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Microstructure of Ethylene−1-Butene Copolymers Produced by Zirconocene/Methylaluminoxane Catalysis

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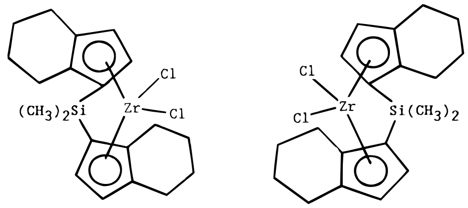
ABSTRACT: Low molecular weight (ca. 2000) ethylene−1-butene copolymers were synthesized at 90 °C using *rac*-(dimethylsilyl)bis(4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride (**I**) catalyst and methylaluminoxane (MAO) cocatalyst. Comonomer composition, triad sequence distribution, and end groups were analyzed by ^{1}H and ^{13}C NMR. The average polymer molecule contains about one double bond and one saturated end group. The unsaturated end groups were formed almost exclusively by transfer from propagating chains containing 1-butene as the terminal unit. At least 98% of the unsaturated end groups are vinylidene and trisubstituted double bonds, which are present in the approximate ratio 3:1. Saturated end groups result from the initiation process. Both ethylene and 1-butene are involved in initiation, but ethylene more than 1-butene. The product is a random copolymer with very short blocks (no longer than 2−3 monomer units) of both ethylene and 1-butene. The comonomer sequence distributions determined by ^{13}C NMR were fitted to first-order Markovian statistics, which allowed calculation of the monomer reactivity ratios. The results are discussed in terms of a reaction mechanism consisting of initiation, propagation, and chain transfer reactions.

Introduction

Studies of the microstructure of ethylene copolymers have focused mostly on comonomer sequence distribution.[1−9] The structural studies have indicated that polymer molecular weight is controlled by various chain transfer reactions, mostly β-hydride transfer but also β-alkyl transfer and chain transfer to aluminum.[10,11] A better understanding of the polymerization mechanism requires not only the polymer sequence distribution, which gives information on the propagation step, but also the polymer end groups, which give information on the initiation and termination steps. Elucidation of the polymer end groups includes the end groups that are saturated or unsaturated (and what type of double bond) and also the sequence of monomer units at the end groups (e.g., for ethylene−(E)-1-butene (B) copolymers, EE, BB, BE, or EB).

This research describes the microstructure of two ethylene−1-butene copolymers synthesized using *rac*-$(CH_3)_2Si(H_4Ind)_2ZrCl_2$ (**I**) catalyst and methylaluminoxane cocatalyst (MAO), $[Al(CH_3)O]_n$. Soluble metallocene catalysts such as **I** are of increasing technological importance because of their potential for finer control of molecular weight, molecular weight distribution, and polymer microstructure.



Ia Ib

Experimental Section

Polymerization. The catalyst−cocatalyst mixture was prepared in a drybox. MAO was obtained as a 10 wt % solution in toluene from Schering and used without further purification. The *rac*-(dimethylsilyl)$(H_4Ind)_2ZrCl_2$ catalyst (**I**) was synthesized according to the literature procedure[12] and used at a concentration of 3.6×10^{-6} M with MAO:Zr molar ratios of 500:1 and 1000:1 for samples 1 and 2, respectively.

[⊗] Abstract published in *Advance ACS Abstracts,* February 15, 1996.

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Ethylene, 1-butene, and butane were obtained from Mathieson and purified by treatment with 4 Å molecular sieves. Copolymerizations of ethylene and 1-butene were carried out at 90 ± 1 °C at about 20 bar in a continuous flow stirred reactor. The feed into the reactor contained 4.3 M 1-butene in butane with ethylene:1-butene molar ratios of 1:4.76 and 1:1.15 for samples 1 and 2, respectively. Gas chromatographic analysis of the reaction mixture showed that the ethylene conversions were 96.2 and 99.4%, respectively, and 1-butene conversions were 43.5 and 69.1%, respectively, for samples 1 and 2. The ethylene:1-butene molar ratio in the reactor was 1:71 and 1:59, respectively, for samples 1 and 2. Thus, the effective ethylene−1-butene molar ratio in the reaction mixture at steady state was much richer in 1-butene than the feed composition because of the greater conversion of ethylene compared to 1-butene, a consequence of the higher reactivity of ethylene relative to 1-butene.

Copolymer samples were obtained by quenching aliquots of the exiting reaction mixture with aqueous NaOH solution. The organic layer was separated and then washed with water several times. Volatile materials were removed using a rotary evaporator, and the polymer was subsequently dried at 45 °C in a vacuum oven (<1 Torr) for 2 days prior to NMR analysis.

NMR Analysis. ^{1}H NMR spectra of the copolymer samples were obtained on a Varian 500 MHz spectrometer; ^{13}C NMR spectra were obtained on a Varian 300 MHz spectrometer. The conditions for quantitative ^{1}H NMR were 10% (wt/vol) sample in CDCl$_3$, 40 °C, 30° pulse angle, 3 s delay between pulses, 12 000 scans, TMS as internal reference. The conditions for quantitative ^{13}C NMR were 20% (wt/vol) sample in CDCl$_3$, 15 mg/mL Cr(AcAc)$_3$ added, 40 °C, 90° pulse angle, inverse gated decoupling with 3 s delay, 50 000 scans, TMS as internal reference. ^{13}C DEPT (135° ^{1}H pulse) was run under the same conditions as the quantitative ^{13}C NMR. Primary (1°) and tertiary (3°) carbons show positive signals, secondary (2°) carbons show negative signals, and quaternary (4°) carbons do not show signals.

^{13}C NMR data were useful for analysis of saturated end groups and sequence distribution; ^{1}H NMR signals were too poorly resolved for this analysis. Analysis of unsaturated end groups employed both ^{1}H and ^{13}C NMR data. The ^{1}H NMR signal assignments for unsaturated end groups were based on comparisons with double bond model compounds. The ^{13}C NMR signal assignments were based on the following principles:

1. Qualitative and quantitative consistency is required between ^{1}H and ^{13}C NMR signal assignments.
2. Internal consistency is required in the ^{13}C NMR signal assignments, e.g., the two carbons of a double bond must have about equal signal areas.
3. The assignments are correlated with the ^{13}C DEPT NMR spectrum.
4. The observed ^{13}C chemical shifts were compared with calculated chemical shifts[13,14] for a wide variety of end groups and monomer sequences.
5. The assignments of major double bond carbon signals were aided by correlation with signal assignments for single bond carbons α and β to the double bond. Chemical shift values of single bond carbons were calculated using the Grant and Paul parameters,[15] the results for carbons α and β to double bonds were corrected using the following correlations: 3−4 ppm correction for 2° and 3° allylic carbons and about 10 ppm correction for 4° allylic carbons.[16] Corrections of up to 1−2 ppm were required for single bond carbons β to a double bond.

Molecular Weight. Molecular weights were determined by size-exclusion chromatography (SEC), NMR, and vapor pressure osmometry (VPO). SEC was performed at ambient temperature using a Waters 150C instrument, THF as the mobile phase, a set of three Ultrastyragel columns (10^4, 10^3, and 500 Å) as the stationary phase, and calibration with polyisobutylene standards. Molecular weights were calculated from ^{1}H and ^{13}C NMR by comparing the signal areas for the single and double bond regions. Molecular weights by VPO were performed using a Jupiter instrument at 50 °C with toluene as the solvent.

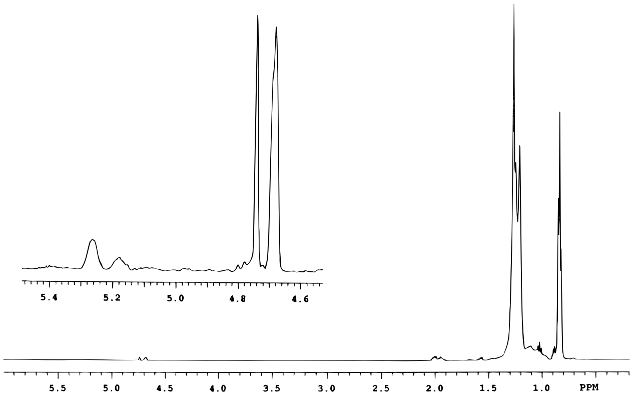


Figure 1. 500 MHz ^{1}H NMR of ethylene−1-butene copolymer sample 2.

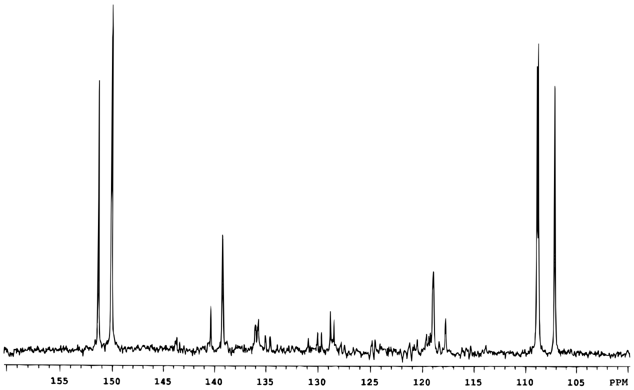


Figure 2. 75 MHz ^{13}C NMR of double bond region of ethylene−1-butene copolymer sample 2.

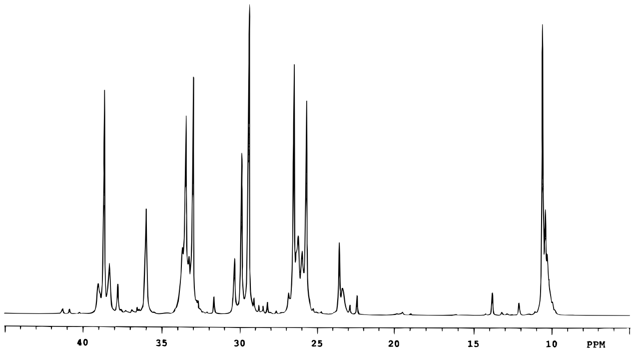


Figure 3. 75 MHz ^{13}C NMR of single bond region of ethylene−1-butene copolymer sample 2.

Results

Copolymer Composition. Figures 1−3 illustrate the NMR spectra of ethylene−1-butene copolymers. The methyl signals of the 1-butene units, upfield from 0.95 and 11 ppm, respectively, in the ^{1}H and ^{13}C NMR, are well separated from other signals and their integration relative to all other signals yielded the copolymer composition (Table 1). The results from ^{1}H and ^{13}C NMR were in good agreement, 32.4 vs 34.8 mol % ethylene for sample 1 and 56.2 vs 58.3 mol % ethylene for sample 2. In good agreement with the NMR results, the copolymer compositions calculated from the overall conversions of ethylene and 1-butene were 32.6 and 55.6 mol % ethylene for the two samples.

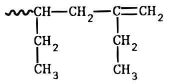
End Groups. End group analysis was facilitated in this study by the use of very low molecular weight (ca.

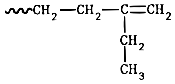
Table 1. Copolymer Composition, Molecular Weight, and Double Bond Composition of Ethylene−1-Butene Copolymers

		sample 1	sample 2
mol % E	^{1}H NMR	32.4	56.2
	^{13}C NMR	34.8	58.3
$\bar{M}_n$	^{1}H NMR	2030	2350
	^{13}C NMR	1810	1920
	SEC	1700	2110
	VPO	2060	2420
MWD (SEC)		2.05	2.17
double bond end groups by ^{1}H NMR	$CH_2{=}C\langle$	75.0	73.1
	$-CH{=}C\langle$	23.0	25.1
	$-CH{=}CH-$	1.0	1.4
	$CH_2{=}CH-$	0	0.4
double bond end groups by ^{13}C NMR	1-type	61.8	43.7
	2-type	11.2	24.4
	3-type	11.7	19.1
	4-type	14.0	11.8
	$-CH{=}CH-$	1.3	1.0

2000) polymers coupled with large numbers of NMR acquisitions. Signals for vinylene, trisubstituted, vinyl, and vinylidene double bonds are expected in the ^{1}H NMR spectrum at 5.5−5.3, 5.3−5.1, 5.1−4.8, and 4.8−4.6 ppm, respectively.[13] Figure 1 shows the ^{1}H NMR spectra of sample 2. Vinylidene is the major double bond end group. Also there is a significant amount of trisubstituted double bond end group (Table 1). Vinylidene and trisubstituted double bonds are in the approximate ratio 3:1. Vinyl and vinylene double bond end groups appear to be present in trace amounts (<1%).

Vinylidene Double Bonds. The major vinylidene ^{1}H NMR signals were identified as a doublet at 4.74 and 4.68 ppm. The ratio of the signal area at 4.68 ppm compared to that at 4.74 ppm was smaller for sample 1, which had the lower ethylene content, than for sample 2. The NMR signals correspond to the two vinylidene end groups **1** and **2**. **1** and **2** have terminal 1-butene units and the penultimate unit is 1-butene for **1** but ethylene for **2**. The geminal vinylidene protons of **2** are very similar and one signal at 4.68 ppm is found. The chemical shifts of the two geminal vinylidene protons of **1** are more different than those of **2**, and separate signals of equal area at 4.74 and 4.68 ppm are found. Copolymer sample 1, containing less ethylene than sample 2, has a lower content of **2**, and this resulted in a smaller signal area at 4.68 ppm. The ratio **1**:**2** is 5.9:1 and 2.1:1 for copolymer samples 1 and 2, respectively.


1

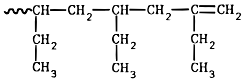

2

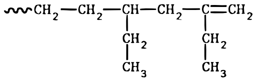
The ^{13}C NMR results verified the assignments for vinylidene end groups **1** and **2** (Figures 2 and 3, Table 2). The pair of signals at 150.2 and 109.1 ppm are assigned to structure **1**, which has calculated chemical shift values of 148.0 and 109.4 ppm. The pair of signals at 151.5 and 107.4 ppm is assigned to structure **2**, which has calculated chemical shift values of 150.3 and 107.9 ppm. These assignments are consistent with the observed ^{13}C DEPT NMR spectrum, which showed that the signals at 151.5 and 150.2 ppm are quaternary carbons and the signals at 109.1 and 107.4 ppm are secondary carbons. For copolymer samples 1 and 2, the ratio **1**:**2** by ^{13}C NMR is 5.9:1 and 2.0:1 for samples 1 and 2, respectively, consistent with the ^{1}H NMR results.

Table 2. ^{13}C NMR End Group and Repeat Unit Assignments

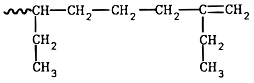
δ (PPM)	assignment	δ (PPM)	assignment
151.5, 107.4	**2**	32.0	**8**
150.2, 109.1	**1**	30.7	S$_{\gamma\gamma}$-BEEB
140.5, 118.1	**3B**	30.2	S$_{\gamma\delta}$-BEEEB
139.4, 119.2	**3A**	29.8	S$_{\delta\delta}$-BEEEEB
138.0, 123.1	**3C**	29.4	**8**
136.2, 128.6	**4D**$_E$	29.1	**7**
135.9, 129.0	**4C**$_E$	28.8	**2**
135.1, 119.4	**4A**	28.5	**1**
134.6, 119.8	**4B**	28.0	**2**
130.9, 127.4	**5A**	27.2	S$_{Br}$-BBBB
136.0, 130.1	**4C**$_Z$	26.8	S$_{\beta\delta}$-EBEE + S$_{Br}$-EBBBE
136.0, 129.7	**4D**$_Z$	26.6	S$_{\beta\delta}$-BBEE + S$_{Br}$-BBBE
41.6	**1A**	26.3	S$_{Br}$-EBBE
41.1	**1B**	26.1	S$_{Br}$-EBE
40.5	**3A**	23.9	S$_{\beta\beta}$-EBEBE
39.4	S$_{\alpha\alpha}$-BBBB	23.7	S$_{\beta\beta}$-BBEBE
39.0	T$_{\delta\delta}$-EBE	23.2	**7**
38.7	S$_{\alpha\alpha}$-BBBE	22.7	**8**
38.1	S$_{\alpha\alpha}$-EBBE	19.7	**11**
36.9	**2**	14.1	**7** + **8**
36.4	T$_{\beta\delta}$-EBB	13.5	**3A**
34.0	T$_{\beta\beta}$-BBB	12.4	**1** + **2**
33.8	S$_{\alpha\gamma}$-EBEB	10.9	CH$_3$-EBE
33.6	S$_{\alpha\beta}$-BBEE	10.7	CH$_3$-BBE
33.4	S$_{\alpha\delta}$-EBEE	10.6	CH$_3$-BBB

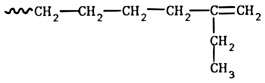
Close inspection of the two ^{13}C NMR signals for **1** showed each signal to be a pair of signals. This was interpreted in terms of end groups **1A** and **1B**,differing in the identity of the penpenultimate unit. **1A** and **1B** have exactly the same calculated double bond carbon and side chain allylic carbon chemical shift values, but different chemical shift values for the backbone allylic carbons. Further support for the presence of **1A** and **1B** came from the ^{13}C NMR single bond region. There are signals at 41.6 and 41.1 ppm for the backbone allylic carbons of **1A** and **1B**, respectively, with calculated chemical shift values of 40.5 and 40.0 ppm. There is one signal at 28.6 ppm for the side chain allylic methylene carbon. The calculated chemical shift value is 28.1 ppm for both **1A** and **1B**. Support for the assignments of **1A** and **1B** was also found from the observations that the sum of the signal areas at 41.6 and 41.1 ppm equals the signal area at 28.6 ppm, and the ratio of the signal area at 41.6 ppm to that at 41.1 ppm decreases with increasing ethylene content in the copolymer.


1A


1B

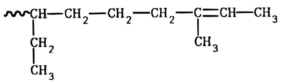
End group **2** may also be present in the corresponding variations **2A** and **2B**, but there was no supporting evidence due to the closeness of chemical shift values of the two structures.


2A


2B

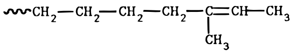
The total vinylidene contents found by ^{13}C NMR, a total of 73.0 and 68.1% for samples 1 and 2, respectively, are in agreement with the results from ^{1}H NMR (75.0 and 73.1%).

Trisubstituted Double Bonds. The 5.1−5.3 ppm region of the ^{1}H NMR spectrum indicated the presence of more than one type of trisubstituted double bond end group (Figure 1). Analysis of the ^{13}C NMR double bond region (Figure 2; Table 2) showed that there are at least six different trisubstituted double bond end groups: end groups **3A**, **3C**, **4A**, **4B**, **4C**, and **4D**for sample 1 and



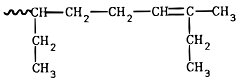
$\sim CH(CH_2CH_3)-CH_2-CH_2-CH_2-C(CH_3)=CH-CH_3$

3A



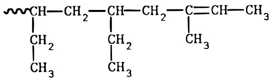
$\sim CH_2-CH_2-CH_2-CH_2-C(CH_3)=CH-CH_3$

3B



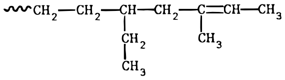
$\sim CH(CH_2CH_3)-CH_2-CH_2-CH=C(CH_2CH_3)-CH_3$

3C



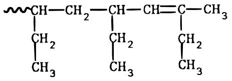
$\sim CH(CH_2CH_3)-CH_2-CH(CH_2CH_3)-CH_2-C(CH_3)=CH-CH_3$

4A



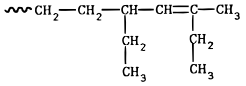
$\sim CH_2-CH_2-CH(CH_2CH_3)-CH_2-C(CH_3)=CH-CH_3$

4B



$\sim CH(CH_2CH_3)-CH_2-CH(CH_2CH_3)-CH=C(CH_2CH_3)-CH_3$

4C



$\sim CH_2-CH_2-CH(CH_2CH_3)-CH=C(CH_2CH_3)-CH_3$

4D

end groups **3A**, **3B**, **4A**, **4B**, **4C**, and **4D** for sample 2. Signals for both *E* and *Z* isomers were assigned for end groups **4C** and **4D** with the *E* isomers in greater abundance. (*E* and *Z* refer to *trans* and *cis* placements, respectively, of the larger alkyl groups on each of the carbons of the double bond.) The *E* and *Z* isomers are indicated by subscripts *E* and *Z* in Table 2. Separate signals for *E* and *Z* isomers of **3A**, **3B**, **3C**, **4A**, and **4B** were not observed. Both *E* and *Z* isomers are assumed to be present but not observed due to the overlapping of signals.

For sample 1, the predominant **3**-type of trisubstituted double bond is **3A** while the predominant **4**-type of trisubstituted double bond is **4A**. For sample 2, the predominant **3**-type of trisubstituted double bond is **3A** with significant amounts of **3B** while the predominant **4**-type of trisubstituted double bond has comparable amounts of **4A** and **4B**. The relative amounts of **3**-type and **4**-type are comparable, somewhat more **4**-type for sample 1 but somewhat less **4**-type for sample 2.

The total trisubstituted double bond contents by ^{13}C NMR, 25.7 and 30.9% for samples 1 and 2, respectively, are in agreement with the results from ^{1}H NMR (23.0 and 25.1%).

Vinylene and Vinyl Double Bonds. NMR indicated the presence of very small amounts (no more than about 1%) of vinylene and vinyl double bonds. The amounts were near the detection limits for both ^{1}H and ^{13}C NMR. ^{13}C NMR spectra identified **5A** as the vinylene end group. Vinyl double bonds **6**, although detected by ^{1}H NMR, were not observed in the ^{13}C NMR.

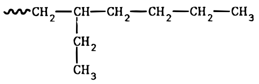
$\sim CH_2-CH_2-CH=CH-CH_3$

5A

$\sim CH=CH_2$

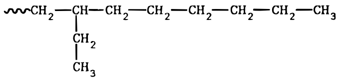
6

Saturated End Groups. The ^{13}C NMR single bond region (the signals upfield of 42 ppm in Table 2) indicated two major saturated end groups, **7** and **8**.



$\sim CH_2-CH(CH_2CH_3)-CH_2-CH_2-CH_2-CH_3$

7



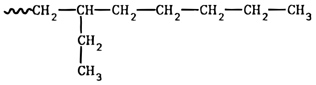
$\sim CH_2-CH(CH_2CH_3)-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$

8

Table 3. Comonomer Distribution Statistics

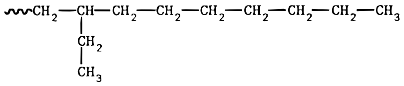
	^{13}C NMR triad distribution		first-order Markovian statistics	
	sample		sample	
	1	2	1	2
[EEE]	0.04	0.19	0.03	0.21
[EEB + BEE]	0.12	0.26	0.12	0.30
[BEB]	0.16	0.14	0.15	0.11
[EBE]	0.11	0.20	0.06	0.18
[BBE + EBB]	0.22	0.13	0.29	0.16
[BBB]	0.36	0.08	0.35	0.04
[E]	0.32	0.59	0.30	0.62
[B]	0.68	0.41	0.70	0.38
n_E	1.5	3.2		
n_B	2.2	1.6		
r_E			30	83
r_B			0.034	0.0078
r_Er_B			1.02	0.65

Structure **8** differs from **7** in having two additional methylene units at the chain end. The chemical shift values assigned to **7** and **8** are also consistent with **9** and **10**,each of which has one additional methylene unit at the chain end compared to **7** and **8**. However, mechanistic considerations (see Discussion) indicate that **7** and **8** exceed **9** and **10** by a factor of about 10 000.



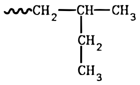
$\sim CH_2-CH(CH_2CH_3)-CH_2-CH_2-CH_2-CH_2-CH_3$

9



$\sim CH_2-CH(CH_2CH_3)-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$

10



$\sim CH_2-CH(CH_2CH_3)-CH_3$

11

Structure **11** was assigned as a minor saturated end group based on the small ^{13}C NMR signals near 20 ppm.

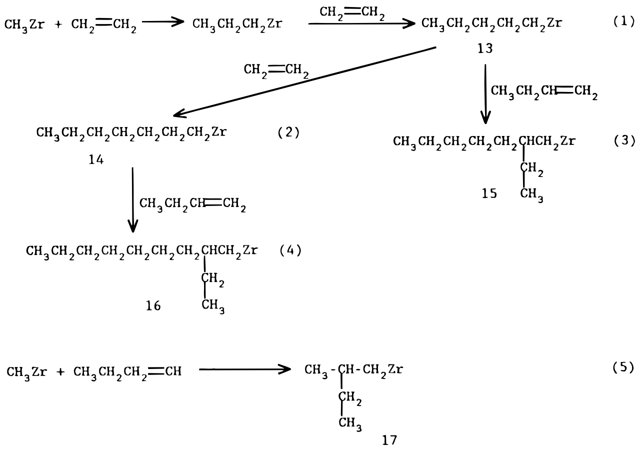
The ratio of saturated end groups **7**:**8**:**11** is 51:41:8 and 34:53:13 for samples 1 and 2, respectively. Overall, the saturated end groups are in excess of the unsaturated end groups by 10–20% for both copolymer samples. Experimental limitations prevent a more precise evaluation of the ratio of saturated to unsaturated end groups because the saturated and unsaturated end groups each comprise only about 2% of the polymer.

Polymer Molecular Weight. SEC yielded $\bar{M}_n$ = 1700 and 2110 for samples 1 and 2, respectively. $\bar{M}_n$ values of 2030 and 2350 were calculated from the ^{1}H NMR data for samples 1 and 2, respectively, assuming an average of one double bond per polymer molecule, by comparison of the double and single bond signal areas. The corresponding values from ^{13}C NMR data were 1810 and 1920. VPO yielded $\bar{M}_n$ = 2060 and 2420, respectively, for samples 1 and 2. The number-average molecular weights by NMR, SEC, and VPO are consistent with each other.

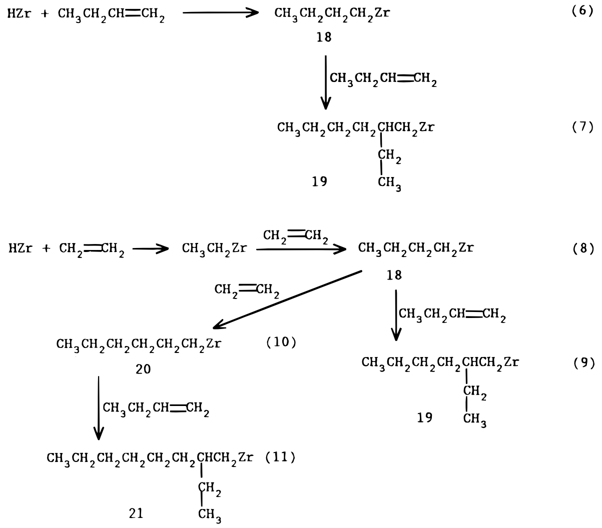
The polymer molecular weight distribution is narrow. SEC yielded $\bar{M}_w/\bar{M}_n$ = 2.05 and 2.17 for samples 1 and 2, indicative of the single-site nature of the zirconocene catalyst.

Repeat Units. The repeat unit microstructure was determined by matching calculated ^{13}C chemical shift values[15] of possible repeat units with observed chemical shift values. Signal assignments were consistent with the results of ^{13}C DEPT NMR, signal area differences between samples 1 and 2, and quantitative correlation between different carbon signals. Predominantly isotactic poly(1-butene) was used as the model for chemical

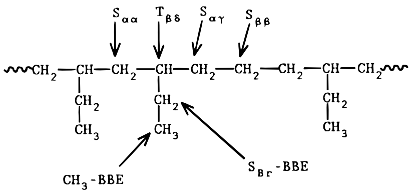
Scheme 1A. Initiation by CH_3Zr



Scheme 1B. Initiation by HZr



shift calculations of copolymer repeat units. The assignments (Table 2) are consistent with Cheng's assignments for ethylene−1-butene copolymer.[7] The nomenclature used for different repeat units is similar to the nomenclature by Carman and co-workers for ethylene/propylene copolymer.[17] The letters S and T represent secondary and tertiary carbons, respectively. Greek subscripts indicate the distance from the designated carbon to the nearest tertiary carbon atoms on the left and right sides of that carbon. The subscript Br designates the CH_2 of the ethyl branches of 1-butene units. Some examples of this nomenclature are shown in structure **12**.



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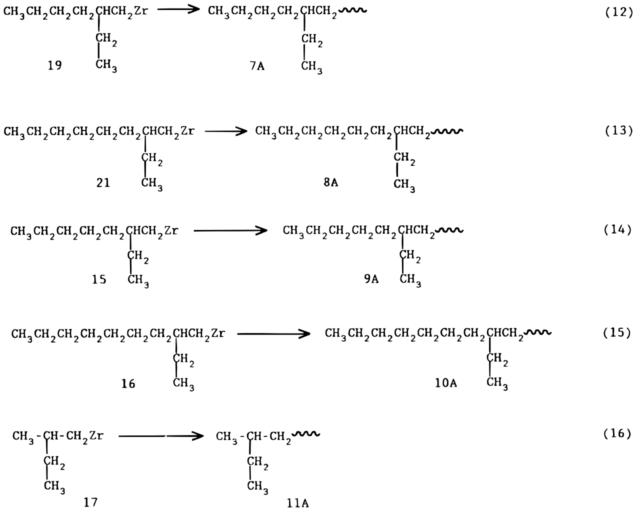
The experimental ^{13}C NMR comonomer triad distributions were determined from the repeat unit assignments (Table 3). This allowed the calculation of the overall comonomer composition, 32 and 59 mol % ethylene, respectively, for samples 1 and 2. These data were in good agreement with those obtained by comparison of the methyl signal to all other signals: ^1H and ^{13}C NMR, respectively, gave 32.4 and 34.8 mol % ethylene for sample 1 and 56.2 and 58.3 mol % ethylene for sample 2 (Table 1). The triad distribution was fitted to first-order Markovian statistics (terminal model of copolymerization) to obtain the four transition probabilities P_{EE}, P_{EB}, P_{BE}, and P_{BB} for chains terminating in ethylene and 1-butene units reacting with monomers ethylene and 1-butene.[9] (P_{XY} is the probability of monomer Y adding to a propagating chain with X as the terminal unit.) The triad distribution calculated from the transition probabilities compares well with the experimental triad distribution (Table 3). The monomer reactivity ratios for ethylene and 1-butene, r_E and r_B, were calculated[18] from the relationships

Scheme 2. Propagation Reactions



$$r_E = \frac{P_{EE}}{X(1 - P_{EE})} \qquad r_B = \frac{XP_{BB}}{(1 - P_{BB})}$$

where *X* is the molar feed ratio of ethylene to 1-butene.

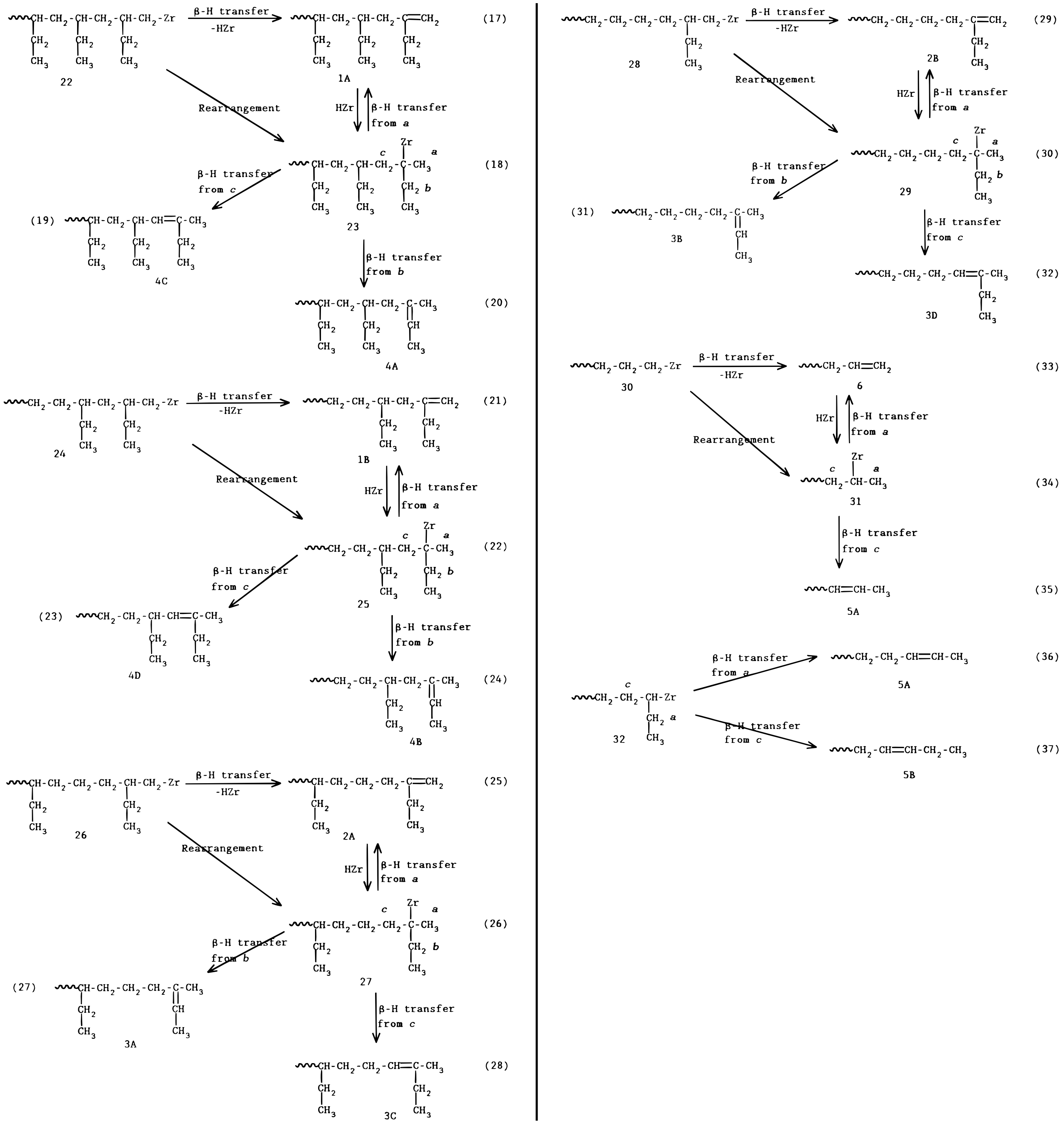
The monomer reactivity ratios are $r_E = 30$, $r_B = 0.034$ and $r_E = 83$, $r_B = 0.0078$, respectively, for samples 1 and 2 (Table 3). The ethylene−1-butene system shows *ideal* behavior: r_E is large while r_B is small, and the product of the two monomer reactivity ratios is near unity. The results are similar to literature observations on ethylene−α-olefin copolymerizations. Heiland and Kaminsky[19] observed $r_E = 29.2$, $r_B = 0.04$, and $r_Er_B = 1.2$ for ethylene−1-butene polymerization at 70 °C with *rac*-$CH_2CH_2(Ind)_2ZrCl_2$. Kaminsky and co-workers[4] observed $r_E = 85$, $r_B = 0.01$, and $r_Er_B = 0.85$ at 80 °C with Cp_2ZrCl_2. Table 3 also gives the average block lengths of ethylene and 1-butene units, n_E and n_B. The ethylene−1-butene copolymers are random with short block lengths of each monomer. 1-Butene has a low reactivity, but there are considerable amounts of 1-butene in the copolymers because of the very large amount of 1-butene relative to ethylene in the reaction mixture.

Discussion

The proposed mechanism for ethylene−1-butene copolymerization by the zirconocene−MAO initiating system is described in Schemes 1−4. The mechanism builds on that proposed for 1-butene homopolymerization.[10] The equations are simplified by showing only one of the ligands for Zr or Al.

MAO alkylates the chloride ligand of the zirconium catalyst to form the initial polymerization sites—zirconium−methyl sites (shown as CH_3Zr in eq 1 in

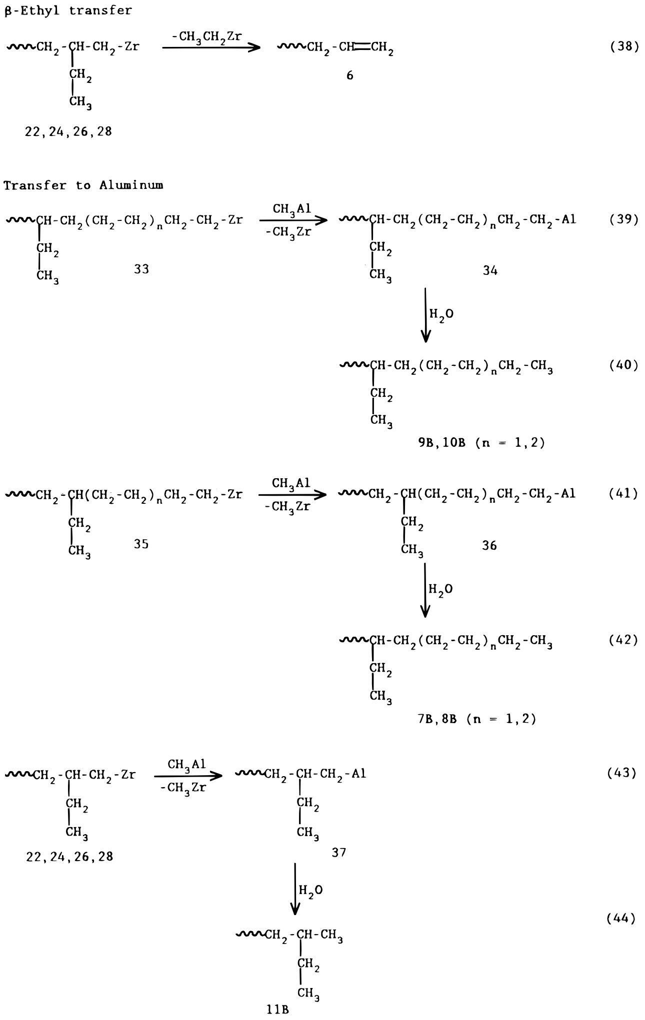
Scheme 3. β-Hydride Chain Transfer Reactions



Scheme 1A). Polymer chains are subsequently initiated by zirconium–hydride sites (shown as ZrH in eqs 6 and 8 of Scheme 1B) formed by various *β*-hydride transfer reactions (Scheme 3). The various species produced by addition of CH_3Zr (**15**, **16**, **17**) or ZrH (**19**, **21**) to monomer differ in the sequence of addition of ethylene and 1-butene monomers. Propagation of **19**, **21**, **15**, **16**, and **17** result in saturated end groups **7A**, **8A**, **9A**, **10A**, and **11**, respectively (Scheme 2). Although end groups **9A** and **10A** cannot be distinguished from **7A** and **8A** by NMR, the catalytic efficiency of the polymerization reaction indicates that initiation is carried to better than 99.99% by **19** and **21**, compared to **15** and **16** (and also compared to **17**). On the assumption that each zirconium atom is active, the calculated moles of polymer per mole of Zr catalyst is 1.69×10^4 and 2.96×10^4 mol of polymer, respectively, for samples 1 and 2. The ratio **7A**:**8A** is 51:41 and 34:53 for samples 1 and 2, respectively. The increase in this ratio for sample 1 relative to sample 2 is a consequence of the lower ethylene content in the feed for sample 1. The fact that comparable amounts of **7A** and **8A** are formed indicates the much lower reactivity of 1-butene relative to ethylene.

The major unsaturated end groups are vinylidene end groups **1** and **2**, which are formed by *β*-hydride transfer from propagating centers **22**, **24**, **26**, and **28** (eqs 17, 21, 25, 29 of Scheme 3). All propagating centers leading to vinylidene end groups have 1-butene terminal units, indicating that ethylene terminal units are much more reactive toward propagation relative to *β*-hydride transfer. Propagating centers **22**, **24**, **26**, and **28** differ only in the identity of the penultimate and pen-penultimate

Scheme 4. Other Chain Transfer Reactions



units. The ends of these chains are BBB, EBB, BEB, and EEB, respectively. Vinylidene end group **1** is formed in excess over vinylidene end group **2** (Table 1), indicative of the increased tendency of propagating chains rich in 1-butene units at penultimate and pen-penultimate positions to undergo β-hydride transfer.

The second most abundant unsaturated end groups, trisubstituted double bonds **3** and **4**, are formed by β-hydride transfer from species **23**, **25**, **27**, and **29**.[20,21] Species **23**, **25**, **27**, and **29** are formed either by rearrangement of propagating species **22**, **24**, **26**, and **28**, respectively, or by reverse addition of zirconium hydride to vinylidene end groups **1A**, **1B**, **2A**, and **2B**, respectively. β-Hydride transfers from *b* and *c* of species **23** yield **4A** and **4C** (eqs 19 and 20). β-Hydride transfers from *b* and *c* of species **25** yield **4B** and **4D** (eqs 23 and 24). β-Hydride transfers from *b* and *c* of **27** yield **3A** and **3C** (eqs 27 and 28). β-Hydride transfers from *b* and *c* of **29** yield **3B** and **3D** (eqs 31 and 32).

^{1}H NMR detected very small amounts of vinyl and vinylene end groups (Table 1). The amounts were so low (no more than about 1% each) that no vinyl signals were observed in the ^{13}C NMR spectra. The most probable route to vinyl end groups is β-hydride transfer from propagating chains possessing ethylene as the terminal unit (**30**, eq 33). An alternative route to vinyl end groups is β-ethyl transfer from propagating species with 1-butene as the terminal unit (**22**, **24**, **26**, and **28**, eq 38 in Scheme 4). The very low vinyl content (0 and 0.4% for samples 1 and 2, respectively) indicates the almost complete absence of β-ethyl transfer reactions. Propagating chains with ethylene as the terminal unit do not undergo β-hydride transfer. β-Hydride transfer occurs almost exclusively through propagating chains possessing 1-butene terminal units. The very small amount of vinylene end groups (1.0 and 1.4% for samples 1 and 2, respectively) indicates the almost negligible extent of the transfer reactions described by eqs 35−37. Again, there is negligible β-hydride transfer from propagating chains possessing ethylene as the terminal unit (eq 35). Further, the very small amount of vinylene end groups indicates there is very little β-hydride transfer from propagating centers of type **32** (eqs 36 and 37), formed by reverse (2,1) addition of 1-butene to propagating centers.

Saturated end groups are formed by the initiation processes as described above. However, chain transfer to aluminum (eqs 39−40, 41−42, 43−44) is a possible second route to saturated end groups. Chain transfer to aluminum involves ligand exchange between zirconium and aluminum from propagating chains terminating in ethylene (eqs 39 and 41) or 1-butene (eq 43). The aluminum-terminated polymers (**34**, **36**, and **37**) are converted to polymers with saturated end groups (**9B**, **10B**, **7B**, **8B**, and **11B**) when the reaction mixture is hydrolyzed. Saturated end groups **7B**, **8B**, **9B**, **10B**, and **11B**, formed by chain transfer to aluminum, are spectroscopically indistinguishable from **7A**, **8A**, **9A**, **10A**, and **11A**, respectively, formed by the initiation reactions, and this does not allow any conclusion regarding the occurrence of chain transfer to aluminum for propagating chains terminating in ethylene. By analogy to their lack of any tendency toward β-hydride transfer, it is reasonable to conclude that propagating chains terminating in ethylene also do not undergo chain transfer to aluminum because of their high reactivity toward propagation. On the other hand, the amount of saturated end group **11** is very much larger than can be accounted for by initiation with CH_3Zr. The high catalytic efficiency (1.69×10^4 and 2.96×10^4 mol of polymer/mol of Zr catalyst for samples 1 and 2, respectively) coupled with the significant amounts of saturated end group **11** (8 and 13% of saturated end groups, respectively, for samples 1 and 2) shows that less than 0.1% of saturated end group **11** (sum of **11A** and **11B**) is formed via initiation by CH_3Zr. More than 99.9% of saturated end group **11** is formed by chain transfer to aluminum for propagating chains terminating in 1-butene. Thus, there is negligible **11A**; the saturated end group **11** is all **11B**.

The extent of chain transfer to aluminum for propagating chains terminating in 1-butene is compatible with both the amount of **11B**-saturated end groups (8 and 13% of total saturated end groups for samples 1 and 2, respectively) and the ratio of saturated to unsaturated end groups [(1.1−1.2):1]. Each act of chain transfer to aluminum produces two saturated end groups: one is at the terminated propagating chain end, and the other occurs when CH_3Zr initiates a new propagating chain. The presence of 8 and 13% of **11B**-saturated end groups for samples 1 and 2, respectively, corresponds to 8 and 13% excess of saturated end groups over unsaturated end groups, close to the 10−20% excess experimentally observed.

The data on the excess of saturated over unsaturated end groups may yield information on the possibility of long chain branching in the ethylene−1-butene copolymer samples. If vinyl end groups **6** were formed (via

β-hydride transfer from propagating chains terminating in ethylene, eq 33 in Scheme 3), subsequent copolymerization of the resulting vinyl-terminated macromer with ethylene and 1-butene would introduce a long chain branch (along with a saturated end group) into the propagating chain. Each incorporated vinyl-terminated macromer would increase the ratio of saturated-to-unsaturated end groups. There were only negligible amounts (<1%) of vinyl end groups found in the copolymer samples. If significant amounts of vinyl end groups, comparable to the vinylidene or trisubstituted end groups, formed and copolymerized during the reaction, the excess of saturated over unsaturated end groups would be considerably higher than experimentally observed. The observed excess of saturated over unsaturated end groups is accounted for almost entirely, within experimental error, by chain transfer to aluminum.

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(20) An alternate mechanism for formation of trisubstituted double bonds, chain transfer to vinylidene end groups, was proposed in our previous work on 1-butene homopolymerization (see eqs 17−19 in ref 10). Recent experiments show that transfer to vinylidene end groups is absent. Performing the polymerization of 1-butene in the presence of approximately 25 mol % of 2-ethyl-1-butene or isobutylene, model compounds for vinylidene end groups, did not alter the identity or amounts of double bonds or saturated end groups.
(21) It has been suggested that trisubstituted double bonds arise by isomerization of vinylidene double bonds by acid generated during workup of the reaction mixture or during the NMR analysis (Rieger, B.; Reinmuth, A.; Roll, W.; Brintzinger, H. H. *J. Mol. Catal.* **1993**, *82*, 67). Various experiments showed that isomerization does not occur in our work. Subjecting 2-heptene and 2-methyl-1-hexene, which are model compounds for vinylene and vinylidene end groups, to our experimental procedures (polymerization, alkaline workup of reaction mixture, and NMR analysis) did not result in any isomerization. There was also no isomerization observed when 3-methyl-2-pentene, a model compound for trisubstituted double bonds, or polymer samples were cycled through the polymerization, workup, and NMR procedures.

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