

## End Groups in 1-Butene Polymerization via Methylaluminoxane and Zirconocene Catalyst

Albert Rossi\*

Exxon Chemical Company, Linden, New Jersey 07036

George Odian\* and Jianbin Zhang

College of Staten Island, City University of New York, Staten Island, New York 10314

Received October 5, 1994; Revised Manuscript Received December 19, 1994\*

**ABSTRACT:** Poly(1-butene) was obtained by polymerization of 1-butene at 100 °C using *rac*-(dimethylsilyl)bis(4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride (I) as catalyst and methylaluminoxane (MAO) as cocatalyst. The product was characterized by NMR (<sup>1</sup>H and <sup>13</sup>C), size exclusion chromatography (SEC), and vapor pressure osmometry (VPO). The number-average molecular weight of the polymer was determined as 1910, 2025, and 2055 by SEC, VPO, and NMR, respectively. The poly(1-butene) is 84% isotactic and has high regioselectivity (ca. 95% 1,2-addition). Both saturated and unsaturated end groups were characterized by NMR. Vinylidene and trisubstituted double bonds comprise approximately 67% and 29%, respectively, of the unsaturated end groups with the remainder consisting of vinylene, vinyl, and tetrasubstituted double bonds. *n*-Butyl and *sec*-butyl groups constitute the saturated end groups in the approximate ratio 10:1. There is a slight excess of saturated end groups relative to unsaturated end groups. These results are discussed in terms of a reaction mechanism of initiation and propagation with various chain-transfer reactions ( $\beta$ -hydride transfers with and without rearrangement, transfer to aluminum, transfer to vinylidene end groups, and  $\beta$ -alkyl transfer).

## Introduction

Both bridged and unbridged metallocene catalysts, e.g., ethylenebis(indenyl)zirconium dichloride and bis(cyclopentadienyl)zirconium dichloride, in the presence of methylaluminoxane (MAO), [O–Al(CH<sub>3</sub>)<sub>3</sub>]<sub>n</sub>, have been studied for the homogeneous polymerization of  $\alpha$ -olefins such as propene and 1-butene.<sup>1–3</sup> These catalysts are single-site catalysts which show high activity coupled with high stereospecificity (usually isospecific) and narrow molecular weight distributions.<sup>4</sup> The mechanism for formation of unsaturated end groups during polymerizations with these catalysts is not well-established, probably because the reaction is very sensitive to monomer, catalyst, cocatalyst, temperature, and other reaction conditions.

$\beta$ -Hydride transfer,  $\beta$ -alkyl transfer, and chain transfer to aluminum have been reported as the molecular weight limiting reactions in propene polymerization, but the relative importance of the three reactions is sensitive to the specific system. Catalyst identity does not appear to be important in the temperature range 0–80 °C unless the catalyst is sterically hindered. Polymerization proceeds exclusively by  $\beta$ -hydride transfer using catalysts such as Cp<sub>2</sub>ZrCl<sub>2</sub> and Cp<sub>2</sub>HfCl<sub>2</sub> (Cp = cyclopentadienyl) and CH<sub>2</sub>CH<sub>2</sub>- and (CH<sub>3</sub>)<sub>2</sub>Si-bridged Ind<sub>2</sub>ZrCl<sub>2</sub> and (H<sub>4</sub>Ind)<sub>2</sub>ZrCl<sub>2</sub> [Ind = 1-indenyl, H<sub>4</sub>Ind = 4,5,6,7-tetrahydro-1-indenyl].<sup>3,5–7</sup> At lower temperatures and/or with more sterically hindered catalysts,  $\beta$ -alkyl transfer and/or chain transfer to aluminum become important. For example, polymerization with (CH<sub>3</sub>)<sub>5</sub>CpCpZrCl<sub>2</sub> proceeds with 80%  $\beta$ -hydride transfer

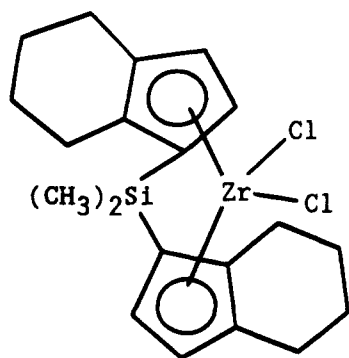
and 20% chain transfer to aluminum at 50 °C, while only chain transfer to aluminum occurs at –30 °C.<sup>2</sup> Polymerization with [(CH<sub>3</sub>)<sub>5</sub>Cp]<sub>2</sub>ZrCl<sub>2</sub> proceeds with 91%  $\beta$ -methyl transfer, 8%  $\beta$ -hydride transfer, and 1% chain transfer to aluminum at 50 °C, while chain transfer to aluminum occurs exclusively at –40 °C.<sup>5</sup> Polymerization by cationic zirconocenes such as [(CH<sub>3</sub>)<sub>5</sub>Cp]<sub>2</sub>ZrR<sup>+</sup>Z<sup>–</sup>, where Z is a stable anion such as BPh<sub>4</sub><sup>–</sup>, proceeds almost exclusively by  $\beta$ -methyl transfer at 0 °C.<sup>8,9</sup>

Much less is available in the literature on mechanisms for formation of unsaturated end groups for 1-butene polymerization.  $\beta$ -Hydride transfer is the exclusive reaction for Cp<sub>2</sub>ZrCl<sub>2</sub> at 0 °C.<sup>5</sup> Chain transfer to aluminum becomes important for polymerization by [(CH<sub>3</sub>)<sub>5</sub>Cp]<sub>2</sub>ZrCl<sub>2</sub>. The ratio of chain transfer to aluminum to  $\beta$ -hydride transfer increases from 1:3 to 2:1 as the polymerization temperature decreases from 50 to 0 °C.<sup>5</sup> Chain transfer to aluminum is the exclusive reaction for CH<sub>2</sub>CH<sub>2</sub>-bridged Ind<sub>2</sub>Ti(CH<sub>3</sub>)<sub>2</sub> at –45 °C.<sup>10</sup>  $\beta$ -Hydride transfer, but exclusively after reverse addition of monomer (all other  $\beta$ -hydride transfers discussed above occur after normal propagation), is the only transfer reaction for polymerization by CH<sub>2</sub>CH<sub>2</sub>-bridged Ind<sub>2</sub>ZrCl<sub>2</sub> at 30 °C.<sup>11</sup> There are very few other reports of transfer reactions in  $\alpha$ -olefin polymerizations except for the report of chain transfer to aluminum as the exclusive reaction in 1,5-hexadiene cyclopolymerization by Cp<sub>2</sub>ZrCl<sub>2</sub> at –25 °C.<sup>12</sup>

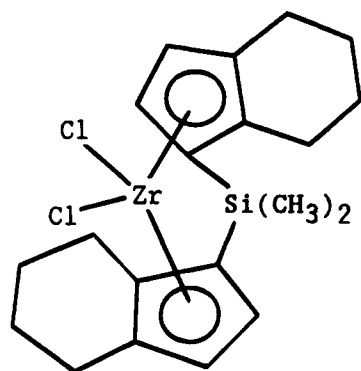
We report here our studies on the chain-transfer reactions which control molecular weight in the polymerization of 1-butene catalyzed by *rac*-(dimethylsilyl)-(H<sub>4</sub>Ind)<sub>2</sub>ZrCl<sub>2</sub> (I) in the presence of methylaluminoxane

\* Abstract published in *Advance ACS Abstracts*, February 15, 1995.

(MAO).  $^1\text{H}$  and  $^{13}\text{C}$  NMR was used for analysis of end groups formed by chain-transfer reactions.



Ia



Ib

## Experimental Section

**Polymerization.** 1-Butene, 98.5% in isobutane, was obtained from Mathieson and polymerized without further purification. MAO was obtained as a 10 wt % solution in toluene from Schering and used without further purification. The zirconocene catalyst I, synthesized according to the literature procedure,<sup>13,14</sup> was used at a concentration of  $7.1 \times 10^{-6}$  M with a MAO:Zr ratio of 1000:1. Various precautions were taken to exclude moisture and perform the polymerization in an inert atmosphere. The catalyst-cocatalyst mixture was prepared in a drybox, and the monomer feed was dried over molecular sieves. Polymerization of 1-butene to an overall conversion of 60% was carried out in a continuous-flow stirred reactor at 100 °C. The reaction mixture was quenched by treatment with aqueous base (10% NaOH) followed by water and then filtered. Water and toluene were removed from the filtrate to yield the poly(1-butene) sample by heating at 140 °C for 2 min at atmospheric pressure followed by drying in a vacuum oven (<1 Torr) for 2 days either at room temperature or 45 °C.

**NMR Analysis.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of polymer samples were obtained on a JEOL 400 MHz instrument. The conditions used for quantitative  $^1\text{H}$  NMR were 10% (wt/vol) sample in  $\text{CDCl}_3$ , 40 °C, 30° pulse angle, 3 s delay between pulses, 500 scans, and TMS as internal reference. The conditions used for quantitative  $^{13}\text{C}$  NMR were 20% (wt/vol) sample in  $\text{CDCl}_3$ , 25 mg/mL  $\text{Cr}(\text{AcAc})_3$  added, 40 °C, 90° pulse angle, inverse gated decoupling with 3 s delay, 12 000 scans, and TMS as internal reference. For both  $^1\text{H}$  and  $^{13}\text{C}$  NMR, it was verified that the 3 s delay was sufficient for quantitative results by performing experiments with 10 s delays.  $^{13}\text{C}$  DEPT NMR (135°  $^1\text{H}$  pulse) was run under the same conditions as the quantitative  $^{13}\text{C}$  NMR. Primary and tertiary (1° and 3°) carbons show positive signals, secondary (2°) carbons show negative signals, and quaternary (4°) carbons do not show signals.

$^{13}\text{C}$ - $^1\text{H}$  shift-correlated 2D NMR was run on the same sample used for quantitative  $^{13}\text{C}$  NMR.

Only  $^{13}\text{C}$  NMR data were useful for analyses of saturated end groups and repeat unit stereochemistry and regioselectivity.  $^1\text{H}$  NMR signals were insufficiently resolved for these analyses. Analysis of unsaturated end groups used both  $^{13}\text{C}$  and  $^1\text{H}$  NMR data. The  $^{13}\text{C}$  NMR signal assignments were based on several considerations.

1. Qualitative and quantitative consistency is needed between  $^{13}\text{C}$  and  $^1\text{H}$  NMR signal assignments.

2. Internal consistency is needed in the  $^{13}\text{C}$  signal assignments; e.g., the two carbons of a double bond must have reasonably equal signal areas.

3. The assignments need to correlate with the DEPT  $^{13}\text{C}$  NMR spectrum.

4. The observed  $^{13}\text{C}$  chemical shifts were compared to calculated chemical shifts for a wide variety of double-bond carbons.<sup>15,16</sup> Signal assignments were considered acceptable if the difference between calculated and observed chemical shifts was no greater than 2–3 ppm.

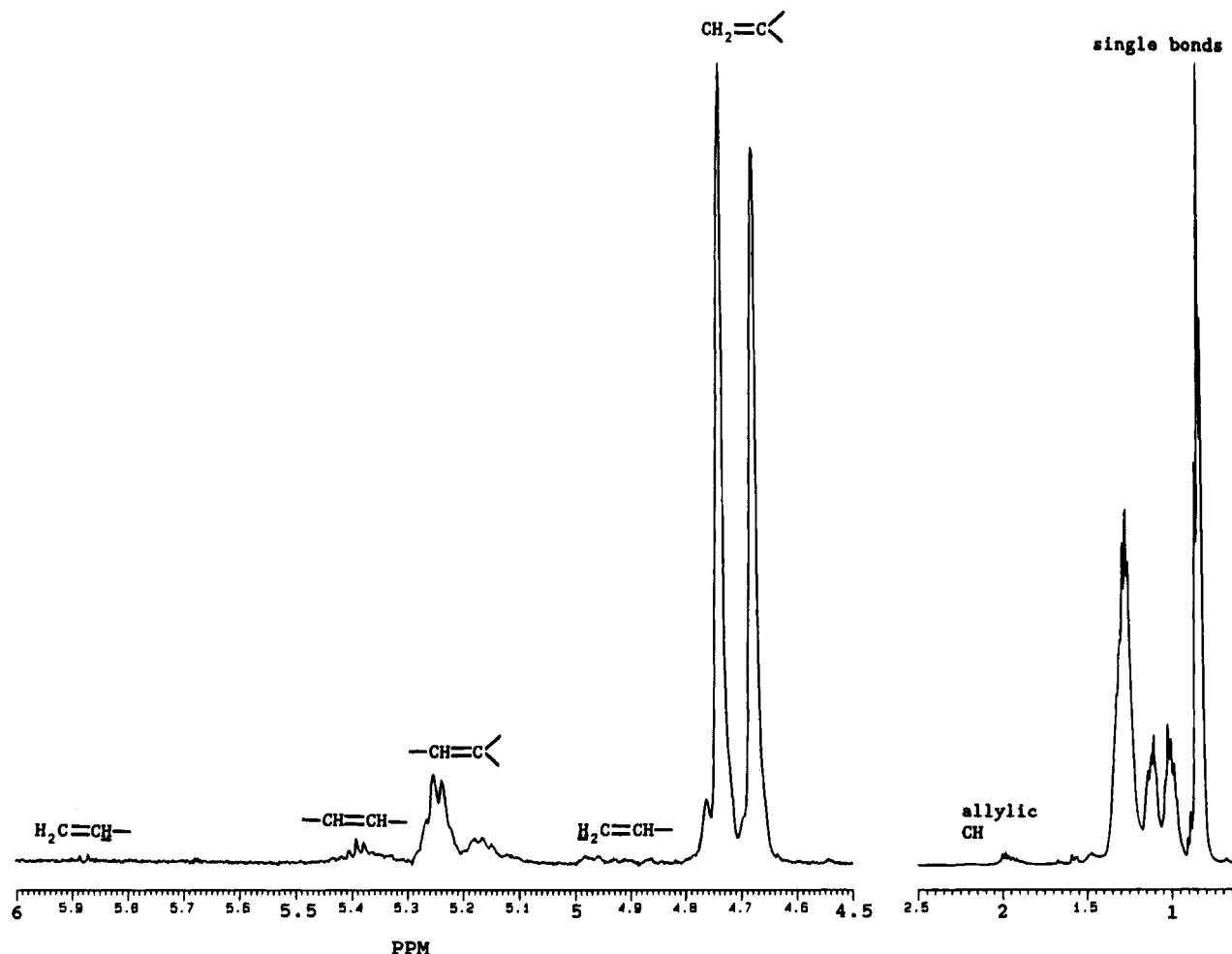
5. The assignments of double-bond carbon signals were aided by correlation with signal assignments for single-bond carbons  $\alpha$  and  $\beta$  to the double bond. However, data from the single-bond region are inherently limited compared to that from the double-bond region because the single-bond region has many more signals—signals for saturated end groups and repeat units in addition to single-bond carbons near double bonds. The presence of so many signals, some poorly resolved from others, makes signal assignments less fruitful. Chemical shift values were calculated using the Grant and Paul parameters<sup>17</sup> followed by correction for the double-bond substituent. Examination for various model compounds showed a 3–4 ppm correction for 2° and 3° allylic carbons  $\alpha$  to a double bond with about a 10 ppm correction for 4° allylic carbons. Smaller corrections were observed for single bond carbons  $\beta$  to a double bond.

**Molecular Weight.** Molecular weight analysis by size-exclusion chromatography (SEC) was performed at ambient temperature using a Waters 150C instrument at ambient temperature, THF as the mobile phase, a set of three Ultrastaygel columns (10<sup>4</sup>, 10<sup>3</sup>, and 500 Å) as the stationary phase, and calibration with polyisobutylene samples standardized by vapor pressure osmometry. Vapor pressure osmometry (VPO) was performed by Galbraith Laboratories using a Knauer VPO with toluene as the solvent at 60 °C. Molecular weights were also obtained by comparison of the signal areas for the single- and double-bond regions in both the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra.

## Results

**End Groups.** Most studies of end groups in metallocene-catalyzed polymerizations of  $\alpha$ -olefins have been carried out on relatively high molecular weight samples and this placed major limits on end-group analysis. End-group analysis was considerably enhanced in the present study by working with a low molecular weight poly(1-butene). The poly(1-butene) was obtained by polymerization of neat 1-butene at 100 °C using  $7.1 \times 10^{-6}$  M dimethylsilyl-bridged ( $\text{H}_4\text{Ind})_2\text{ZrCl}_2$  with a MAO:Zr ratio of 1000:1. The poly(1-butene) produced under these conditions contains a much wider range of double-bond types than previously reported for  $\alpha$ -olefin polymerizations. Figure 1 shows the 400 MHz  $^1\text{H}$  NMR of the poly(1-butene) sample. The double-bond region contains proton signals for vinylene, trisubstituted, vinyl, and vinylidene double bonds at 5.5–5.3, 5.3–5.1, 5.1–4.8, and 4.8–4.6 ppm, respectively.<sup>15</sup> Structural details on the various double bonds were obtained from  $^{13}\text{C}$  NMR (Figure 2). There are eighteen different signals, i.e., nine different double bonds, including signals for tetrasubstituted double bonds which are not observable by  $^1\text{H}$  NMR.

**Vinylidene Double Bonds.** The major unsaturated end groups are vinylidene.  $^1\text{H}$  and  $^{13}\text{C}$  NMR indicate 69.7% and 63.1% vinylidene, respectively (Table 1).  $^1\text{H}$  NMR indicates two different vinylidene groups. The



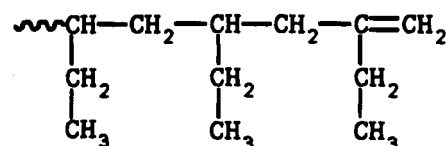
**Figure 1.** 400 MHz  $^1\text{H}$  NMR of poly(1-butene). The double-bond region is shown on expanded scale relative to the single-bond region.

**Table 1. Double Bonds in Poly(1-butene)**

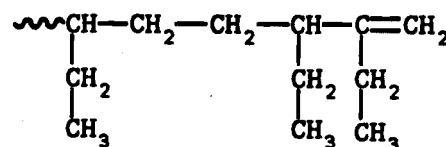
type of double bond	% by NMR	
	$^1\text{H}$	$^{13}\text{C}$
$\text{H}_2\text{C}=\text{CR}_1\text{R}_2$	69.7	63.1
$\text{R}_1\text{CH}=\text{CR}_2\text{R}_3$	26.9	31.7
$\text{R}_1\text{CH}=\text{CHR}_2$	2.8	1.6
$\text{R}_1\text{R}_2\text{C}=\text{CR}_3\text{R}_4$		3.6
$\text{H}_2\text{C}=\text{CHR}$	0.6	

major vinylidene signal is a pair of doublets at 4.74 and 4.68 ppm (the splitting of each signal into a doublet is barely visible). The minor vinylidene signal, only partially resolved from the major vinylidene signal, is at slightly lower field—see the signal at 4.76 ppm in Figure 1. The minor vinylidene  $^1\text{H}$  NMR signal area is 3–5% of the major vinylidene signal area. The major vinylidene signal was assigned to end-group 1 while the minor vinylidene signal was assigned to 2 and/or 3 based on mechanistic considerations (see below). 2 and 3 differ from 1 in having reverse placement of the penultimate and pen-penultimate unit, respectively.

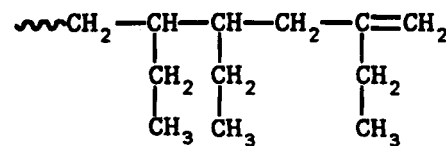
The  $^{13}\text{C}$  NMR results verify 1 as the major double bond. The pair of signals at 150.5 and 109.4 ppm, the largest  $^{13}\text{C}$  NMR signals in the double bond region, are close to the values (148.0 and 109.4 ppm, respectively) calculated for 1 and the DEPT experiment shows the carbons to be  $4^\circ$  and  $2^\circ$  carbons, respectively. The  $^{13}\text{C}$  NMR single-bond region supports the assignment of 1 as noted by signals at 33.7, 41.6, 28.6, and 12.4 ppm for the carbons of the penultimate unit (Figure 3). Still further verification for 1 came from the  $^{13}\text{C}$ – $^1\text{H}$  shift-correlated 2D NMR experiment which showed cross-



1



2



3

peaks between side-chain and in-chain allylic carbon signals at 28.6 and 41.6 ppm, respectively, and allylic protons at 2 ppm. No signal was observed in the  $^{13}\text{C}$  NMR for minor vinylidene end-groups 2 and 3. We assume that signals for the minor vinylidene end groups are buried under the signal for the major vinylidene end group, indicating that the major and minor vinylidene groups have very nearly the same chemical shifts. The

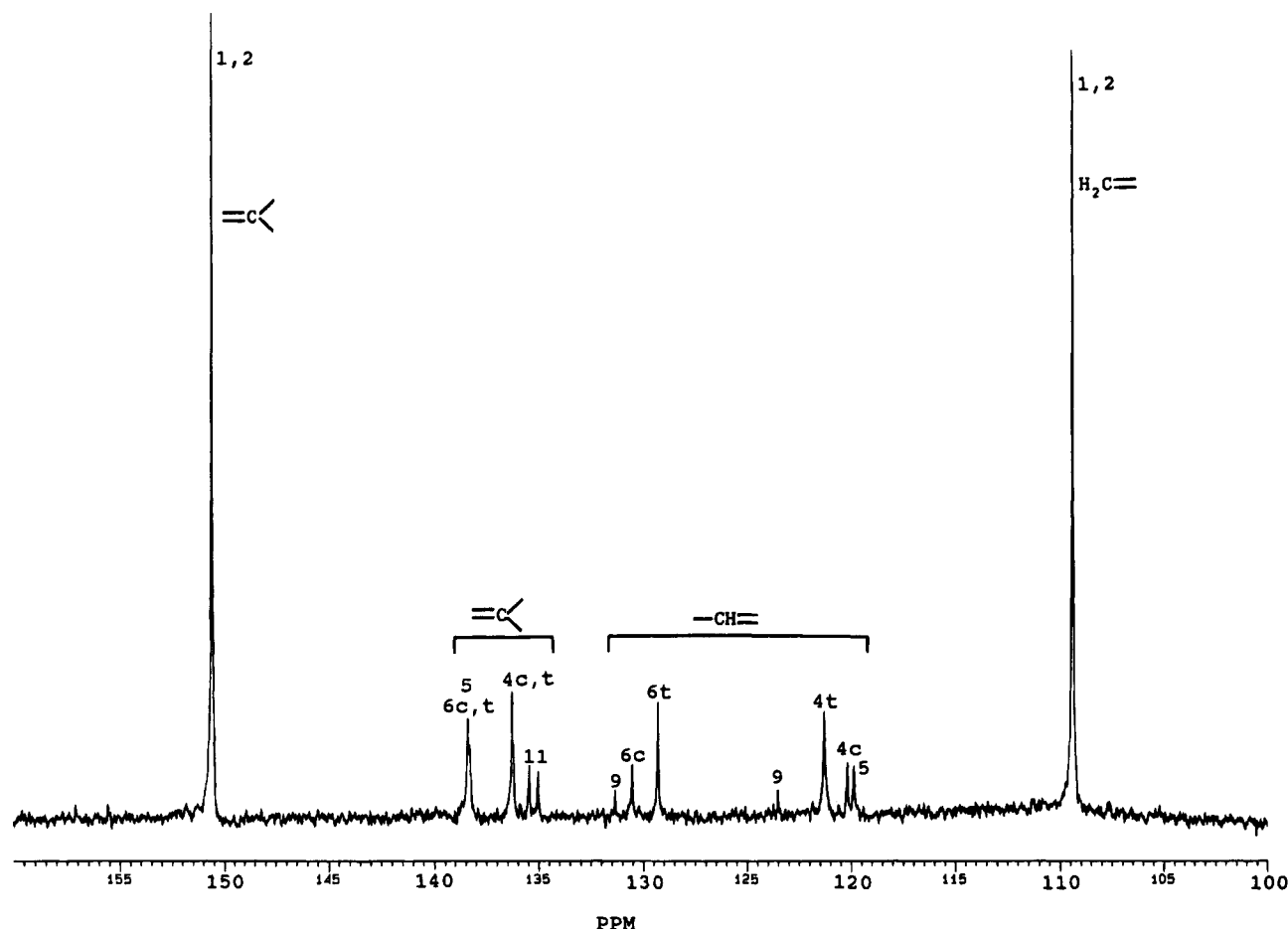


Figure 2. 100 MHz  $^{13}\text{C}$  NMR of double-bond region of poly(1-butene).

Table 2. Assignments of Double-Bond  $^{13}\text{C}$  NMR Signals

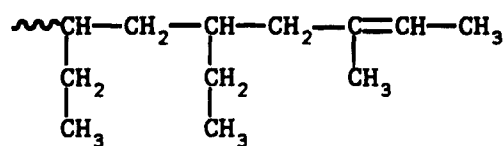
$\delta$ (ppm)	no. signals <sup>a</sup>	carbon type	signal area <sup>b</sup>	assignments <sup>c</sup>
150.5	1	$4^\circ (>\text{C}=\text{})$	100	1, 2, 3
138.3	3	$4^\circ (>\text{C}=\text{})$	27.0	6c,t, 5 (7)
136.3	2	$4^\circ (>\text{C}=\text{})$	21.5	4c,t (7)
135.5	1	$4^\circ (>\text{C}=\text{})$	6.9	11
135.0	1	$4^\circ (>\text{C}=\text{})$	4.5	11
131.3	1	$3^\circ (-\text{CH}=\text{})$	2.5	9 or 10
130.5	1	$3^\circ (-\text{CH}=\text{})$	8.2	6c (7)
129.3	1	$3^\circ (-\text{CH}=\text{})$	13.5	6t (7)
123.5	1	$3^\circ (-\text{CH}=\text{})$	2.6	9 or 10
121.3	1	$3^\circ (-\text{CH}=\text{})$	16.7	4t (8)
120.2	1	$3^\circ (-\text{CH}=\text{})$	6.0	4c (8)
119.9	1	$3^\circ (-\text{CH}=\text{})$	7.1	5 (8)
109.4	1	$2^\circ (\text{H}_2\text{C}=\text{})$	98.9	1, 2, 3

<sup>a</sup> Number of signals at that chemical shift. <sup>b</sup> Based on 100 for the signal at 150.5 ppm. <sup>c</sup> c and t refer to cis and trans isomers.

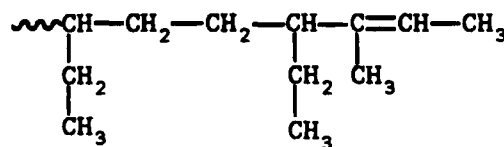
calculated chemical shifts for the double-bond carbons of **3** are exactly the same as for **1**. **2** has very close but not exactly the same calculated chemical shifts.

**Trisubstituted Double Bonds.** Trisubstituted double bonds are the next most abundant double bonds, 26.9% and 31.7%, respectively, by  $^1\text{H}$  and  $^{13}\text{C}$  NMR (Table I). Trisubstituted double bonds have not been previously reported in  $\alpha$ -olefin polymerizations. The  $^1\text{H}$  NMR is quite complex in the region (5.3–5.1 ppm) for trisubstituted double-bond protons, indicating the presence of more than one type of trisubstituted double bond. This is verified by the  $^{13}\text{C}$  NMR which shows the presence of at least five different trisubstituted double bonds. Two different sets of trisubstituted double bonds are compatible with the  $^{13}\text{C}$  NMR data: (1) trisubstituted double-bond end groups and (2) internal trisubstituted double bonds.

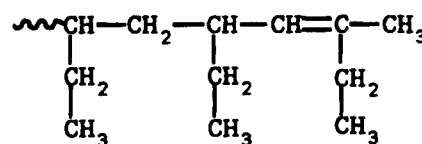
**4–6** are the trisubstituted double-bond end groups compatible with the calculated  $^{13}\text{C}$  chemical shift values and the DEPT experiment (for both single and double



4



5



6

bond carbons). Specific signal assignments are shown in Table 2 and Figures 2 and 3. **4–6** can each exist as cis and trans isomers, but only five sets of signals are observed. The five sets of signals are assigned to a combination of **5** and the cis and trans isomers of **4** and **6**. The signals assigned to **5** may be for a combination of the cis and trans isomers or only the trans isomer

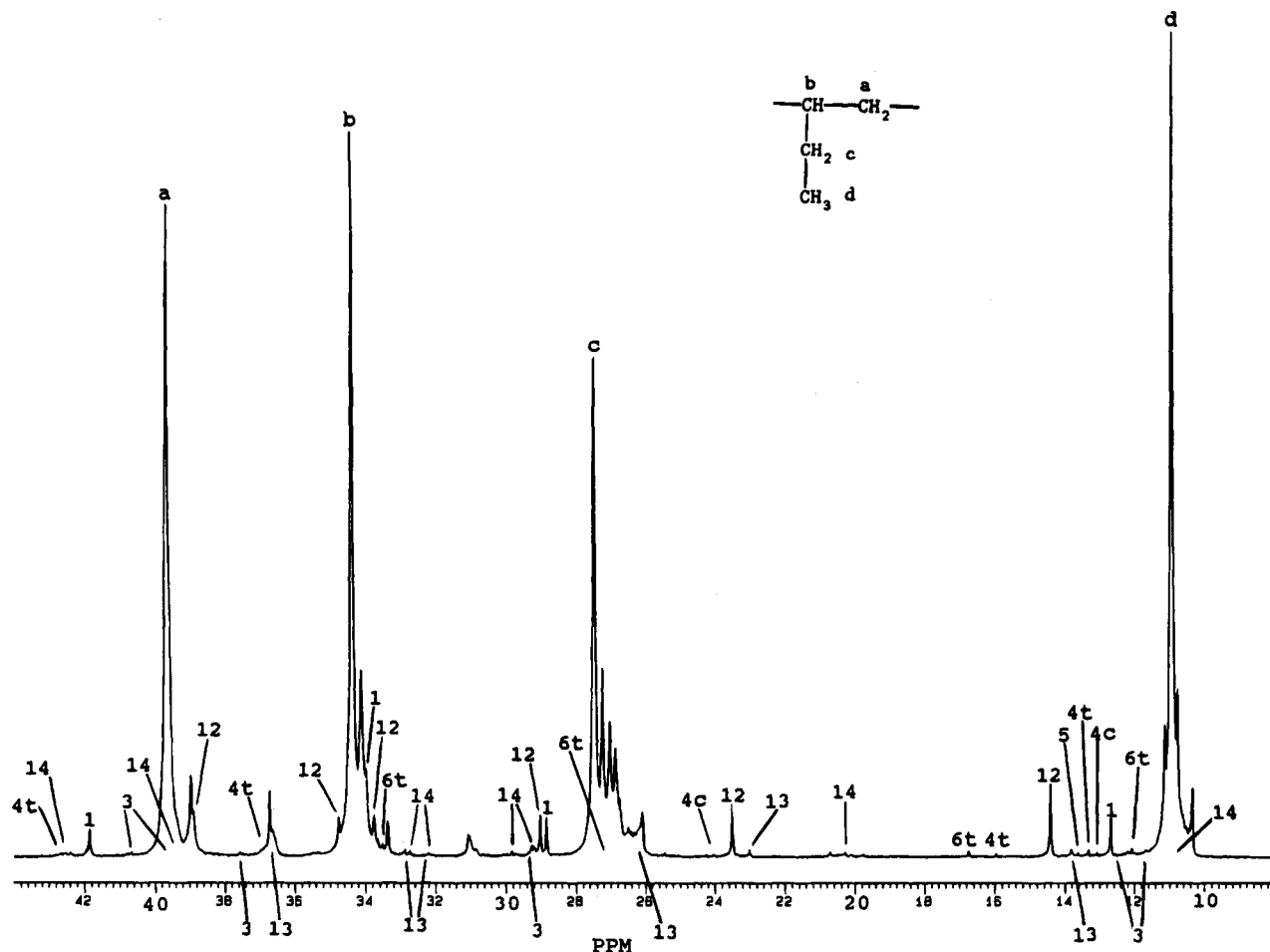
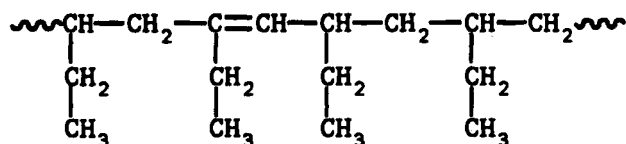


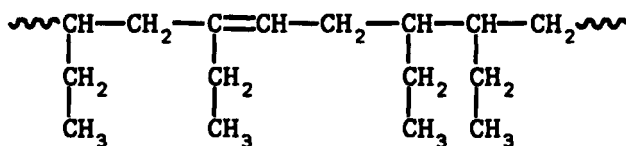
Figure 3. 100 MHz  $^{13}\text{C}$  NMR of single-bond region of poly(1-butene) with assignments for saturated and unsaturated end groups.

(with signals for the cis isomer not observed due to low concentration).

The  $^{13}\text{C}$  NMR data are also compatible with the presence of internal trisubstituted double bonds 7 and 8. (Internal trisubstituted double bonds are located "inside" the polymer chain, not at the ends of the



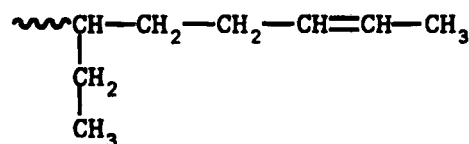
7



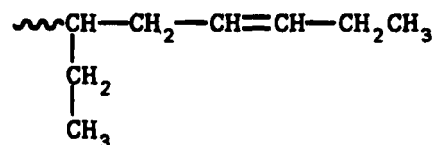
8

polymer chain.) Signal assignments for 7 and 8 are shown in parentheses in Table 2 but are not noted in Figure 2. Both 7 and 8 can exist as cis and trans isomers, which means that four of the five sets of trisubstituted double bond signals can be accounted for by internal trisubstituted double bonds. The broadest interpretation of the trisubstituted double bond region is the presence of 7 and 8 in addition to 4–6, with cis and trans isomers of any one of these units being unresolved from each other.

**Vinylene Double Bonds.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR indicate a small amount (2.8 and 1.6%, respectively) of vinylene end groups. The best fit between calculated and observed  $^{13}\text{C}$  chemical shift values assigns this group as 9. 10 cannot be ruled out as an alternate to 9 although



9

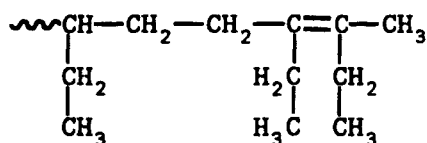


10

the calculated chemical shifts do not fit as well.

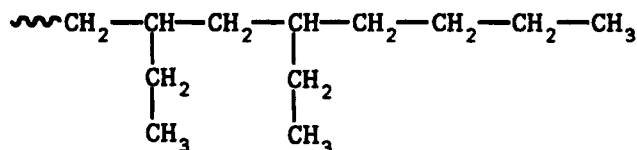
**Tetrasubstituted Double Bonds.** The small amount (3.6%) of tetrasubstituted end groups is assigned to 11. (Tetrasubstituted end groups are not observed in the  $^1\text{H}$  NMR because of the absence of protons on the double-bond carbons.)

**Vinyl Double Bonds.** A very small amount (0.6%) of vinyl double bonds are observed by  $^1\text{H}$  NMR but not  $^{13}\text{C}$  NMR. The absence of vinyl signals in the  $^{13}\text{C}$  NMR is compatible with their low concentration. There is no analytical basis for assigning any specific structure for the vinyl groups.

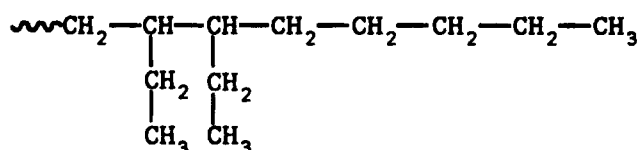


11

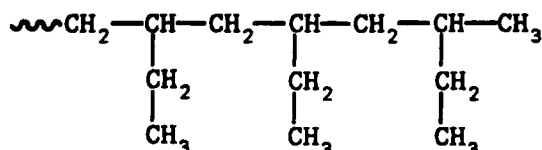
**Saturated End Groups.** Figure 3 shows the  $^{13}\text{C}$  NMR assignments for saturated end groups, based on chemical shift values, signal areas, and the DEPT experiment. The major saturated end group is 12,



12



13



14

referred to as an *n*-butyl end group. 13 and 14 are minor saturated end groups. 13, also an *n*-butyl end group, differs from 12 in having a reverse placement of the penultimate unit. 14 is referred to as a *sec*-butyl end group. The relative amounts of the saturated end groups are in the approximate ratio 12:13:14 = 18:3:2.

**Polymer Molecular Weight.** There was good agreement among SEC, NMR, and VPO measurements of the number-average molecular weight of the poly(1-butene) sample. SEC yielded  $\bar{M}_n = 1910$ .  $\bar{M}_n$  values of 2090 and 2020 were calculated from the  $^1\text{H}$  and  $^{13}\text{C}$  NMR data, respectively, assuming an average of one double bond per polymer molecule, by comparison of the double- and single-bond signal areas. VPO yielded  $\bar{M}_n = 2025$ , indicating that the assumption of one double bond per molecule is valid within experimental error. The polymer molecular weight is narrow. SEC yielded  $\bar{M}_w/\bar{M}_n = 1.88$ , indicative of the single-site nature of the zirconocene catalyst. Heterogeneous Ziegler-type catalysts are multisite catalysts and yield broader molecular weight distributions.

Table 3. Relative Amounts of  $\beta$ -Transfer Reactions

end group	eq <sup>a</sup>	%
Vinylidene		
1	5	60
2	9 }	3
3	5 }	
Trisubstituted		
4	7	14
5	11	4
6	8	13
Tetrasubstituted		
11	12	4
Vinylene		
9	13 }	2
10	14 }	

<sup>a</sup> Chain-transfer reaction in Scheme 3.

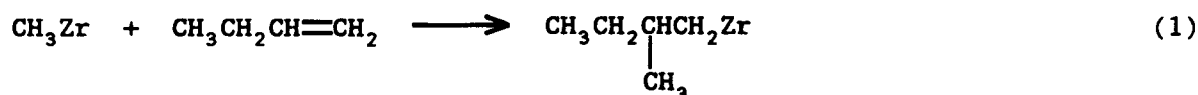
Table 4. Pentad Stereochemistry of Poly(1-butene)

pentad	$\delta$ (ppm)	fraction
mmmm	27.1	0.581
mmmr	26.9	0.192
rmmr	26.7	0.109
mmrr		
mmrm	26.6	0.080
rmrr		
mrmm	26.4	0.024
rtrr	26.1	0.014
mrtr		
rrrm		

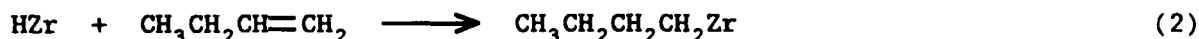
**Structure of the Repeat Unit.** Analysis of the repeat unit structure involved simultaneous analysis of regioselectivity and stereoregularity. Chemical shift values for various repeat unit sequences of normal (or 1,2 or primary) and reverse (or 2, 1 or secondary) insertions were calculated by the Grant and Paul parameters.<sup>17</sup> The calculations of Asakura and co-workers<sup>18,19</sup> were used for different stereochemical arrangements of butene repeat units. Figure 4 shows the assignment of signals for repeat unit regioselectivity and stereoregularity. Of the four signals for the repeat unit of 1-butene, the signal for the side chain  $\text{CH}_2$  carbon is the most sensitive to stereochemistry while the signal for the backbone  $\text{CH}_2$  carbon is the least sensitive. There is a spread of about 1 ppm among the various pentad arrangements for the side chain  $\text{CH}_2$  carbon signal and only 0.2 ppm for backbone  $\text{CH}_2$  carbon signal. The side chain  $\text{CH}_2$  carbon signal was used for stereochemical analysis. The stereoisomeric pentad fractions are shown in Table 4. The meso and racemic dyad fractions were calculated<sup>20</sup> as 0.84 and 0.16, respectively; i.e., the poly(1-butene) is 84% isotactic.

B and  $\bar{B}$  refer to normal and reverse insertions, respectively. Small amounts of isolated reverse repeat units (BBBB) are observed, but there is no evidence of reverse units being near each other, either adjacent reverse units (BB $\bar{B}$ B) or two reverse units separated by a normal unit (B $\bar{B}$ BB). Most of the signals for

Scheme 1. Initiation Reactions



15



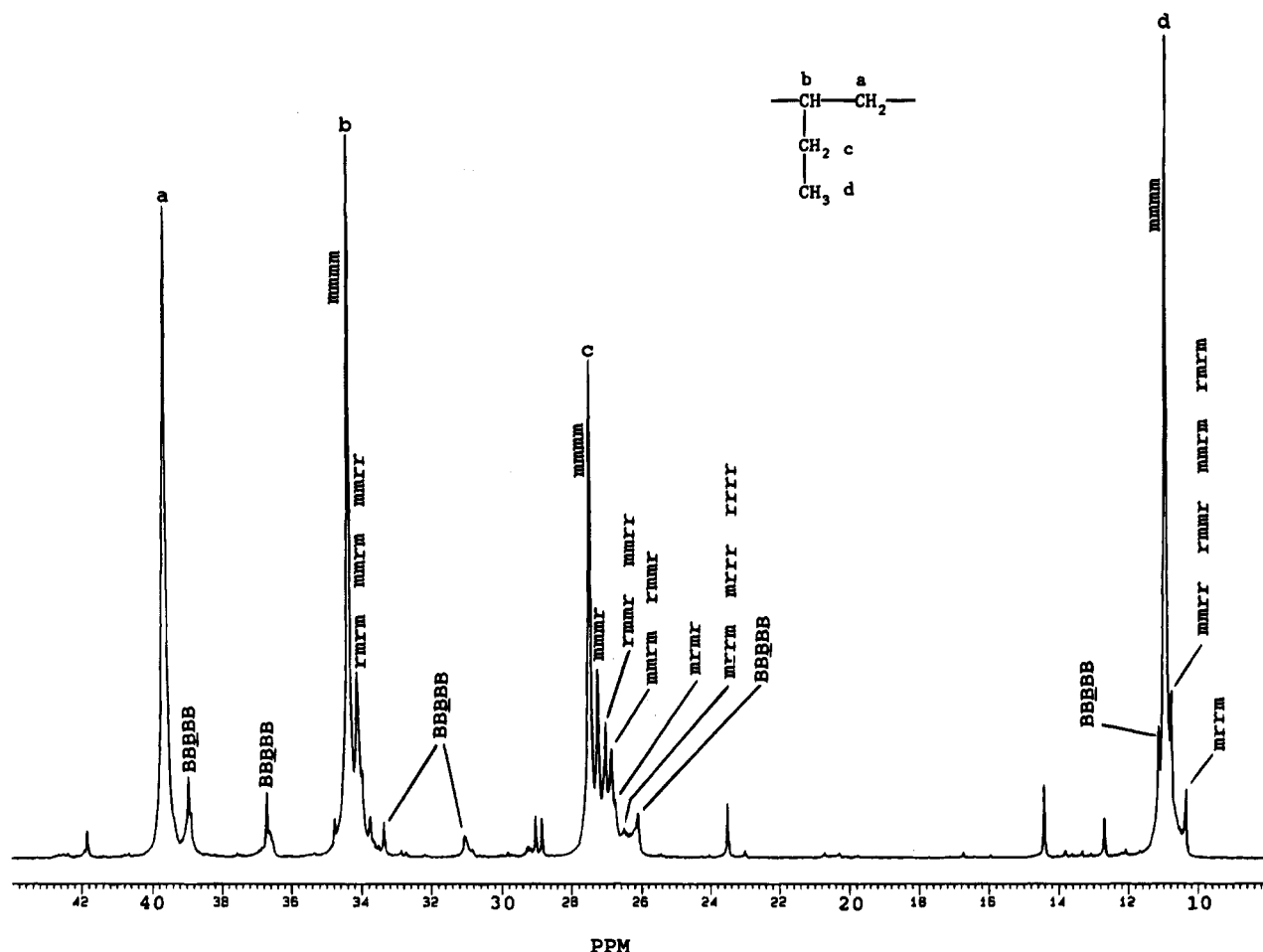
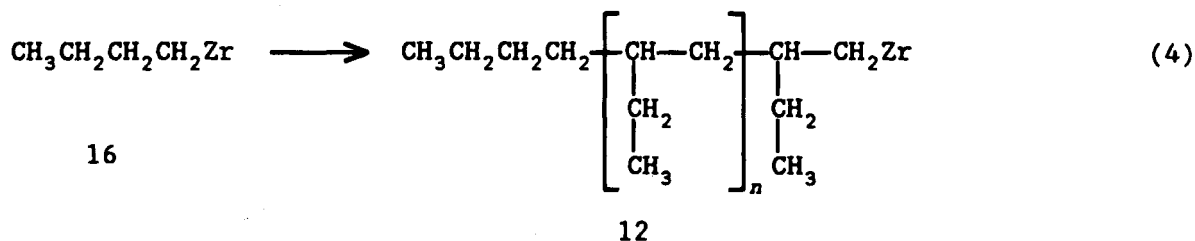
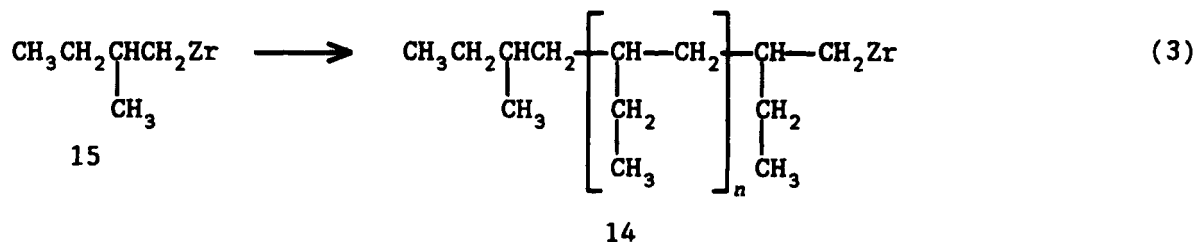


Figure 4. 100 MHz  $^{13}\text{C}$  NMR of single-bond region of poly(1-butene) with assignments for repeat unit regioselectivity and stereoregularity.

#### Scheme 2. Propagation Reactions



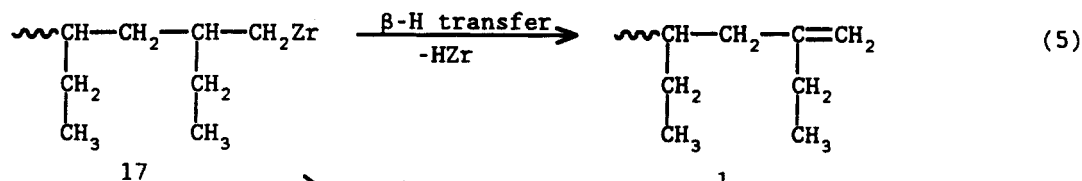
BBBBB are poorly resolved from other signals and this limits quantification of the extent of reverse repeat units and, to some extent, confidence in these assignments. We estimate between 0.5 and 2 reverse repeat units per polymer molecule, not counting the end groups. Overall, this means that the number-average polymer molecule has a degree of polymerization of 36 and contains two end groups and 34 repeat units, of which 0.5–2 are reverse repeat units.

#### Discussion

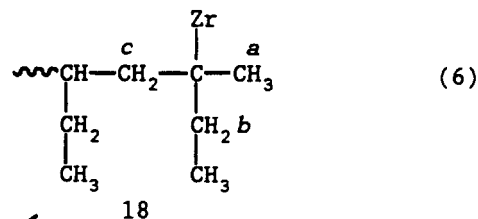
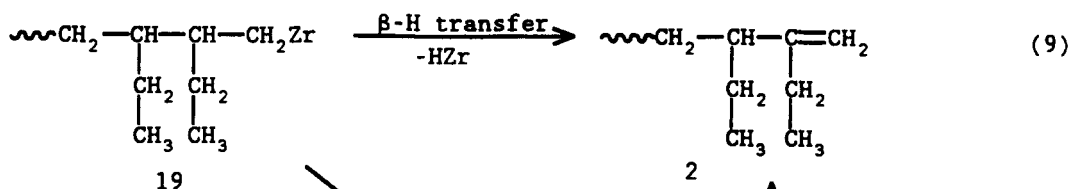
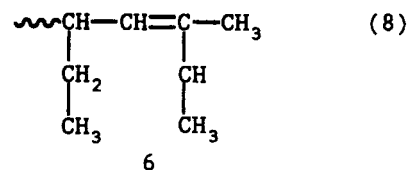
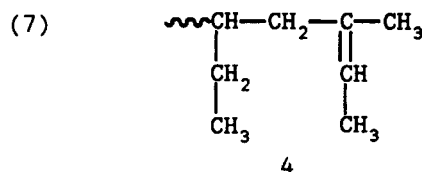
Proposed initiation, propagation, and chain-transfer reactions are described in Schemes 1–3, respectively.

The various equations are simplified by showing only one of the ligands of Zr or Al. It is assumed that MAO alkylates the zirconium chloride ligands to form the initial polymerization sites: zirconium–methyl sites (shown as  $\text{CH}_3\text{Zr}$  in eq 1). Most polymer chains are subsequently initiated by zirconium–hydride sites (shown as  $\text{ZrH}$  in eq 2) formed by various  $\beta$ -hydride-transfer reactions (Scheme 3). The two initiation reactions result in propagation (eqs 3 and 4) to yield polymer with *sec*-butyl (14) and *n*-butyl (12 and 13) end groups, respectively. 13, not shown in eq 4, differs from 12 only in having reverse placement of the first monomer unit added.

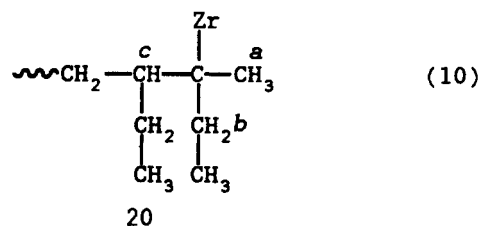
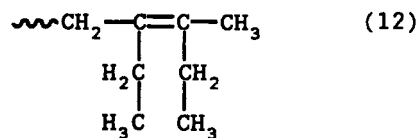
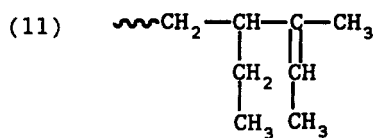
## Scheme 3. Chain-Transfer Reactions

 $\beta$ -Hydride Transfer Reactions

Rearrangement

 $\beta$ -H transfer from a $\beta$ -H transfer from b $\beta$ -H transfer from c

Rearrangement

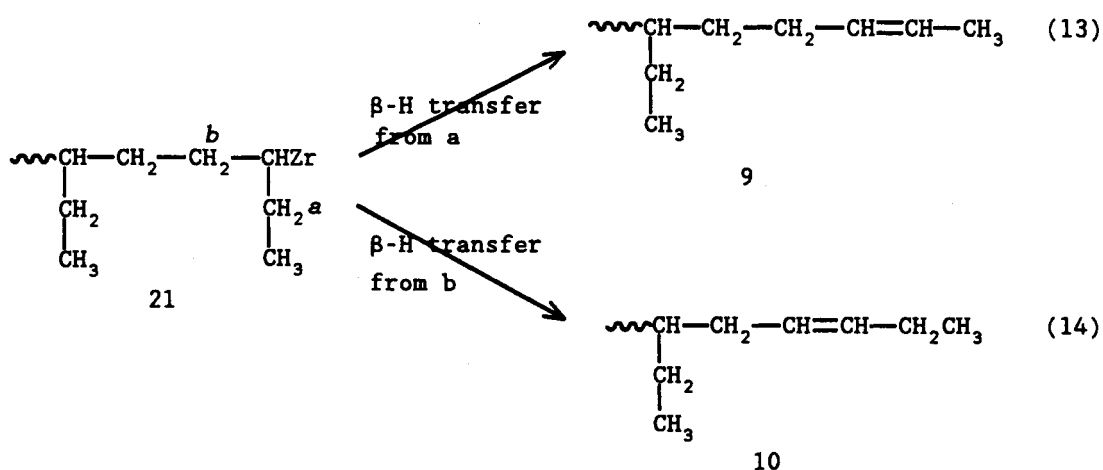
 $\beta$ -H transfer from a $\beta$ -H transfer from b $\beta$ -H transfer from c

Propagation involves insertion of 1-butene into zirconium-carbon sites with almost exclusively normal addition coupled with isospecificity. The major unsaturated end group (vinylidene group 1) is formed by

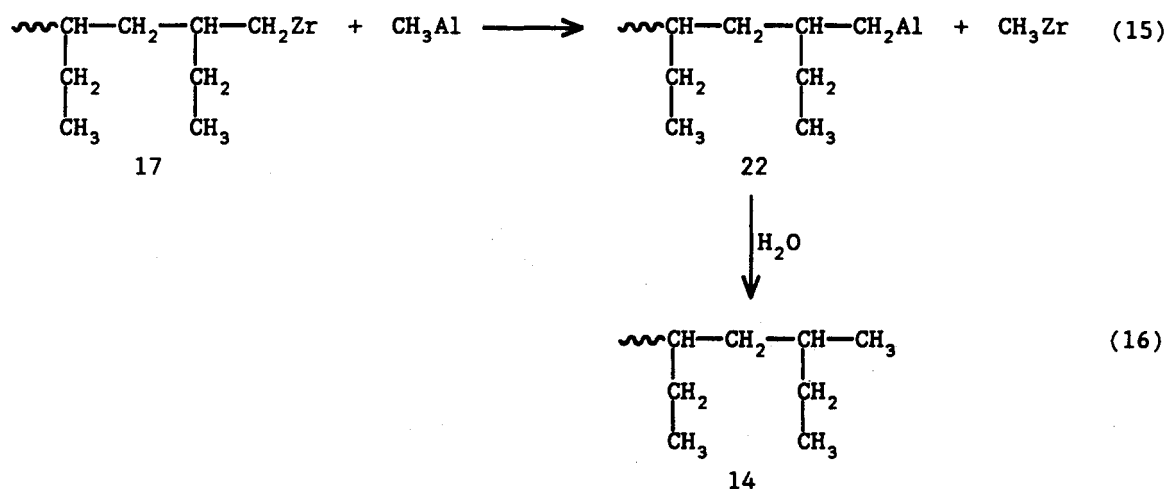
$\beta$ -hydride transfer from normal propagating sites (17) (eq 5). Vinylidene end-group 2 is formed by  $\beta$ -hydride transfer from propagating sites (19) in which the penultimate unit is reversed (eq 9). Vinylidene end-



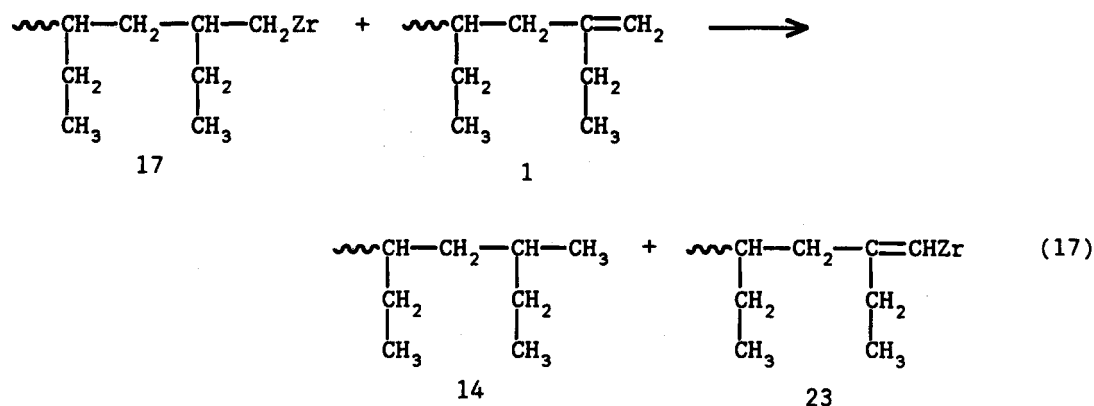
Scheme 3 Cont'd.



## Transfer to Aluminum



## Transfer to Vinylidene End-Group

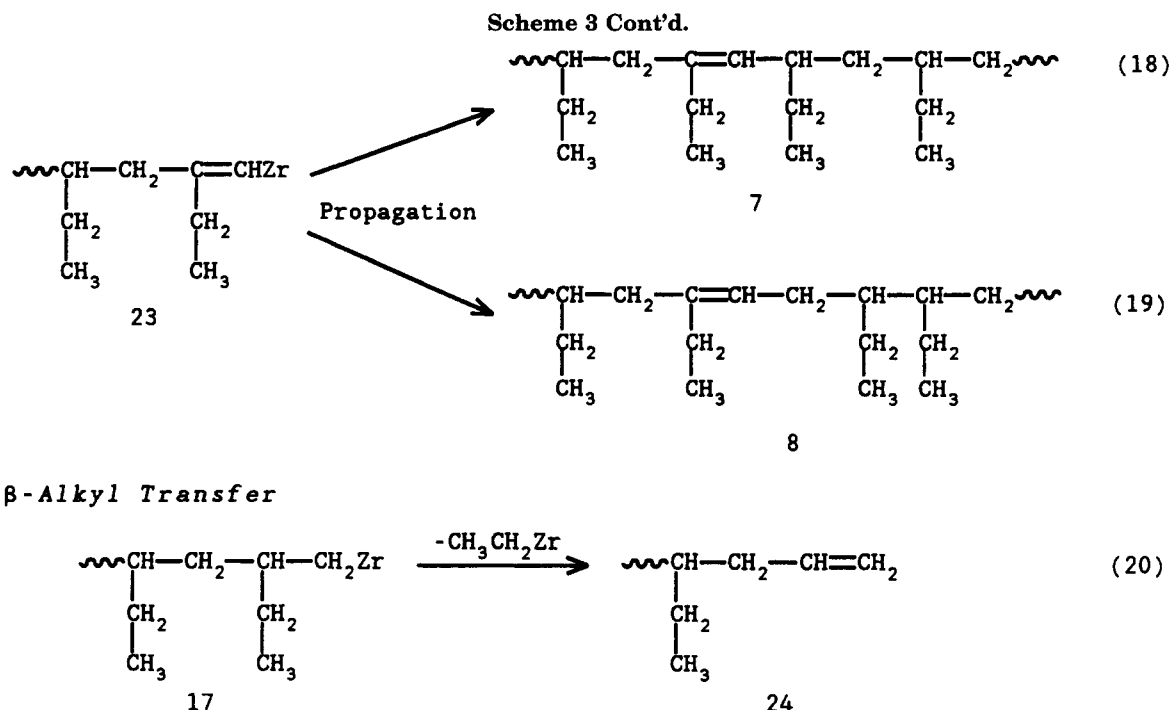


group 3 which may be present is formed by  $\beta$ -hydride transfer from propagating sites in which the penultimate unit is reversed. The amounts of 2 plus 3 are no more than 3–5% of the total vinylidene content.

Rearrangement of propagating site 17 to 18 followed by  $\beta$ -hydride transfer from *b* and *c*, respectively, yields trisubstituted double-bond end-groups 4 and 6 (eqs 7 and 8). (Transfer from *a* yields 1.) Similarly, rearrangement of propagating site 19 to 20 followed by  $\beta$ -hydride transfer from *b* and *c*, respectively, yields

trisubstituted double-bond end-group 5 and tetrasubstituted end-group 11 (eqs 11 and 12). (Transfer from *a* yields 2.) The formation of trisubstituted double bonds in metallocene-initiated polymerization of  $\alpha$ -olefins was first reported in our patent application for copolymerizations of ethylene with  $\alpha$ -olefins<sup>21</sup> and more recently by others for the polymerization of 1-hexene.<sup>22</sup>

Vinylene end groups (9 and 10) are formed by  $\beta$ -hydride transfer from propagating sites (21) in which the last unit is reversed (eqs 13 and 14). This was reported



to be the only chain-transfer reaction in the polymerization of 1-butene by (ethylene)Ind<sub>2</sub>ZrCl<sub>2</sub> at 30 °C.<sup>11</sup>

Transfer to aluminum results in *sec*-butyl end groups. Each act of transfer to aluminum results in two *sec*-butyl end groups (14). Transfer to aluminum (eq 15) results in aluminum-terminated polymer **22** and zirconium-methyl sites. One *sec*-butyl end group is formed when zirconium-methyl initiates polymerization (eq 1). The other *sec*-butyl end group is formed at the end of the polymerization process when **22** is hydrolyzed. (Transfer to aluminum may involve transfer to aluminum-methyl bonds in MAO as well as transfer to the residual trimethylaluminum present in MAO.)

The formation of internal trisubstituted double bonds of **7** and **8** (if present) involves transfer to vinylidene end groups to form propagating center **23** (eq 17). Subsequent propagation of **23** yields **7** and **8** (eqs 18 and 19).

The very small amount (<1%) of vinyl end groups is probably formed by  $\beta$ -ethyl transfer (eq 20).

The relative amounts of the various  $\beta$ -hydride transfer reactions are shown in Table 3. The relative amounts of **1**–**3** were obtained from the <sup>1</sup>H NMR which showed the minor vinylidene signals to be no more than 5% of the major vinylidene signal. All other values were obtained from the <sup>13</sup>C NMR signals areas (Table 2). (This analysis assumes that the trisubstituted double bonds are end groups, not internal double bonds.)

The amount of chain transfer to aluminum relative to  $\beta$ -hydride transfer reactions was obtained from the relative amounts of the three saturated end groups (**12**:**13**:**14** = 18:3:2). **12** and **13** (*n*-butyl) result from initiation via  $\beta$ -hydride transfer. *sec*-Butyl end group **14** is formed via three routes: (1) the very-first act (i.e., at the beginning of polymerization) of initiation by zirconium-methyl sites (eq 1 followed by eq 3); (2) chain transfer to aluminum (eq 16); (3) Chain transfer to vinylidene end groups (eq 17). Note that the *sec*-butyl end-group **14** in eq 3 appears to be different from the *sec*-butyl end-group **14** in eqs 16 and 17, but they are not different end groups. The apparent difference arises because **14** in eq 3 is an end group at the initiation end of the polymer chain while **14** in eqs 16 and 17 is an end group at the terminal end of the polymer chain.

Chain transfer to aluminum results in two *sec*-butyl groups per transfer. If chain transfer to aluminum and chain transfer to vinylidene end groups are unimportant, the ratio *n*-butyl:*sec*-butyl should be close to the catalytic efficiency of the polymerization process since one *n*-butyl end group is formed for each  $\beta$ -hydride transfer while one *sec*-butyl end group is formed for each Zr atom initially present. The experimentally determined catalytic efficiency for this polymerization is 33 000 mol of polymer/mol of Zr. However, the *n*-butyl:*sec*-butyl ratio is far smaller, being about 10, which indicates the occurrence of a significant amount of chain transfer to aluminum and/or chain transfer to vinylidene end groups.

The *n*-butyl:*sec*-butyl ratio of 10 indicates about 5% chain transfer to aluminum or 10% chain transfer to vinylidene end groups. (The difference between 5% and 10% for the two transfers results from the fact that chain transfer to aluminum yields twice the number of *sec*-butyl end groups as chain transfer to vinylidene end groups.) The overall result is that the ratio of saturated:unsaturated end groups is not 1, but is greater than 1. Some of the polymer molecules, 5% or 10% depending on whether chain transfer to aluminum or chain transfer to vinylidene is important, have two saturated end groups and no double-bond end groups. We expect a saturated:unsaturated ratio of about 1.1 on the basis of the *n*-butyl:*sec*-butyl ratio of 10. Direct evaluation of the saturated:unsaturated ratio from the <sup>13</sup>C NMR signal areas for the various double-bond and saturated end groups gives a ratio of 1.3. The difference between 1.1 and 1.3 is probably not experimentally significant. Each ratio is the ratio of the summations of several small signals.

Calculations from the catalytic efficiency, saturated:unsaturated end-group ratio, and the *n*-butyl:*sec*-butyl end-group ratio show that the amount of *sec*-butyl formed by the very-first act (i.e., at the beginning of polymerization) of initiation by zirconium-methyl sites (eq 1 followed by eq 3) is negligible (<0.1%). Essentially all of the *sec*-butyl is formed by some combination of chain transfer to aluminum and chain transfer to vinylidene. The relative extent of chain transfer to aluminum relative to chain transfer to vinylidene is

unclear. Calculations show that chain transfer to vinylidene alone can account for the *sec*-butyl content while chain transfer to aluminum alone cannot account for the *sec*-butyl content. The amount of MAO (and trimethylaluminum) present in the polymerization system is such that it can account for no more than 60% of the *sec*-butyl content.

## References and Notes

- (1) Kaminsky, W.; Kulper, K.; Brintzinger, H.; Wild, F. R. W. P. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 507.
- (2) Ewen, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 6355.
- (3) Grassi, A.; Zambelli, A.; Resconi, L.; Albizzati, E.; Mazzocchi, R. *Macromolecules* **1988**, *21*, 617.
- (4) Kaminsky, W.; Bark, A.; Spiehl, R.; Moller-Lindenhoff, N.; Niedoba, S. In *Isotactic Polymerization of Olefins with Homogeneous Zirconium Catalysts*; Kaminsky, W., Sinn, H., Eds.; Transition Metals and Organometallics as Catalysts for Olefin Polymerization; Springer-Verlag: Berlin, 1988; pp 291-301.
- (5) Resconi, L.; Pietmontesi, F.; Franciscano, G.; Abis, L.; Fiorani, T. *J. Am. Chem. Soc.* **1992**, *114*, 1025.
- (6) Cheng, H. N.; Ewen, J. A. *Makromol. Chem.* **1989**, *190*, 1931.
- (7) Tsutsui, T.; Mizuno, A.; Kashiwa, N. *Polymer* **1989**, *30*, 428.
- (8) Yang, X.; Stern, C. L.; Marks, T. J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1375.
- (9) Eshuis, J. J. W.; Yong, Y. T.; Meetsma, A.; Teuben, J. H. *Organometallics* **1992**, *11*, 362.
- (10) Longo, P.; Grassi, A.; Pellecchia, C.; Zambelli, A. *Macromolecules* **1987**, *20*, 1015.
- (11) Kioka, M.; Mizuno, A.; Tsutsui, T.; Kashiwa, N. In *Catalysis in Polymer Synthesis*; Vandenberg, E. J., Salamone, J. C., Eds.; ACS Symposium Series 490; American Chemical Society: Washington, DC, 1992; Chapter 5.
- (12) Mogstad, A.-L.; Waymouth, R. M. *Macromolecules* **1992**, *25*, 2282.
- (13) Welborn, H. C. European Patent Application (Exxon), No. 89302675.7, Publ. No. 0 344 887 A2, December 6, 1989.
- (14) Spaleck, W.; Antberg, M.; Rohrmann, J.; Winter, A.; Bachmann, B.; Kiprof, P.; Behm, J.; Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1347.
- (15) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 5th ed.; Wiley: New York, 1991; pp 215, 237-238.
- (16) Wehrli, F. W.; Wirthlin, T. *Interpretation of Carbon-13 NMR Spectra*; Wiley: New York, 1976; pp 41-43.
- (17) Grant, D. M.; Paul, E. G. *J. Am. Chem. Soc.* **1964**, *86*, 2984.
- (18) Asakura, T.; Omaki, K.; Zhu, S.; Chujo, R. *Polym. J.* **1984**, *16*, 717.
- (19) Asakura, T.; Demura, M.; Yamamoto, K.; Chujo, R. *Polymer* **1987**, *28*, 1037.
- (20) Odian, G. *Principles of Polymerization*, 3rd ed.; Wiley: New York, 1991; pp 622-623.
- (21) Rossi, A.; Rea, S.; Stanat, J.; Wright, L.; Kaufman, K. L.; Frederick, J. W.; Koros, R. M. Exxon Chemical Patent, International Pat. Appl. No. 94/13715, filed U.S. December 17, 1992, published June 23, 1994.
- (22) Babu, G. N.; Newmark, R. A.; Chien, J. C. W. *Macromolecules* **1994**, *27*, 3383.

MA945053D