes of stirring, the anilinium solution was added to the off-white $Li(C_6F_5)_4$ suspension. A separate white precipitate began to crash out of solution almost immediately, but the reaction was continued for 6 h. At this point, the slurry was filtered through Celite to remove LiCl, and the solution was concentrated to 15 mL and placed in the −15 °C freezer for 2 days. This produced 3.8 g (80% yield) of white cubic crystals which were pure by elemental analysis. Anal. Calcd for $C_{32}H_{12}NF_{20}BLi$: C, 47.97; B, 1.35; N, 1.75; F, 47.42; H, 1.51. Found: C, 48.41; B, 1.48; N, 1.97; F, 47.19; H, 1.77. ^{1}H NMR (400 MHz, C_6D_6): δ 6.71 (m, 3H), 6.16 (m, 2H), 1.55 (s, 6H). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (m, 3H), 7.33 (m, 2H), 3.32 (s, 6H). N*H* could not be detected in both solvents.

General Polymerization Procedure. Polymerizations with Dimethylmetallocene/Borate. Hexene (2 mL, 15.99 mmol) was combined with 4.0 mL of toluene and a few drops of decane (internal standard) in a 25-mL Schlenk tube in the drybox. To the Schlenk tube, which was equipped with a stir bar and a septum was added an appropriate amount of the borate cocatalyst to give approximately a 1:1 molar ratio with the metallocene. After stirring for 5 min, a GC aliquot was taken from the solution and the Schlenk tube was then removed from the drybox and placed in a large water bath at 22 °C. In the drybox, the appropriate amount of the selected catalyst was dissolved in 1.0 mL of toluene and placed in a gastight syringe. The catalyst solution was added to the monomer solution under an argon atmosphere. This brings the polymerization concentrations to 2.46 M in monomer and approximately 3.0 mM in catalyst. Within seconds of catalyst addition, the colorless monomer solution turns an intense golden yellow color. The polymerization was sampled at 10 min and quenched with methanol. The polymerization was stopped after 1 h (to ensure high conversion) by the addition of methanol. The polymer was washed with methanol to remove impurities, extracted with hexane, and dried in vacuo to yield a viscous oil. The percent conversion of monomer to polymer was measured by GC, and the polymer was analyzed by ^{1}H NMR, ^{13}C NMR, and GPC.

All amine monomers were, in general, further purified just prior to use by filtration through activated alumina (neutral alumina, 20 mesh; heated to 250 °C under vacuum) in the drybox. 5-(*N*,*N*-Diisopropylamino)-1-pentene (2 mL, 8.86 mmol), for example, was combined with 3 mL of toluene and a few drops of decane in a 25-mL vial in the drybox. An appropriate amount of the borate cocatalyst was added to the vial, which was equipped with a stir bar, to give approximately a 1:1 molar ratio with the metallocene. After stirring for 5 min, a GC aliquot was removed from the solution. To this stirring solution was added the selected catalyst as a crystalline powder. This brings the polymerization concentrations to 1.86 M in monomer and approximately 4.0 mM in catalyst. Within seconds of catalyst addition, the colorless monomer solution turns an intense golden brown color. The polymerization was sampled at 30 min and quenched with silica gel. It was stopped at high conversion of monomer by the addition of methanol. The polymer was washed with methanol to remove impurities, extracted with hexane, and dried in vacuo. The percent conversion of monomer to polymer was measured by GC, and the polymer was analyzed by ^{1}H and ^{13}C NMR, DSC, viscometry, and elemental analysis. Anal. Calcd for $C_{11}H_{23}N$: C, 78.11; H, 13.61; N, 8.28. Found: C, 78.25; H, 13.73; N, 8.25. Molecular weights were measured by ^{1}H NMR end-group analysis and viscosity as analysis of these polyamines by GPC proved highly irreproducible, possibly due to adventitious protonation of the amine causing changes in the hydrodynamic radii.

Standardized Polymerizations with Dimethylmetallocene/Borate (Method B). In addition to the description above, the following changes were made:

1-Hexene and 5-(*N*,*N*-diisopropylamino)-1-pentene polymerizations were carried out as toluene solutions (20 mL) at 22.5 °C in 25 mL vials in the drybox. Decane (5 vol %) was used as the internal standard for GC measurements. Polymerization concentrations were 0.5 M in monomer and 0.5 mM in catalyst, with a zirconocene/borate ratio of approximately 1. The appropriate amount of borate was added as a solid to the vials. Toluene stock solutions of the zirconocenes were freshly prepared from single crystals. Aminopentene polymerizations were started by adding the zirconocene solution to the other starting materials. Due to the bad solubility of the anilinium borate in decane/hexene/toluene solutions, hexene polymerizations were started by adding hexene to the vial after the zirconocene and borate were allowed to stir in decane/toluene for 30 min. To record the monomer conversion by GC, 0.1-mL samples were taken from the main vial after 5, 10, 15, 20, and 30 min, diluted with 0.2 mL of toluene in small vials, and quenched outside the box with methanol. The initial monomer/decane ratio of aminopentene polymerizations was determined from a sample taken just before zirconocene addition. To determine the initial ratio of hexene/decane, a sample with the same weight percent of hexene, decane, and toluene was prepared. After 1 h the main vials were brought out of the box and the polymerization was stopped by addition of methanol. From GC measurements we obtained the percentage monomer conversion of each sample. At high monomer conversions we used the first time segment to calculate the maximum velocity and activity. The 60-min segment was used for calculations at low monomer conversions (≤25% after 1 h).

Polymerizations with Metallocene/MAO. $Cp^*_2ZrMe_2$ (20.3 mg, 51.8 μmol) was combined with 268 mg of MAO (Akzo type 4) as a white powder, 8.61 mL of toluene, and 0.48 mL of decane in a 25-mL vial in the drybox. The suspension was stirred 30 min and became lemon yellow colored. Addition of 5-(*N*,*N*-diisopropylamino)-1-pentene (2 mL, 1.575 g) started the polymerization and changed the color of the suspension to golden yellow. Amine addition brought the polymerization concentrations to 4.55 mM in catalyst and 0.83 M in monomer with an Al:Zr ratio of 89:1. To measure the initial conditions by GC, decane, toluene, and aminopentene were mixed with the same ratio of weight percent. One sample was taken after 1 h and the polymerization stopped after 6 h by addition of methanol. The polymer was washed with methanol to remove impurities, extracted with hexane, and dried in vacuo to yield a viscous oil. The percent conversion of monomer to polymer was measured by GC, and the polymer was analyzed by ^{1}H NMR (in $CDCl_3$ at room temperature).

Polymerizations with $TiCl_3$/TiBAl. $TiCl_3$ (0.270 g, 1.8 mmol), which was purchased "aluminum free" from Strem Chemical and used as received, was combined with 5-(*N*,*N*-diisopropylamino)-1-pentene (3.39 mL, 20 mmol) and 18 mL of benzene or with 1-hexene (15 mL, 119.95 mmol) and 15 mL of toluene in a 50-mL Schlenk tube in the drybox. After stirring for 5 min, a GC aliquot was taken from the solution and the Schlenk tube was removed from the drybox. The aminopentene-containing flask was placed in a silicon oil bath at 60 °C, and with constant stirring, the TiBAl (1.29 g, 6.5 mmol) was added. This brought the polymerization concentrations to 0.9 M in monomer and approximately 72.0 mM in catalyst, with an Al:Ti ratio of 3.7:1. The flask containing hexene was placed in a water bath at 23 °C. Addition of TiBAl (0.5 g, 2.52 mmol) brought the polymerization concentrations to 3.9 M in monomer and approximately 21.0 mM in catalyst, with an Al:Ti ratio of 3.9:1. Within seconds of cocatalyst addition, the colorless monomer solution, with suspended purple catalyst crystals, turns black. The aminopentene polymerization was sampled after 3.5 h and quenched with silica gel, and the polymerization was stopped after approximately 18 h at 100% conversion of monomer by the addition of methanol. The poly(aminopentene) was washed with methanol to remove impurities, extracted with hexane,

and dried in vacuo to yield a sticky white solid. This raw polymer was further fractionated with refluxing acetone (to yield acetone-soluble and acetone-insoluble fractions). The percent conversion of monomer to polymer was measured by GC, and the polymer was analyzed by ^{1}H and ^{13}C NMR, DSC, and viscometry. The hexene polymerization was stopped after approximately 1 min at 100% conversion of monomer by the addition of methanol. The polyhexene was washed with 2-propanol to remove impurities, extracted with toluene, and dried in vacuo to yield an opaque solid. The percent conversion of monomer to polymer was measured by GC, and the polymer was analyzed by ^{1}H NMR, ^{13}C NMR, and GPC.

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