# Metallocene/Borate-Catalyzed Copolymerization of 5-*N*,*N*-Diisopropylamino-1-pentene with 1-Hexene or 4-Methyl-1-pentene

**Udo M. Stehling, Kevin M. Stein, David Fischer, and Robert M. Waymouth***

*Department of Chemistry, Stanford University, Stanford, California 94305*

*Received June 1, 1998; Revised Manuscript Received October 27, 1998*

ABSTRACT: Metallocene/borate catalysts, generated from zirconocene dimethyl compounds, $L_nZrMe_2$, and anilinium borate, $[HNMe_2Ph]^+[B(C_6F_5)_4]^-$, were used to copolymerize 5-*N*,*N*-diisopropylamino-1-pentene with 1-hexene and 4-methyl-1-pentene. The selected zirconocenes, bis(pentamethylcyclopentadienyl)zirconium(IV) dimethyl ($Cp^*_2ZrMe_2$) and *rac*-ethylenebis(4,5,6,7-tetrahydroindenyl)zirconium(IV) dimethyl (*rac*-EB(THI)$ZrMe_2$), provided atactic and isotactic materials, respectively. The isotactic polymers produced were amorphous or crystalline depending of the monomer. The calculated reactivity ratios for the copolymerization of 5-*N*,*N*-diisopropylamino-1-pentene with 1-hexene and metallocene *rac*-EB(THI)$ZrMe_2$ indicate that this system approximates an ideal azeotropic copolymerization with $r_1 = 1.11$ and $r_2 = 0.87$. Estimates for the reactivity ratios for the copolymerization of 5-*N*,*N*-diisopropylamino-1-pentene with 4-methyl-1-pentene were $r_1 = 3$ and $r_2 = 1$ for *rac*-EB(THI)$ZrMe_2$ and $r_1 = 5$ and $r_2 = 0.5$ for $Cp^*_2ZrMe_2$. The polymerization of 1-hexene in the presence of the saturated 1-*N*,*N*-diisopropylaminopentane with *rac*-EB(THI)$ZrMe_2$/borate was compared with analogous copolymerizations of 1-hexene/5-*N*,*N*-diisopropylamino-1-pentene. The aminopentene was more effective than the aminopentane in inhibiting the rate of total monomer conversion, implicating both intra- and intermolecular mechanisms for inhibition by the amine. Copolymers of 4-methyl-1-pentene/5-*N*,*N*-diisopropylamino-1-pentene produced with *rac*-ethylenebisindenyl zirconium(IV) dimethyl (*rac*-EBI$ZrMe_2$)/borate have higher decomposition temperatures with increasing amounts of aminopentene. This copolymer can be protonated with HCl to yield a methanol-soluble material.

## Introduction

The stability of poly(α-olefins) to solvolysis, photodegradation, microbial growth, and biodegradation is largely due to their lack of functionality along the polymer backbone. The lack of chemical functionality becomes a liability for many applications, particularly those which depend on the polymer's adhesive properties, affinity for dyes and paints, gas permeability, and compatibility with more polar polymers, metal, and glass. Often only a small percentage of functionality (<2%) in a poly(α-olefin) can dramatically improve these latter properties.[1]

Two approaches can be envisioned for the synthesis of a functionalized poly-α-olefins: modification of the preformed polyolefin and direct copolymerization of an olefin with a functionalized monomer. Free-radical grafting reactions (with maleic anhydride for example) is a common approach to introducing functionality into polyolefins; however, this poorly controlled reaction often leads to polymer degradation, cross-linking, and nonuniform incorporation of the desired functionality. Other methods include ionic treatment (both anionic and cationic), plasma induced modifications, treatment with ionizing radiation, oxidation (acidic treatment), and halogenation.[1−3]

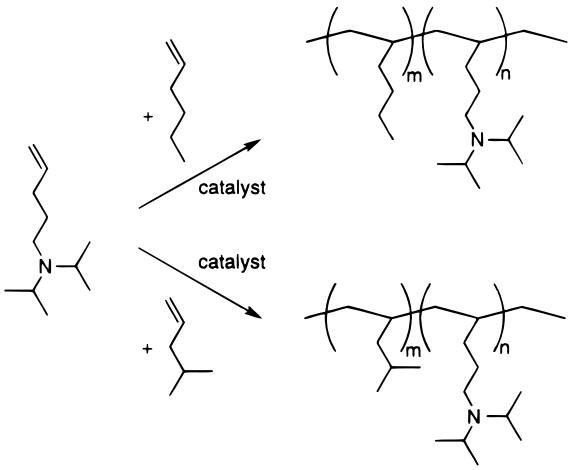
The second method of functionalized poly(α-olefin) synthesis consists of the direct copolymerization of functionalized olefins. An example of this method is the free radical copolymerization of ethylene with acrylic acid to yield the ionomer Surlyn (DuPont, 1964). Unfortunately, this rather effective technique is limited to monomers without α-hydrogens (e.g.: ethylene, styrene, acrylic acid, etc.) due to rapid chain-transfer reactions for monomers that contain allylic hydrogens. This disadvantage can be overcome by using coordination-type catalysts. Copolymerization of ethylene and propylene with alkyl acrylates using palladium(II) catalysts, for example, gave high molar mass polymers under mild and controlled conditions.[4]

A well-known limitation of conventional Ziegler−Natta catalyst systems is their intolerance to most functional groups (ethers, esters, amines, alcohols, and carboxylic acids).[5] Previous attempts to directly homo- or copolymerize various functionalized α-olefin monomers met with limited success due to a severe loss of activity caused by catalyst deactivation.[6−11] On the other hand, zirconocene/methylalumoxane (MAO) catalysts were to a certain extent successful in copolymerizing ethylene and propylene with 1-hydroxy-10-undecene,[12,13] 1-chloro-10-undecene,[14] *N*,*N*-bis(trimethylsilyl)-1-amino-10-undecene,[15] silsesquioxane-functionalized decene,[16] an *o*-heptenylphenol derivative,[17] and borane-functionalized α-olefins.[18,19]

The direct synthesis of cationic, group 4 metallocene complexes has led to catalysts which show some tolerance for Lewis basic solvents.[20−24] Furthermore these catalysts made possible the polymerization of olefins in the absence of alkylaluminum cocatalysts in solvents such as anisole, *N*,*N*-dimethylaniline, and chlorobenzene.[25,26] These studies provided the precedent for our efforts to carry out the homopolymerization of α-olefins containing silyl-protected alcohols and different tertiary amines.[27,28] In this paper we describe the copolymerization of 5-*N*,*N*-diisopropylamino-1-pentene with 1-hexene and 4-methyl-1-pentene using cationic group 4 metallocenes. Comparison of hexene/aminopentene copolymerizations with related hexene homopolymerizations in the presence of a saturated amine provided

10.1021/ma980856c CCC: $18.00 
Published on Web 12/10/1998

**Scheme 1. Copolymerization of 5-*N*,*N*-Diisopropylamino-1-pentene with 1-Hexene or 4-Methyl-1-pentene**




some information on the origins of the lower productivities in the presence of monomers containing tertiary amines.

## Results

Two zirconocenes, bis(pentamethylcyclopentadienyl)-zirconium(IV) dimethyl ($Cp^*_2ZrMe_2$) and *rac*-ethylene-bis(4,5,6,7-tetrahydroindenyl)zirconium(IV) dimethyl (*rac*-EB(THI)$ZrMe_2$), were treated with *N*,*N*-dimethylanilinium tetrakis(pentafluorophenyl)borate, $[HNMe_2Ph]^+[B(C_6F_5)_4]^-$, to generate the active catalysts $[Cp^*_2ZrMe]^+[B(C_6F_5)_4]^-$ and [*rac*-EB(THI)ZrMe]$^+[B(C_6F_5)_4]^-$. Both catalysts were utilized to copolymerize 5-*N*,*N*-diisopropylamino-1-pentene with 1-hexene and 4-methyl-1-pentene (Scheme 1). Catalysts were selected to prepare atactic and isotactic copolymers. The monomers were chosen to provide functionalized amorphous and crystalline materials.

The copolymerizations of 5-*N*,*N*-diisopropylamino-1-pentene with 1-hexene and 4-methyl-1-pentene were carried out at five different monomer ratios. After polymerization times of from 3 up to 30 min a conversion of 10−53% amine for copolymerizations with 1-hexene and a conversion of 7−17% amine for copolymerizations with 4-methyl-1-pentene were observed (see Supporting Information). The monomer composition and % conversion were determined by gas chromatography (GC), and the final polymer composition was determined by $^1H$ and $^{13}C$ NMR or elemental analysis. Estimates for the copolymerization parameters,[29,30] $r_1$ (amine) and $r_2$ (1-hexene or 4-methyl-1-pentene), were obtained from a direct fit of $f_{amine}$ (composition of the monomer feed) to $F_{amine}$ (resultant copolymer compositions) utilizing the Marquardt−Levenberg algorithm for nonlinear curve fitting and are reported in Table 1.

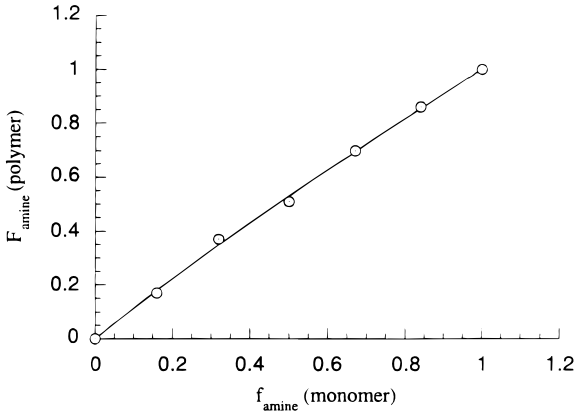



**Figure 1.** Copolymerization diagram for the 5-*N*,*N*-diisopropylamino-1-pentene and 1-hexene copolymerization with *rac*-EB(THI)$ZrMe_2$/borate.

A representative copolymerization diagram is presented in Figure 1 (monomer 1 = aminopentene), and the copolymerization parameters are listed in Table 1. As shown in Figure 1 the *rac*-EB(THI)$ZrMe_2$/borate catalyst system exhibits a similar preference for both the amine and 1-hexene monomers. The product of the reactivity ratios $r_1r_2 = 0.99$ reveals an almost ideal copolymerization, indicating that both monomers are readily incorporated into the copolymer to give a Bernoullian distribution of comonomers.

Copolymerizations of the amine with 4-methyl-1-pentene indicate a preference for insertion of the amine for both *rac*-EB(THI)$ZrMe_2$/borate ($r_1 \sim 3$) and the $Cp^*_2ZrMe_2$/borate ($r_1 \sim 5$) catalyst systems. These kinetic selectivities are particularly notable in light of our previous measurements which show that the activity for hexene is approximately 30 times higher than that of 5-*N*,*N*-diisopropylamino-1-pentene (activity = 546 mol of amine/mol of Zr × [amine] × h vs 15570 mol of hexene/mol of Zr × [hexene] × h) with the *rac*-EB(THI)$ZrMe_2$/borate catalyst.[28,41]

The high incorporation selectivities for the olefinic amines despite their much lower activity in homopolymerization prompted us to investigate the inhibition of hexene polymerization by tertiary amines more generally. To that end, the rate of total monomer conversion in the presence of the 5-*N*,*N*-diisopropylamino-1-pentene comonomer was compared to the rate in the presence of a saturated 1-*N*,*N*-diisopropylaminopentane. The results are summarized in Table 2. Polymerizations were carried out in vials in a glovebox to facilitate GC sampling under oxygen free (≤3 ppm $O_2$) and moisture-free conditions during the polymerizations. This procedure provided limited temperature control which may explain the variable molecular weights particularly for the hexene homopolymerizations at amine:monomer ratios smaller than 0.7 and for

**Table 1. Copolymerization of 5-*N*,*N*-Diisopropylamino-1-pentene with 1-Hexene and 4-Methyl-1-pentene from Metallocene/Borate Catalysis[a]**

| | | | copolymerization parameters[d] | | |
|---|---|---|---|---|---|
| metallocene[b] | monomers[c] | % conv amine | $r_1$(amine) | $r_2$[e] | $r_1r_2$ |
| *rac*-EB(THI)$ZrMe_2$ | aminopentene/hexene | 13−50 | 1.1 | 0.9 | 0.99 |
| | aminopentene/methylpentene | 6−17 | ∼3[f] | ∼1[f] | 3[f] |
| $Cp^*_2ZrMe_2$ | aminopentene/methylpentene | 13−17 | ∼5[f] | ∼0.5[f] | 2.5[f] |

[a] Copolymerizations in toluene in a dry box or Schlenk flasks at $T = 22$ °C. [b] Metallocene/aniliniumborate ratio was approximately 1. [c] Initial monomer composition was varied from 0 to 0.96 mole/l amine in seven different concentrations and vice versa for hexene and methylpentene. [d] Calculated from copolymer composition data, which were determined by $^{13}C$ NMR or $^1H$ NMR analysis. [e] 1-Hexene or 4-methyl-1-pentene. [f] High conversion limits accuracy of reactivity ratios (ref 29).

**Table 2. Homo- and Copolymerization Data of 1-Hexene with 1-*N*,*N*-Diisopropylaminopentane Inhibitior or 5-*N*,*N*-Diisopropylamino-1-pentene Comonomer from *Rac*-EB(THI)ZrMe$_2$/Borate[a]**

| | monomer composition[b] | | | monomer conversion | |
|---|---|---|---|---|---|
| entry | 1-hexene, $(mol/L)_{av}$ | 5-*N*,*N*-Diisopropylamino-1-pentene, $(mol/L)_{av}$ | 1-*N*,*N*-Diisopropylamino-pentane, $(mol/L)_{av}$ | ratio [amine]:[monomer$_{total}$] | velocity$_{max}$ of monomer conversion ($mol_{mon}$/L s) | activity[41] (h c[mon$_{tot}$]$_{av}$)$^{-1}$ |
| 1 | 0.338 (±0.060) | | | 0 | $1.16 \times 10^{-3}$ ($\pm 0.15 \times 10^{-3}$) | 24231 (±5179) |
| 2 | 0.243 | | $6.79\ 10^{-3}$ | 0.028 | $5.72 \times 10^{-4}$ | 16875 |
| 3 | 0.325 | | $39.6 \times 10^{-3}$ | 0.122 | $4.52 \times 10^{-4}$ | 10040 |
| 4 | 0.384 | | 0.101 | 0.263 | $3.39 \times 10^{-4}$ | 6309 |
| 5 | 0.345 | | 0.149 | 0.432 | $3.32 \times 10^{-4}$ | 6828 |
| 6 | 0.386 | | 0.250 | 0.648 | $2.29 \times 10^{-4}$ | 4916 |
| 7 | 0.467 | | 0.494 | 1.058 | $1.31 \times 10^{-4}$ | 2323 |
| 8 | 0.264 | $2.81 \times 10^{-3}$ | | 0.011 | $6.45 \times 10^{-4}$ | 17414 |
| 9 | 0.430 | $37.6 \times 10^{-3}$ | | 0.080 | $4.18 \times 10^{-4}$ | 6478 |
| 10 | 0.459 | 0.092 | | 0.167 | $3.08 \times 10^{-4}$ | 4011 |
| 11 | 0.478 | 0.146 | | 0.234 | $1.91 \times 10^{-4}$ | 2328 |
| 12 | 0.242 | 0.163 | | 0.402 | $5.61 \times 10^{-5}$ | 998 |
| 13 | 0.163 | 0.249 | | 0.605 | $4.98 \times 10^{-5}$ | 868 |
| 14 | | 0.438 (±0.002) | | 1 | $3.87 \times 10^{-5}$ ($\pm 0.40 \times 10^{-5}$) | 635 (±66) |

[a] See Experimental Section for polymerization conditions; see Supporting Information for additional results of hexene or aminopentene homopolymerizations in Schlenk flasks in a waterbath at 21.5 or 28.0 °C. [b] All concentrations are average concentrations of the time segments used for calculations. [c] Determined by $^1$H NMR spectroscopy (vinylidene end groups).

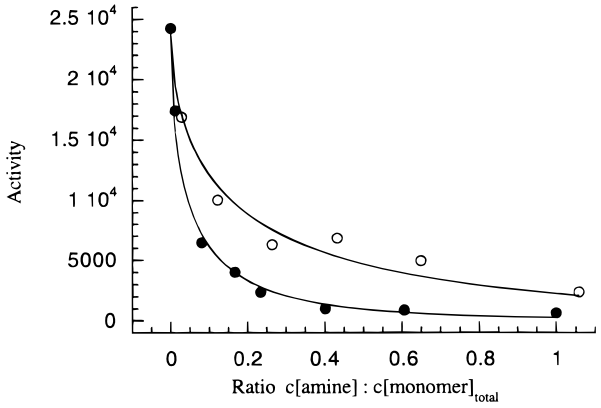



**Figure 2.** Activity of 1-hexene homopolymerizations with 1-*N*,*N*-diisopropylaminopentane inhibition (○) and 1-hexene/5-*N*,*N*-diisopropylamino-1-pentene copolymerizations (•) from *rac*-EB(THI)ZrMe$_2$/borate.

hexene/aminopentene copolymerizations at amine:monomer ratios smaller than 0.2 (Table 2).[31]

The decrease in activity with increasing ratio of the amine concentration to the total monomer concentration is plotted in Figure 2. The influence of the added amine on the activity can be fit to the expressions

$$\ln[A] = 10.1 - 2.4(x_1)^{0.541} \quad (1)$$

for the polymerization of hexene in the presence of the amine and

$$\ln[A] = 10.1 - 4.7(x_2)^{0.541} \quad (2)$$

for the aminopentene/hexene copolymerizations where $A$ = the activity in mol polymer/(mol of Zr)(h)([olefin]) and $x$ = ratio of the amine concentration to the total monomer concentration. For hexene polymerization in the presence of the aminopentane, the activity drops to half for $x_1 = 0.100$; for the copolymerization, the activity drops in half at a much lower ratio $x_2 = 0.029$. These data clearly show the aminopentene is a more potent inhibitor than the amine lacking a polymerizable group. In general, the ratio of olefinic amine/hexene must be a factor of 3.5 smaller than the ratio of saturated amine/hexene to reach a comparable rate.[42]

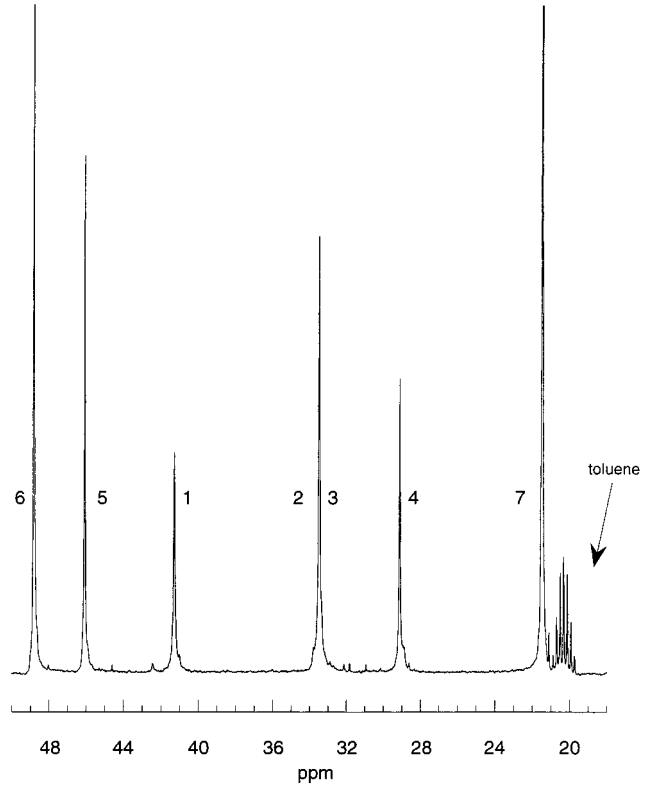



**Figure 3.** $^{13}$C NMR of isotactic poly(5-*N*,*N*-diisopropylamino-1-pentene) from *rac*-EBIZrMe$_2$/borate.

The isospecific copolymerization of 5-*N*,*N*-diisopropylamino-1-pentene with 4-methyl-1-pentene was repeated with the *rac*-ethylenebisindenylzirconium(IV) dimethyl (*rac*-EBIZrMe$_2$)/anilinium borate catalyst system to obtain a higher molecular weight, stereoregular copolymer sample for further characterization. 4-Methyl-1-pentene was chosen as the comonomer for these investigations as the homopolymers are crystalline, whereas all 1-hexene homopolymers are amorphous (independent of stereochemistry).[32]

The $^{13}$C NMR spectra of isotactic poly(5-*N*,*N*-diisopropylamino-1-pentene) and of the methylpentene/ami-

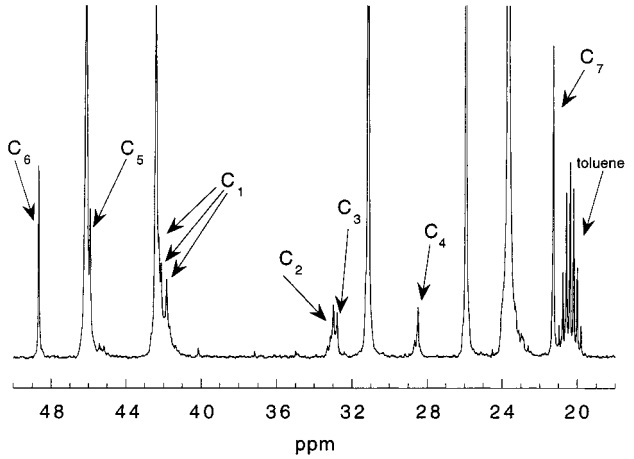



**Figure 4.** $^{13}C$ NMR of 5-*N*,*N*-diisopropylamino-1-pentene/4-methyl-1-pentene copolymer from *rac*-EBIZrMe$_2$/borate with 12.5% incorporated amine monomer (amine peaks are identified).

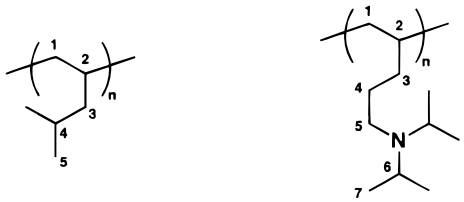



**Figure 5.** Assignment of $^{13}C$ NMR chemical shifts of isotactic poly(4-methyl-1-pentene) and isotactic poly(5-*N*,*N*-diisopropylamino-1-pentene).

nopentene copolymer with 12.5 mol % amine incorporation are shown in Figures 3 and 4. The chemical shifts of poly(4-methyl-1-pentene) were assigned from the literature,[32,33] and those for the amine homopolymer were assigned through the use of data of model α-olefin polymers[28,34] and DEPT experiments (Figure 5). The NMR spectra (Figures 3 and 4) indicate that for these two monomers the catalyst is highly stereoselective. By comparison of the amine homopolymer spectrum (Figure 3) with the copolymer spectrum (Figure 4), it becomes apparent that in the copolymer spectrum carbons 2 and 3 are resolved into their individual chemical shifts and carbon 1 is split into several peaks. This observation arises from an altered environment about amine carbons 1, 2, and 3 from the presence of the comonomer 4-methyl-1-pentene. Specifically, amine carbon 1 appears to be the most sensitive to such changes in the polymer backbone.

The melting points and decomposition temperatures of homo- and copolymers synthesized from the catalytic system *rac*-EBIZrMe$_2$/Borate are listed in Table 3. With increasing amounts of the amine comonomer, the melting point and crystallinity decreased but the decomposition temperature increased. At the 2.5% monomer incorporation level, a 43 °C increase in the decomposition temperature was achieved, and for the 12.5% level, a 59 °C increase was realized over the homopolymer of 4-methyl-1-pentene.

Treatment of the 2.5% amine/4-methyl-1-pentene copolymer with HCl produced a methanol-soluble material which could also be swelled with water to produce a gel. The same copolymer was previously hexane and toluene soluble but insoluble in polar solvents.

**Table 3. Thermal Transition Data for Homo- and Copolymers Synthesized with *rac*-EBIZrMe$_2$/Borate**

| polymer | mp,[a] °C ($\Delta H_{fus}$, J/g) | dec temp,[b] °C | $M_n$[c] |
|---|---|---|---|
| poly(4M1P)[d] | 223 (34.5) | 342 | 16 200 |
| copolymer(2.5% amine/4M1P)[e] | 186 (10.3) | 385 | >14 000[g] |
| copolymer(12.5% amine/4M1P)[e] | 159 (4.9) | 400.6 | >14 000[g] |
| poly(amine)[f] | 115 (12.4) | 401.7 | >14 000[g] |

[a] Peak melting points reported. [b] Determined in $N_2$ as the onset of 100% degradation. [c] Determined by $^1H$ NMR vinylidene end group analysis. [d] Isotactic poly(4-methyl-1-pentene). [e] The copolymers are isotactic poly(4-methyl-1-pentene-*co*-5-*N*,*N*-diisopropylamino-1-pentene) [f] Isotactic poly(5-*N*,*N*-diisopropylamino-1-pentene). [g] The upper limit of detection for this technique for the amine polymers is about 14 000.

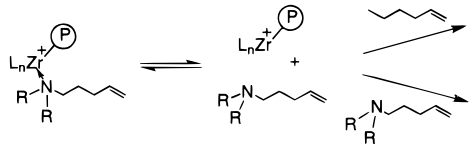
## Discussion

The copolymerization of α-olefins is an important technique for the preparation of novel materials but also provides important mechanistic information on the relative reactivity of the comonomers. The behavior of monomers in copolymerization reactions is especially useful for studying the effect of chemical structure on reactivity. We had previously investigated and compared the homopolymerization of the amine-functionalized olefin 5-*N*,*N*-diisopropylamino-1-pentene with hexene;[28] herein, we examine the copolymerization behavior of this amino olefin and describe some novel functionalized olefin copolymers.

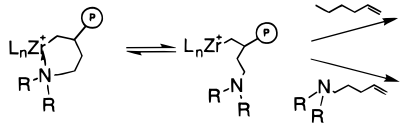
Two catalyst systems, *rac*-EB(THI)ZrMe$_2$/borate and Cp*$_2$ZrMe/borate were investigated for the copolymerization of 5-*N*,*N*-diisopropylamino-1-pentene/1-hexene and 5-*N*,*N*-diisopropylamino-1-pentene/4-methyl-1-pentene. The copolymerization parameters reveal that these copolymerizations are close to ideal for hexene in the presence of *rac*-EB(THI)ZrMe$_2$/borate ($r_1r_2 = 0.99$), with reactivity ratios for the aminopentene ($r_1 = 1.1-5$, Table 1) which indicate that the functionalized monomer can be readily incorporated into the polymer. These data reveal that an entire range of copolymers are quite readily prepared. The slight preference for incorporation of the amine in aminopentene/4-methyl-1-pentene copolymers (Table 1) for the Cp$_2$*ZrMe$_2$/borate system suggest that the selectivity for incorporation is related to the steric accessibility of the olefin rather than the presence of the tertiary amine. This is consonant with the observation that 4-methyl-1-pentene shows a lower preference for incorporation into copolymers than 1-hexene with Ziegler−Natta type initiators.[35] Therefore, it is not surprising that the reactivity ratios for 4-methyl-1-pentene are lower than for 1-hexene for copolymerizations with the amine monomer.

The selectivity for incorporation of the aminopentene into the copolymer can be contrasted to the different productivities observed for the respective homopolymerization reactions; we have previously observed that the rate of hexene polymerization with the *rac*-EB(THI)ZrMe$_2$/borate catalyst system is approximately 30 times higher than that of 5-*N*,*N*-diisopropylamino-1-pentene.[28,36,41] In addition, the copolymerization rate drops with increasing concentration of amine in the feed (entries 8−13, Table 2). The fact that the relative rates of homopolymerization do not match the relative selectivities in copolymerization suggests that inhibition of the rate by the amine is unrelated to the olefin insertion step: these processes are two distinct kinetic events. Two possible inhibition processes are illustrated in Scheme 2: an intermolecular coordination of the ter-

**Scheme 2. Two Potential Inhibition Mechanisms**



**A:** Intermolecular Coordination



**B:** Intramolecular Coordination

tiary amine and an intramolecular coordination of the tertiary amine from the last inserted monomer unit. Both processes compete with olefin insertion. Precedent for the former process derives from the well-documented inhibitory effect of coordinating functional groups on the polymerization activity of cationic metallocenes.[24,37] Support for the latter mechanism comes from our observation that the polymerization of 4-*N*,*N*-diisopropylamino-1-butene is approximately 4 times slower than that of 5-*N*,*N*-diisopropylamino-1-pentene.[28]

In an attempt to decouple these two mechanisms, homopolymerizations of 1-hexene in the presence of the saturated monomer analogue, 1-*N*,*N*-diisopropylaminopentane, with the *rac*-EB(THI)$ZrMe_2$/borate catalyst system were investigated and compared to hexene/aminopentene copolymerizations. The inhibitory effect of the aminopentane implies that intermolecular coordination of the amine is a potent mechanism for inhibition. However, the fact that hexene homopolymerization with the aminopentane inhibitor could accommodate approximately 3.5 higher amine concentration and attain a productivity equal to the hexene/aminopentene copolymerizations suggests that intramolecular coordination of the amine following the insertion of the aminoolefin is also an effective inhibition mechanism that competes with olefin insertion. This result is anticipated by our previous studies which show the aminopentene is polymerized more rapidly than an aminobutene containing one less methylene spacer between the olefin and the functional group. Thus, it would appear that both mechanisms A and B (Scheme 2) are responsible for the lower productivity in the copolymerization of olefins and aminoolefins.

The near ideal copolymerization behavior of these systems was employed to produce a stereoregular copolymer of 4-methyl-1-pentene/amine. An isotactic poly(4-methyl-1-pentene-*co*-5-*N*,*N*-diisopropylamino-1-pentene) copolymer was produced utilizing the *rac*-EBI$ZrMe_2$/borate catalyst system. This crystalline copolymer exhibits a high melting point and a higher decomposition temperatures than that recorded for the homopolymer of 4-methyl-1-pentene. Such an improvement may be a consequence of the ability of hindered amines to act as antioxidants and inhibit radical chain scission,[38] one of the major mechanisms of thermal polymer degradation.[39]

These novel copolymers can be protonated to produce ionomer type materials which are soluble in methanol and could be swelled with water. Such materials might provide access to a new family of ionomer type materials from α-olefins, whose physical properties must still be defined.

## Conclusion

The direct copolymerization of functionalized α-olefins with other monoalkenes utilizing a homogeneous cationic metallocene catalyst system is described. Analysis of the copolymerization behavior reveal reactivity ratios approaching unity for the copolymerization of hexene with 5-*N*,*N*-diisopropylaminopentene in the presence of *rac*-ethylenebis(4,5,6,7-tetrahydroindenyl)zirconium-(IV) dimethyl. This behavior allows for a complete complement of functionalized copolymers to be synthesized directly utilizing these homogeneous metallocene catalyst systems.

The novel copolymers synthesized in this work contain a hindered amine, a family of materials which are known to act as antioxidants.[38] In addition, the added polarity should enhance the chemical reactivity of the polymer, including its adhesive properties, compatibility with more polar polymers, and affinity for functionalized additives (eg: dyes, paints, antioxidants, flame retardant, etc.).

The productivity for the copolymerizations of olefins with amino olefins is suppressed as a consequence of both intramolecular coordination of the amine following insertion of an amino olefin and an intermolecular coordination of the amino group. Both processes are competitive with olefin insertion and thus inhibit the rate. Although activity dropped in half using 3% of an amino functionalized comonomer, polyolefins with this range of comonomer contents are expected to exhibit properties considerably different from those of the analogous homopolymers. Thus for those systems where a diminution in productivity can be tolerated, metallocene/borate catalysts provide an attractive strategy for the synthesis of stereoregular, functionalized polyolefins.

## 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% dimethyl polysiloxane, 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. Nuclear magnetic resonance spectroscopy (NMR) was performed on Varian XL-400 and on Gemini 200 spectrometers. Data on polymer samples were obtained at 75 °C in toluene-$d_8$ or at 18 °C in $CDCl_3$. The copolymer composition was determined by $^1H$ or $^{13}C$ NMR spectroscopy. Composition evaluations from $^{13}C$ NMR spectra are based on the hexene signal at 29.67 ppm and the amine signal at 29.12 ppm. The spectra were run under standard conditions and corrected

by multiplication with an empirical correction coefficient. The coefficient was determined from an experiment with long relaxation delay (15 s) and reversed gated decoupling (sample: copolymer from 1:1 monomer mixture). This experiment gave an amine/hexene ratio (incorporated units) of 1.054 instead of 1.143 from the standard experiment. Therefore all amine/hexene ratios from standard experiments were corrected as follows: $(\text{amine/hexene})_{cor} = 0.92213(\text{amine/hexene})_{standard}$. Copolymer composition evaluations from $^1$H NMR spectra are based on the integrals ($I_i$) of the following three areas: $I_1$ at 3.0 ppm (2H of aminopentene), $I_2$ at 2.32 ppm (2H of aminopentene), and $I_3$ of the area 2.1−0.6 ppm (19H of aminopentene (AP) and 12H of hexene (H) or methylpentene (MP)); the integral of vinylidene end group protons was neglected. The equations $I_{AP} = ((I_1 + I_2):4) \times 23$ and $I_H$ (or $I_{MP}$) $= (\sum I_i) - I_{AP}$ were employed. The ratio of aminopentene/hexene (or methylpentene) was then calculated from $(I_{AP}:23)/(I_H:12)$. Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) were 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, and TGA data were collected in a nitrogen atmosphere at 20 °C/min from 35 to 1000 °C. Elemental analyses were performed by E & R Microanalytical Laboratory, Inc., Corona, NY. The analysis of the copolymer data, to elucidate the copolymerization equation and determine the reactivity ratios for each catalyst system, was performed using a Marquardt−Levenberg algorithm for nonlinear curve fitting in KaleidaGraph 3.0.1. The confidence level for the reactivity ratios, derived from NMR data of the copolymers, is ± 7%.[40]

**Monomer and Catalyst Synthesis.** 1-Hexene (density = 0.673 g/mL) and 4-methyl-1-pentene (density = 0.665 g/mL) are commercially available. 5-*N*,*N*-Diisopropylamino-1-pentene (density = 0.75 g/mL), bis(pentamethylcyclopentadienyl)-zirconium(IV) dimethyl ($Cp^*_2ZrMe_2$), *rac*-ethylenebis(4,5,6,7-tetrahydroindenyl)zirconium(IV) dimethyl (*rac*-EB(THI)$ZrMe_2$), *rac*-ethylenebisindenylzirconium(IV) dimethyl (*rac*-EBI$ZrMe_2$), and *N*,*N*-dimethylanilinium tetrakis(pentafluorophenyl)borate ($[HNMe_2Ph]^+[B(C_6F_5)_4]^-$) were synthesized from published procedures.[28]

**1-*N*,*N*-Diisopropylaminopentane.** This synthesis is similar to that reported for the 5-*N*,*N*-diisopropylamino-1-pentene.[28] 2-(Diisopropylamino)ethyl chloride (24.5 g, 0.15 mol) was 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. To the flask, under an argon atmosphere, was added 100 mL of dry THF. Propylmagnesium chloride was added to this solution with constant stirring as a 2.0 M solution in $Et_2O$ (77 mL, 0.154 mol, 3% 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 extracted three times with 100 mL of $Et_2O$. The combined yellow organics were dried over anhydrous $MgSO_4$ and distilled from $CaH_2$. This yielded 22.8 g (89% yield) of a pungent clear liquid, which was characterized by GC and $^1$H NMR. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 2.95 (m, 2H), 2.35 (m, 2H), 1.45 (m, 2H), 1.3 (m, 4H), 0.95 (d, 12H), 0.85 (t, 3H). The amine reagent was further purified just prior to use by filtration through activated alumina (neutral alumina, 20 mesh; heated to 250 °C under vacuum) in the drybox.

**General Polymerization Procedures. Copolymerization of Amino-1-pentene with 1-Hexene or 4-Methyl-1-pentene.** The unfunctionalized α-olefin and 5-*N*,*N*-diisopropylamino-1-pentene were copolymerized at 5 different monomer ratios (16, 33, 67, and 84 mol % of 1-hexene). Polymerizations with $Cp^*_2ZrMe_2$/borate were carried out at 22 °C in a drybox. The monomers were combined with the appropriate amount of toluene, and a few drops of decane (internal standard), in a 25 mL vial equipped with a stir bar. The borate cocatalyst was added to give approximately a 1:1 molar ratio with the metallocene. After the reaction was stirred for 5 min, a GC aliquot was taken from the solution and removed from the drybox. In the drybox, the appropriate amount of $Cp^*_2ZrMe_2$ was dissolved in 0.5 mL of toluene and added to the reaction vial via a syringe. This brings the polymerization concentrations to 0.96 M in combined monomer, approximately 1.3 mM in catalyst (3 mM in catalyst for the aminopentene/methylpentene system), with a total solution volume of approximately 10 or 11.5 mL. Within seconds of catalyst addition, the colorless monomer solution turns an intense yellow/brown color. The polymerizations were stopped by addition of methanol within a time frame of from 3 up to 30 min after the reactions were started. All polymerizations with *rac*-EB(THI)$ZrMe_2$/borate were carried out at 22 °C in Schlenk tubes. The solid borate, toluene, and the monomers were added in this order into a dry 100 mL Schlenk tube (equipped with a magnetic stir bar) in the drybox. A small sample was taken (reference for the GC evaluation) and the Schlenk tube was sealed with a rubber septa. It was brought out of the drybox and connected to the argon/vacuum line. The polymerization was started by addition of one equivalent of *rac*-EB(THI)$ZrMe_2$ as 50 mmol/L stock solution (total volume after this addition: 25.0 mL; total monomer concentration: 0.96 mol/L). The polymerization was stopped by addition of MeOH. The polymer was washed with methanol to remove impurities, extracted with hexane, and dried in vacuo to yield a viscous oil (or a tacky solid with *rac*-EB(THI)$ZrMe_2$ for the aminopentene/methylpentene system). The percent conversion of monomer to polymer was measured by GC. The polymer was analyzed by $^1$H and $^{13}$C NMR analysis. From $^1$H NMR vinylidene end group analysis, the $M_n$ of the copolymers was determined as ≤2000 for the $Cp^*_2ZrMe_2$ catalyst and ≤10000 for the *rac*-EB(THI)$ZrMe_2$ catalyst.

**Copolymerization of Amino-1-pentene/4-Methyl-1-Pentene, Preparative Scale.** The monomers 4-methyl-1-pentene (9.182 g, 109.1 mmol) and 5-*N*,*N*-diisopropylamino-1-pentene (0.36 g, 2.126 mmol) were combined with toluene (12.33 mL) and a few drops of decane (internal standard) in a 100 mL vial in the drybox. The borate cocatalyst (28 mg, 0.035 mmol) was then added to the vial, which was equipped with a stir bar. After the reaction was stirred for 5 min, a GC aliquot was taken from the solution and removed from the drybox. In the drybox, the appropriate amount of the *rac*-EBI$ZrMe_2$ (22 mg, 0.058 mmol) was then added to the reaction vial. This brought the polymerization concentrations to 4.2 M in combined monomer (1.9 mol % amine), and approximately 2.3 mM in catalyst. Within seconds of catalyst addition, the colorless monomer solution turned an intense yellow/brown color. The polymerization was stopped after 12 h (100% conversion) and quenched with methanol. The polymer was washed with methanol to remove impurities, extracted with hexane, and dried in vacuo to yield 8.504 g (89% yield after workup) of an off-white solid. The percent conversion of monomer to polymer was measured by GC, and the polymer was analyzed by $^1$H and $^{13}$C NMR, elemental analysis, and DSC/TGA. Anal. Found: C, 85.55; H, 14.15; N, 0.43. (This indicated a 2.64 mol % amine incorporation.) $M_n > 14\,000$ from $^1$H NMR, mp = 186 °C ($\Delta H_m = 10.33$ J/g).

**Homopolymerization of 5-*N*,*N*-Diisopropylamino-1-pentene or 4-Methyl-1-pentene.** Homopolymerizatons were carried out as described in ref 28. *rac*-EBI$ZrMe_2$ was used to prepare poly-5-*N*,*N*-diisopropylamino-1-pentene ($^{13}$C NMR (100 MHz, toluene-$d_8$): $\delta$ 48.8, 46.1, 41.3, 33.4, 29.1, and 21.6), and poly-4-methyl-1-pentene ($M_n = 16\,200$ from $^1$H NMR end-group analysis; mp = 223 °C (34.5 J/g); $^{13}$C NMR (100 MHz, toluene-$d_8$) $\delta$ 46.2, 42.3, 31.3, 26.9, and 23.5).

**Polymerization of 1-Hexene in the Presence of 1-*N*,*N*-Diisopropylaminopentane or 5-*N*,*N*-Diisopropylamino-1-pentene.** 1-Hexene was polymerized in the presence of an increasing amount of 1-*N*,*N*-diisopropylaminopentane or 5-*N*,*N*-diisopropylamino-1-pentene (Tables 2 and S5). Polymerizations were carried out as toluene solutions (10 mL) at 22.5 °C in 15 mL vials in the drybox. Decane (5 vol %) was used as an internal standard for GC measurements. Polymerization concentrations were 0.5 M in monomer and 0.5 mM in catalyst, with an 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 or aminopentane-containing 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 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 toluene in small vials, and quenched outside the box with methanol. The initial monomer/decane ratio of aminopentene or aminopentane containing 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 stopped by addition of methanol. The average percentage of monomer conversion was generally obtained for each sample from three GC measurements. At high monomer conversions the first time segment was used to calculate the maximum velocity and activity.[41] The 60 min segment was used for calculations at low monomer conversions (≤25% after 1 h). The polymers were analyzed by $^1$H NMR to determine $M_n$ (vinylidene end groups).

**Acknowledgment.** The authors gratefully acknowledge financial support from the NSF-NYI Program (DMR 9258324), the Department of Education for a GAANN Fellowship, Raychem Corporation and BASF AG. R.M.W. is a recipient of the Waterman Award from NSF (CHE-9615699) for which he is grateful.

**Supporting Information Available:** Five tables and four copolymerization diagrams containing additional copolymerization data (6 pages). See any current masthead page for ordering and Internet access instructions.

## References and Notes

(1) Simonazzi, T.; Nicola, A. D.; Aglietto, M.; Ruggeri, G. In *Comprehensive Polymer Science*; Aggarwal, S. L., Russo, S., Eds.; Pergamon Press: New York, 1992; 1st Supplement, Chapter 7, pp 133−158.
(2) Jagur-Grodzinski, J. *Prog. Polym. Sci.* **1992**, *17*, 361−77.
(3) Singh, R. P. *Prog. Polym. Sci.* **1992**, *17*, 251−98.
(4) Johnson, L. K.; Mecking, S.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 267−268.
(5) Boor, J. *Ziegler−Natta Catalysts and Polymerization*; Academic Press: New York, 1979.
(6) Padwa, A. R. *Prog. Polym. Sci.* **1989**, *14*, 811−833.
(7) Collette, J. W.; Ro, R. S. Y.; Sonnenberg, F. M. U. S. Pat. 4017669, 1977.
(8) Vogl, O. *J. Macromol. Sci., Chem.* **1985**, *A22*, 541−59.
(9) Purgett, M. D.; Vogl, O. *J. Polym. Sci., Part A: Polym. Chem.* **1988**, *26*, 677−700.
(10) Purgett, M. D.; Vogl, O. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 2051−63.
(11) Giannini, U.; Brückner, G.; Pellino, E.; Cassata, A. *J. Polym. Sci.: Part C* **1968**, *22*, 157−175.
(12) Aaltonen, P.; Löfgren, B. *Macromolecules* **1995**, *28*, 5353−5357.
(13) Aaltonen, P.; Fink, G.; Löfgren, B.; Seppälä, J. *Macromolecules* **1996**, *29*, 5255−5260.
(14) Bruzaud, S.; Cramail, H.; Duvignac, L.; Deffieux, A. *Macromol. Chem. Phys.* **1997**, *198*, 291−303.
(15) Schneider, M. J.; Schäfer, R.; Mülhaupt, R. *Polymer* **1997**, *38*, 2455−2459.
(16) Tsuchida, A.; Bolln, C.; Sernetz, F. G.; Frey, H.; Muelhaupt, R. *Macromolecules* **1997**, *30*, 2818−2824.
(17) Wilén, C.-E.; Näsman, J. H. *Macromolecules* **1994**, *27*, 4051−4057.
(18) Chung, T. C.; Rhubright, D. *Macromolecules* **1993**, *26*, 3019−3025.
(19) Chung, T. C.; Lu, H. L. *J. Mol. Catal., A: Chem.* **1997**, *115*, 115−127.
(20) Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1996**, 255−270.
(21) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143−56.
(22) Alelyunas, Y. W.; Guo, Z. Y.; Lapointe, R. E.; Jordan, R. F. *Organometallics* **1993**, *12*, 544−553.
(23) Marks, T. J. *Acc. Chem. Res.* **1992**, *25*, 57−65.
(24) Jordan, R. F. *Adv. Organomet. Chem.* **1991**, *32*, 325−387.
(25) Eshuis, J. J. W.; Tan, Y. Y.; Teuben, J. H.; Renkema, J. *J. Mol. Catal.* **1990**, *62*, 277−287.
(26) Eshuis, J. J. W.; Tan, Y. Y.; Meetsma, A.; Teuben, J. H.; Evens, G. G. *Organometallics* **1992**, *11*, 362−369.
(27) Kesti, M. R.; Coates, G. W.; Waymouth, R. M. *J. Am. Chem. Soc.* **1992**, *114*, 9679−80.
(28) Stehling, U. M.; Stein, K. M.; Kesti, M. R.; Waymouth, R. M. *Macromolecules* **1998**, *31*, 2019−2027.
(29) The high conversions observed for the 4-methylpentene copolymerizations (up to 17%) introduce some error into the estimates for the reactivity ratios due to the possibility of compositional drift in the feed ratios. However, the accuracy of the reactivity ratios for the aminopentene/hexene copolymerizations with (EBTHI)$ZrCl_2$/MAO system are not likely to be influenced by compositional drift due to the nearly ideal copolymerization behavior for this system (Figure 1) that is close to the azeotropic condition.
(30) Odian, G. *Principles of Polymerization*, 3rd ed.; John Wiley and Sons: New York, 1991; p 768.
(31) The average temperature of the glovebox atmosphere was 22 °C (±0.5 °C) and temperature of the toluene solution was 28 °C (±0.8 °C) before and after the polymerizations due to heat from the magnetic stirrer. We determined an increase of the temperature for hexene homopolymerizations from 27.2 to 37.3 °C within the first 4 min after addition of hexene while the temperature increased from 28.4 to 30.2 °C within the first 9 min in the case of aminopentene. Therefore, we carried out homopolymerizations in Schlenk flasks in a waterbath outside the glovebox and stopped the polymerizations after 5 min (hexene) or 1 h (aminopentene) to get activities and molecular weights under isothermal conditions. These control experiments suggest that the tertiary amines have little influence on the degree of polymerization (Table S5 in Supporting Information).
(32) Asanuma, T.; Nishimori, Y.; Ito, M.; Uchikawa, N.; Shiomura, T. *Polym. Bull.* **1991**, *25*, 567−570.
(33) Ma, S.; Chen, M.-C.; Wang, S.-P. *J. Appl. Polym. Sci.* **1994**, *51*, 1861−1874.
(34) Asakura, T.; Demura, M.; Nishiyama, Y. *Macromolecules* **1991**, *24*, 2334−2340.
(35) Soga, K.; Yanagihara, H.; Lee, D. *Makromol. Chem.* **1989**, *190*, 37−40.
(36) For the $Cp_2$*$ZrMe_2$/borate catalyst system, the activities for aminopentene and hexene were similar.
(37) Jordan, R. F.; Bajgur, C. S.; Willett, R.; Scott, B. *J. Am. Chem. Soc.* **1986**, *108*, 7410−11.
(38) Rabek, J. F. *Photostabilization of Polymers: Principles and Applications*, 1st ed.; Elsevier Applied Science: London, 1990; p 595.
(39) Kulshreshtha, A. K. In *Handbook of Polymer Degradation*; Hamid, S. H., Amin, M. B., Maadhah, A. G. Eds.; Environmental Science and Pollution Control Series; Marcel Dekker: New York, 1992; pp 55−94.
(40) In the case of hexene/aminopentene copolymerizations with the catalyst system EB(THI)$ZrMe_2$/borate polymer compositions were determined from monomer consumption (monitored by GC measurement) and $^{13}$C NMR measurements independently. The GC measurements showed a poor reproducibility of the amine concentration which is reflected in a large standard deviation of the calculated reactivity ratios ($r_1$(amine) = 1.23 ± 0.35, and $r_2$ = 0.72 ± 0.22). The NMR-evaluation method seemed to be more reliable ($r_1$(amine) = 1.11 ± 0.08, and $r_2$ = 0.87 ± 0.07) and was therefore used for all copolymerizations.
(41) Activities were calculated in this paper by using average monomer concentrations of the chosen polymerization time segments. This results in higher activity numbers compared to calculations from initial monomer concentrations (as done in ref 28).
(42) By setting eq 1 equal to eq 2, it can be easily seen that $x_1 = 3.5x_2$.
(43) Stehling, U. M.; Malmstrom, E. E.; Waymouth, R. M.; Hawker, C. J. *Macromolecules* **1998**, *31*, 4396−4398.

MA980856C