

## 2D-INADEQUATE Structural Assignment of Polybutene Oligomers

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The structure of polybutene oligomers has been unambiguously determined using NMR techniques. We used 2D-INADEQUATE to show that the major polybutene isomer synthesized via  $\text{BF}_3$  catalysis has the expected structure with a *tert*-butyl group at the beginning of the chain and the expected methylvinylidene double bond at the other end. Surprisingly, we found that the main isomer of polybutene synthesized from  $\text{AlCl}_3$  catalysis has an isopropyl group at the beginning of the chain. A trisubstituted double bond structure has been assigned at the other end of the chain. Structural information about several minor polybutene isomers has also been determined. Formation of an isopropyl group can be rationalized by assuming a protonated cyclopropane intermediate in the propagation step. Previously, the mechanism of formation of polybutene via  $\text{AlCl}_3$  catalysis was thought to involve exclusively the *tert*-butyl carbenium ion. It now appears that the mechanism is more complicated than previously thought.

## Introduction

The formation of polybutene from isobutylene using Lewis acid catalysts has been carried out commercially since the 1930's.<sup>1</sup> Low molecular weight polybutene oligomers with  $M_n$  of 360–3000 are important raw materials for lubricating oil, fuel additives, sealants, caulks, adhesives, laminates, and lubricants for the paper and food industries.<sup>2</sup> The mechanism of formation of polybutene has been studied for years and is generally thought to be a classic example of a carbocationic polymerization involving the *tert*-butylcarbenium ion intermediate.<sup>2</sup> Recent work in the area of the polymerization of isobutylene has studied: living polymerization;<sup>3</sup> the role of metal centers in the initiation process;<sup>4</sup> polymerization in the gas phase, in the liquid phase, and in clusters;<sup>5</sup> polymerization in supercritical carbon diox-

ide;<sup>6</sup> different methods of initiation;<sup>7</sup> and polymerization in the presence of proton scavengers.<sup>8</sup>

A complete structural assignment of polybutene has been a difficult goal because polybutene is not a single molecule but a broad molecular weight distribution of oligomers, and each oligomer has a number of isomers with different olefin end group structures. We have been interested in the structure of polybutene because it is one of the basic raw materials in the synthesis of ashless dispersants for the lubricating oil and fuel additives industry.

Recently, structural assignments were made for six double bond isomers in polybutene.<sup>9</sup> These authors used various NMR techniques, calculated chemical shifts, and model olefin chemical shifts. In order to explain the structure assignments, the authors assumed that tail to tail addition of isobutylene was required<sup>9a</sup> or that carbenium ion rearrangements were occurring.<sup>9b</sup> In these studies, the emphasis has been placed on the determination of the olefin end group structures alone.

We now present the complete structural assignment of both ends of the major isomers from two types of commercial polybutene resulting from  $\text{BF}_3$  and  $\text{AlCl}_3$

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catalysis. We utilized the following NMR techniques: 2D-INADEQUATE (incredible natural abundance double quantum transfer experiment),<sup>10a</sup> APT (attached proton test),<sup>10b</sup> DEPT (distorsionless enhancement by polarization transfer),<sup>10c</sup> and HETCOR (heteronuclear chemical shift correlation),<sup>10d</sup> as well as quantitative <sup>13</sup>C NMR using chromium (acac)<sub>3</sub> relaxation agent.

### Experimental Section

A sample of Parapol 950 polybutene was provided by Exxon Chemical Co. Indopol H100-H polybutene was provided by Amoco Chemicals. The Ultravis 10 polybutene was supplied by BP Chemical Co., and the Glissopal 1000 polybutene was provided by BASF. The PB 24 was obtained from Chevron Chemical Co.

The 500 MHz proton (125 MHz carbon) NMR spectra were acquired in 10 mm tubes on approximately 30 wt % solutions in chloroform-*d* on a Varian Unity Plus instrument using a Nalorac 10 mm broadband probe. The probe temperature was controlled at approximately 26 °C. Broadband proton decoupling was achieved using WALTZ modulation of a 3.2 KHz B<sub>2</sub> field. The  $\pi/2$  pulse in the carbon channel was 9.5  $\mu$ s. All carbon relaxation times in molecules containing adjacent <sup>13</sup>C's will be less than those measured for molecules containing isolated <sup>13</sup>C's because the dipolar interaction between two <sup>13</sup>C's will provide an additional relaxation mechanism. INADEQUATE spectra were taken on nonspinning samples. The two-dimensional INADEQUATE data were obtained using the basic pulse sequence originally proposed by Bax et al.<sup>10a</sup> optimized for  $J_{CC} = 50$  Hz with a 4 s recycle time. Adequate S/N for visual interpretation of the spectrum was achieved with 256 increments in the double quantum dimension and 128 transients of 16 384 complex points each per increment. A spectral width of 20 161.3 Hz in both dimensions was used. Two such data matrices were collected by shifting the phase of the preparation pulses by zero or  $\pi/4$  to produce a zero or  $\pi/2$  phase shift in the amplitude modulation of the interferograms at the double quantum frequency. The 2D data matrices corresponding to these two cases then were stored separately to form a hypercomplex data set and processed according to the prescription of States et al.<sup>10e</sup> and manually phased in both dimensions to give a pure absorption mode 2D spectrum. The limited sampling in the DQ-direction leads to severe truncation wiggles around the peaks after FFT. Gaussian function with a time constant of 5.38 ms was applied to the  $t_1$  domain signal, and 1.62 Hz of Lorentzian line broadening was applied in the  $t_2$  domain. Zero filling in the DQ-direction to 1024 points was applied, but no zero filling was used in the chemical shift dimension. A 1D carbon spectrum was obtained under these same conditions in order to accurately establish the resonance frequencies of the various carbons.

The INADEQUATE experiment displays carbon-carbon connectivities as pairs of antiphase doublets in f1 slices. The separation between the doublets in a single pair are the carbon-carbon coupling constants for connected carbons (approximate values: 35 Hz for sp<sup>3</sup>-sp<sup>3</sup>, 50 Hz for sp<sup>3</sup>-sp<sup>2</sup>, and 70 Hz for sp<sup>2</sup>-sp<sup>2</sup>). The f2 values for each doublet pair are the chemical shifts of the connected carbons. The f1 (double quantum) axis is twice the spectral width of the f2 axis. Using f2 as the abscissa and f1 as the ordinate, the pairs of doublets will be displaced symmetrically about the positive sloping diagonal of the 2D plot; i.e., the diagonal intersects the f1 slice at f2 equal to the average chemical shift of the connected carbons. In practice, the spectral width of the f1 axis is restricted to being equal to the f2 axis so that f1 spectral information is folded in from outside nominal spectral width. The pairs of doublets are still displaced symmetrically about a line, but there are usually three such lines whose trajectories

need to be calculated. Fortunately, the lines are parallel lines. Determining the trajectory of one of the lines effectively determines the trajectories of the others. Knowing the trajectories of these lines means that detecting one antiphase doublet determines the position of the other (within the resolution of the f1 axis—about 0.6 ppm in our experiments). The INADEQUATE data were evaluated by finding the intense antiphase doublets associated with the polybutene backbone. The quaternary carbons (38.0 ppm) are connected to methylenes (59.4 ppm) and to methyls (31.2 ppm). The pairs of antiphase doublets appear in different f1 slices (numbers 409 and 499, respectively) for each of these connections. The f1 slice number vs f2 shift line could be constructed from this data. Other connectivities were determined manually. For the BF<sub>3</sub>-catalyzed polybutene, all major pairs were found and assigned. For the AlCl<sub>3</sub> polybutene, there were a few cases where only one of the pairs gave a detectable signal. However, the other information (f1 slice number, average chemical shift, and coupling constant) left no ambiguity in the assignments.

Pulse delays for HETCOR were chosen based on a proton T<sub>1</sub> of about 1 s. All pulse sequences were standard Varian sequences. Instrument parameters for the HETCOR experiment were as follows: relaxation delay 1.0 s, 0.208 s acquisition time, 512 increments,  $J_{HC} = 140$  Hz. The spectral widths were 6.5 and 156 ppm for H and C, respectively. The relaxation delay was chosen to be about equal to the average proton T<sub>1</sub> of the sample.

Quantitative <sup>13</sup>C NMR spectra were obtained on a 300 MHz Varian Gemini NMR (75 MHz carbon) using 1.0 g of sample dissolved in 3.0 mL of 0.5 M chromium(acac)<sub>3</sub> in chloroform-*d*. The transmitter pulse sequence (delay (2.2 s), 90° pulse-acquisition (0.853 s)) was employed with the decoupler (WALTZ-16) gated off during the delay and on during acquisition. cursory examination of the T<sub>1</sub>'s for the quaternary carbons at our Cr(acac)<sub>3</sub> levels indicated they were about 0.4–0.5 s. Thus, the relaxation delay was always more than four times the longest T<sub>1</sub>. We believe this is sufficient to allow residual NOE to die away between pulse excitations even though the decoupler duty cycle is above the recommended 5–10% range for quantitative experiments. Integration of the <sup>13</sup>C NMR spectrum was carried out with no base-line correction. The average of at least two separate integrations was used in this report.

Gel permeation chromatography was carried out on a 600 mm Polymer Labs PLgel 3  $\mu$ m Mixed-E column using THF as solvent. A refractive index detector was used, and the system was calibrated with narrow molecular weight polybutene standards.<sup>11</sup>

### Results and Discussion

**Structure of BF<sub>3</sub>-Catalyzed Polybutene Major Isomer 1.** Ultravis 10, made using BF<sub>3</sub>-catalysis technology,<sup>12</sup> was examined. This polybutene, which has been commercially available only since the 1980's, had  $M_n = 943$  and  $M_w/M_n = 1.35$ .

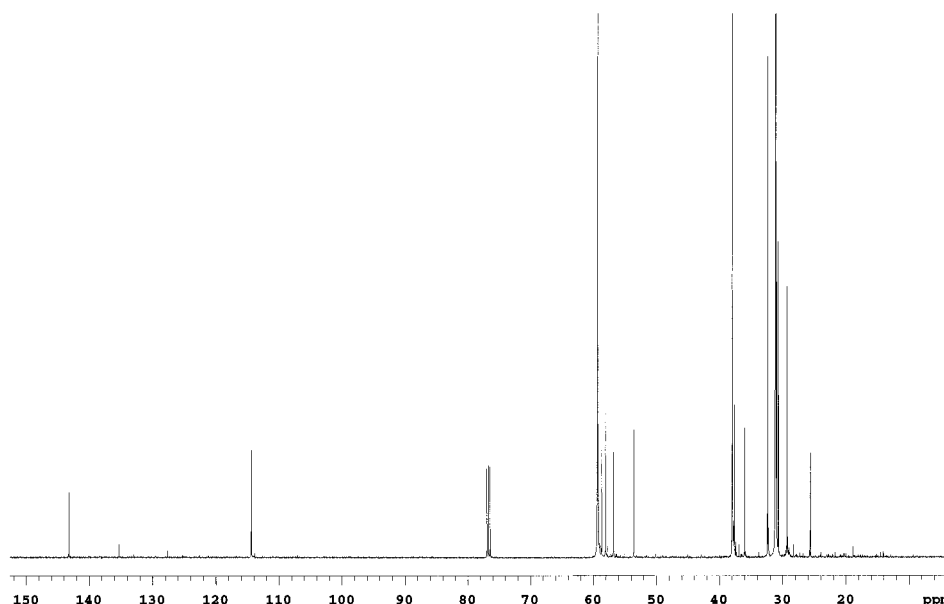
The 125 MHz <sup>13</sup>C NMR spectrum of the Ultravis 10 is shown in Figure 1. This material consisted of a major isomer, **1** (double bond carbons at  $\delta$  143.21 and 114.39), and a minor isomer, **2** (double bond carbons at  $\delta$  135.39 and 127.73). The structure for these double bond isomers has been assigned previously.<sup>9</sup> For the major isomer **1**, the chemical shift listing for the peaks that could be resolved and the carbon/hydrogen correlations obtained from the HETCOR experiment are shown in Table 1.

The complete carbon/carbon connectivity for isomer **1** was determined from the 2D-INADEQUATE experiment (see Figure 2). Starting from the double bond at  $\delta$  114.39, we were able to establish the carbon/carbon connectivity

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(11) We are grateful to AMOCO Chemicals for supplying us with polybutene standards and the GPC method for this analysis.

(12) We thank BP Co. for supplying us with a sample of this material.



**Figure 1.** 125 MHz  $^{13}\text{C}$  NMR spectrum of Ultravis 10.

**Table 1.** 125 MHz NMR Structure Assignment of Polybutene 1

carbon chem shift <sup>a</sup>	carbon type <sup>b</sup>	$^1\text{H}$ chem shift <sup>c</sup>	neighbors <sup>d</sup> ( $J_{\text{C,C}}$ ) <sup>e</sup>
143.21	C		114.39 (70.1), 53.56 (41.8), 25.63 (41.8)
114.39	$\text{CH}_2$	4.85, 4.64	143.21 (70.1)
59.35	$\text{CH}_2$	1.41	37.97 (34.5)
59.25	$\text{CH}_2$	1.41	
59.22	$\text{CH}_2$	1.41	
58.66	$\text{CH}_2$	1.41	37.60 (34.5), 37.90 (34.5)
58.05	$\text{CH}_2$	1.37	37.60 (35.7), 32.39 (35.7)
56.81	$\text{CH}_2$	1.33	36.01 (34.5), 37.68 (34.5)
53.56	$\text{CH}_2$	1.99	143.21 (41.8), 36.01 (33.2)
37.97	C		31.14 (35.7), 59.35 (34.5)
37.93	C		
37.90	C		58.66 (34.5), 30.97 (35.7)
37.68	C		56.81 (34.5), 31.07 (35.7)
37.60	C		58.05 (35.7), 30.69 (35.7), 58.66 (34.5)
36.01	C		56.81 (34.5), 29.29 (35.7), 53.56 (33.2)
32.39	C		58.05 (35.7), 32.37 (nd)
32.37	$\text{CH}_3$	0.99	32.39 (nd)
31.14	$\text{CH}_3$	1.11	37.97 (35.7)
31.07	$\text{CH}_3$	1.11	37.68 (35.7)
30.97	$\text{CH}_3$	1.11	37.90 (35.7)
30.69	$\text{CH}_3$	1.11	37.60 (35.7)
29.29	$\text{CH}_3$	1.03	36.01 (35.7)
25.63	$\text{CH}_3$	1.78	143.21 (41.8)

<sup>a</sup> ppm downfield from TMS internal standard. <sup>b</sup> Obtained from DEPT and APT experiments. <sup>c</sup> Obtained from HETCOR experiment. <sup>d</sup> In ppm, obtained from INADEQUATE experiment. <sup>e</sup> In Hz, from INADEQUATE experiment.

for six carbon atoms in from the end of the chain. These are listed in Table 1. The carbon/carbon connectivity at the other end of the polybutene chain, beginning with a methyl group at  $\delta$  32.37, could be established for six carbon atoms in from the end. All of the carbon/carbon coupling constants observed in the INADEQUATE experiment (Table 1) were consistent with our structural assignments, i.e.,  $\text{sp}^3\text{-sp}^3 \cong 35$  Hz,  $\text{sp}^3\text{-sp}^2 \cong 42$  Hz, and  $\text{sp}^2\text{-sp}^2 \cong 70$  Hz.

The methyl and quaternary carbons of the beginning terminal *tert*-butyl group were barely resolved at 125 MHz (see Figure 3). They were better resolved at the conditions used in the 75 MHz experiment. Quantitative

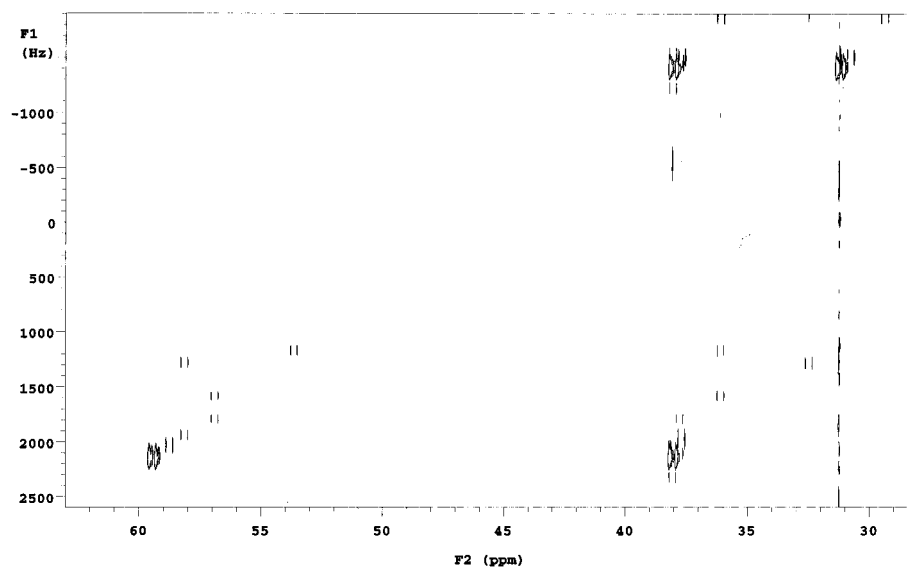
$^{13}\text{C}$  NMR experiments established a 3:1 ratio for the two peaks. The quaternary carbon atom of the *tert*-butyl end group of isomer **1** had a chemical shift position at  $\delta$  32.39. This assignment of the *tert*-butyl group was further confirmed by DEPT and APT experiments. The carbon/carbon connectivity of the methyl and the quaternary carbons of the *tert*-butyl group from the INADEQUATE experiment was made more difficult by the similar chemical shift positions. The INADEQUATE spectrum showed the methyl carbon/quaternary carbon connection as a single peak at  $\delta$  32.38 (close AB pattern) due to the fact that the chemical shift difference was only about 3 Hz while the coupling constant was expected to be about 35 Hz.

**Structure of  $\text{AlCl}_3$ -Catalyzed Polybutene Major Isomer 3.** Parapol 950, an  $\text{AlCl}_3$ -catalyzed polybutene, was analyzed next. The sample of Parapol 950 had a  $M_n$  of 930 and a  $M_w/M_n$  of 1.60. This sample of polybutene was chosen for study because it contained 37% of a single end group isomer **3** that had been characterized by double bond carbons at  $\delta$  122.60 and 133.46. Previous workers<sup>9</sup> have identified this isomer as one of a number of olefin end group structures for the  $\text{AlCl}_3$ -catalyzed polybutene.

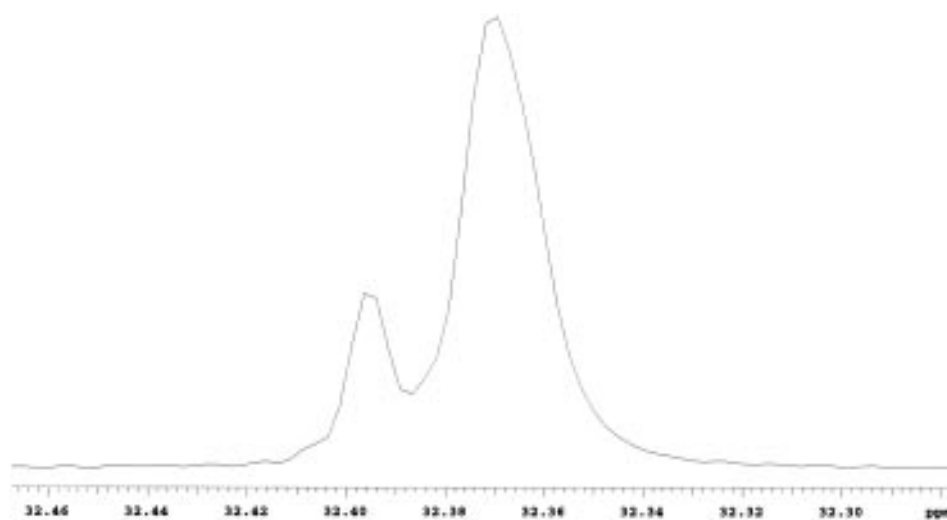
The  $^{13}\text{C}$  NMR of Parapol 950 is shown in Figure 4. In addition to the major peaks at  $\delta$  122.62 and 133.48, the Parapol 950 contained several minor isomers in the double-bond region including peaks at  $\delta$  122.28 and 134.15 (labeled isomer **4**) and  $\delta$  121.28 and 133.02 (labeled isomer **5**). In addition, there are a large number of peaks in the region  $\delta$  7–60 in the spectrum of Parapol 950 compared to Ultravis 10.

Table 2 lists the chemical shifts for the peaks that could be resolved for isomer **3** in the Parapol 950. Peak intensities were the major criterion in selecting isomer **3** carbon atoms, since isomer **3** was the major isomer in the Parapol 950. In addition, the carbon/hydrogen connectivity obtained from the HETCOR experiment is also listed.

Carbon/carbon connectivities were also established for isomer **3** of the Parapol 950 using the INADEQUATE NMR technique. Starting from the double bond carbon at  $\delta$  122.60, we were able to establish the carbon/carbon



**Figure 2.** 2D-INADEQUATE spectrum of the aliphatic region of Ultravis 10.



**Figure 3.** 125 MHz  $^{13}\text{C}$  NMR of the *tert*-butyl region of Ultravis 10.

connectivity for seven carbons in from the end of the chain. These are listed in Table 2.

Quite surprisingly, isomer **3** did not contain a *tert*-butyl group at the other end of the chain. Instead, we have identified an isopropyl group (methyl,  $\delta$  25.77, and methine,  $\delta$  24.06) at the end of the chain in isomer **3** and have established the carbon-carbon connectivities for six carbon-carbon bonds in from the end. Our structure assignment for isomer **3** is shown in Chart 1.<sup>13</sup> This structure avoids the need to postulate anomalous carbon numbers<sup>14</sup> or to assume a tail to tail addition of the last isobutylene unit in the polybutene<sup>9a</sup> to account for the olefin end group structure.

This result is surprising because all polybutene isomers were previously believed to have a *tert*-butyl group at the end of the chain.<sup>2</sup> A recent publication<sup>9b</sup> had identified an isopropyl group in the structure of polybutene with methyl groups at  $\delta$  25.9 and a methine group at  $\delta$  24.0 but had attributed this structure to a saturated polymer

that formed from a transfer of an allylic hydrogen from 1-butene to the growing chain end during the polymerization process.

**Minor Isomers.** A sample of Ultravis 10 polybutene that had increased levels of minor isomer **2** was examined to assign the structure of isomer **2**.<sup>12</sup> We found that the relative intensity of *tert*-butyl end groups in mixtures of **1** and **2** equaled the sum of the relative intensities of isomers **1** and **2** present in the mixture. We conclude that both isomers **1** and **2** contain the *tert*-butyl end group. The NMR structural information obtained from  $^{13}\text{C}$ ,  $^1\text{H}$ , HETCOR, DEPT, and APT experiments for isomer **3** on the 75 MHz instrument are reported in Table 3. (Chemical shifts for some of the carbons were shifted relative to the 125 MHz NMR results.) Our proposed structure assignment for isomer **2** is shown in Chart 1.

Parapol 950 was also examined further in an attempt to learn more about the minor isomers that were present. The first minor isomer **4**, with double-bond chemical shifts at  $\delta$  122.28 and 134.15, had been assigned a structure that differs from isomer **3** only by the position of the substituents on the double bond.<sup>9</sup> Examination of the  $^{13}\text{C}$  NMR spectrum of different samples of Parapol 950 that contained different amounts of isomer **4** indi-

(13) The INADEQUATE NMR technique was unable to determine the stereochemistry about the carbon-carbon double bond. We therefore use the stereochemistry assigned in ref 9b for this isomer with the methyl group *cis* to the alkyl chain.

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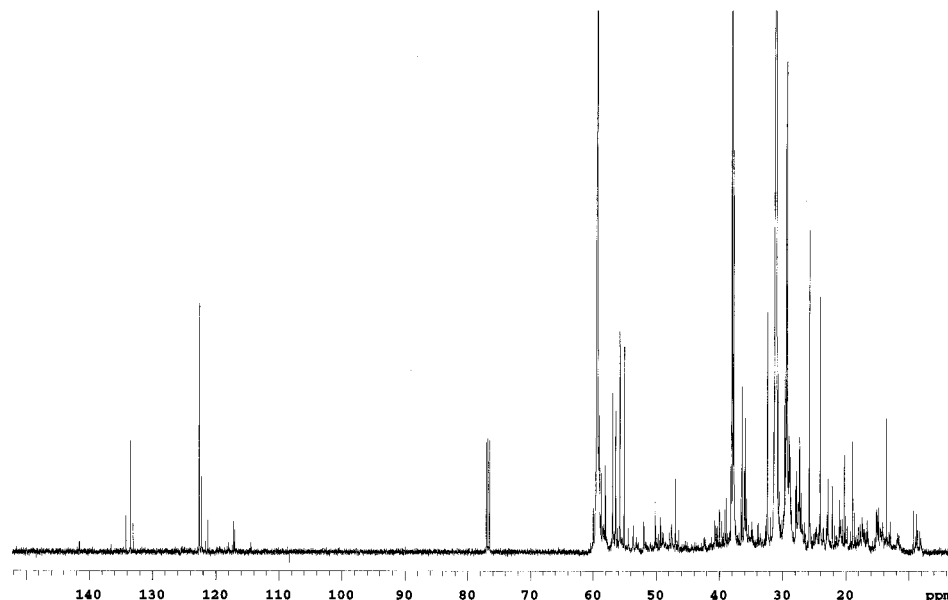


Figure 4. 125 MHz  $^{13}\text{C}$  NMR spectrum of Parapol 950.

Table 2. 125 MHz NMR Structure Assignment of Polybutene 3

carbon chem shift <sup>a</sup>	carbon type <sup>b</sup>	$^1\text{H}$ NMR <sup>c</sup>	neighbors <sup>d</sup> ( $J_{\text{C,C}}$ ) <sup>e</sup>
133.48	C		122.62 (73.3), 55.74 (41.5), 18.93 (43.8)
122.62	CH	5.15	133.48 (73.3), 13.60 (44.0)
59.41	CH <sub>2</sub>	1.40	38.02 (36.6)
56.91	CH <sub>2</sub>	1.33	37.74 (34.2), 36.41 (34.2)
56.45	CH <sub>2</sub>	1.32	35.90 (34.2), 37.85 (34.2)
55.74	CH <sub>2</sub>	1.94	133.48 (41.5), 36.42 (34.2)
55.07	CH <sub>2</sub>	1.16	24.06 (34.2), 35.90 (34.2)
38.02	C		31.17 (36.6), 59.41 (36.6)
37.85	C		56.45 (34.2)
37.74	C		56.91 (34.2)
36.41	C		55.74 (34.2), 29.30 (36.6), 56.91 (34.2)
35.90	C		56.45 (34.2), 55.07 (34.2), 29.47 (34.2)
31.17	CH <sub>3</sub>	1.11	38.02 (36.6)
29.47	CH <sub>3</sub>	0.98	35.90 (34.2)
29.30	CH <sub>3</sub>	0.97	36.41 (36.6)
25.77	CH <sub>3</sub>	0.90	24.06 (36.6)
24.06	CH	1.68	25.77 (36.6), 55.07 (34.2)
18.93	CH <sub>3</sub>	1.63	133.48 (43.8)
13.60	CH <sub>3</sub>	1.56	122.62 (44.0)

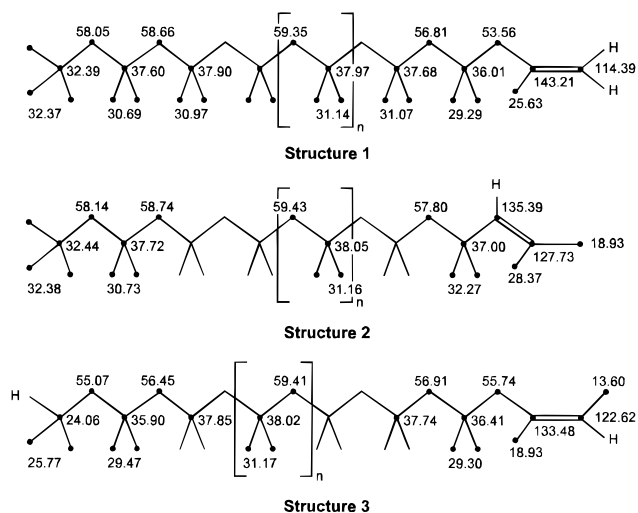
<sup>a</sup> ppm downfield from TMS internal standard. <sup>b</sup> Obtained from DEPT and APT experiments. <sup>c</sup> Obtained from HETCOR experiment. <sup>d</sup> In ppm, obtained from INADEQUATE experiment. <sup>e</sup> In Hz, from INADEQUATE experiment.

cated that the intensity of isopropyl groups equaled the sum of the intensities of isomers **3** and **4**. This indicated that isomer **4**, like isomer **3**, began with an isopropyl group.

The  $^{13}\text{C}$  NMR spectrum of a sample of polybutene with elevated levels of isomer **5** ( $\delta$  121.28 and 133.02)<sup>12</sup> showed an elevated level of *tert*-butyl end group. This indicated that isomer **5**, which contained a tetrasubstituted double bond,<sup>9</sup> like isomers **1** and **2**, also began with a *tert*-butyl group. HETCOR experiments on isomer **5** point toward three methyl groups and an unknown connection to the main polymer chain on the double bond. However, due to the low intensity of isomer **5** peaks in the mixtures examined, the complete structure of isomer **5** has not yet been confirmed by INADEQUATE experiments.

The  $^{13}\text{C}$  NMR spectrum of Parapol 950 contained a number of unassigned peaks in the region of  $\delta$  7–60. In

Chart 1



particular, peaks in the region of  $\delta$  7–9 are characteristic of the methyl carbon in the  $\text{R}_3\text{CCH}_2\text{CH}_3$  end group, and the peaks in the region of  $\delta$  10–12 are characteristic of the methyl carbon in the  $\text{R}_2\text{CHCH}_2\text{CH}_3$  end group.<sup>15</sup> These end groups may be an indication that some of the other isomers in the Parapol 950 may contain substituted ethyl end groups.

**Quantitative  $^{13}\text{C}$  NMR Experiments.** Solutions of chloroform-*d* with 0.5 M chromium (acac)<sub>3</sub> have been used so that quantitative integration of  $^{13}\text{C}$  NMR spectra could be obtained for the samples of polybutene analyzed above. By obtaining the integral of the total double bond region ( $\delta$  150 to 110), the *tert*-butyl group region ( $\delta$  32.39 for the quaternary carbon plus  $\delta$  32.37 for the three methyl carbons), and the isopropyl group region ( $\delta$  24.06 for the methine carbon), we were able to estimate the relative percentage of *tert*-butyl and isopropyl groups as a function of total olefin in the samples of polybutene. This procedure gave a somewhat high value for the percentage of *tert*-butyl groups in samples that contained large quantities of isomer **2** because isomer **2** contains a

(15) Priola, A.; Corno, C.; Cesca, S. *Macromolecules* **1980**, *13*, 1110–1113.

**Table 3.** 75 MHz NMR Structure Assignment of Polybutene 2

carbon chem shift <sup>a</sup>	carbon type <sup>b</sup>	<sup>1</sup> H chem shift <sup>c</sup>
135.39	CH	5.15
127.73	C	
59.43	CH <sub>2</sub>	1.42
58.74	CH <sub>2</sub>	1.42
58.14	CH <sub>2</sub>	1.33
57.80	CH <sub>2</sub>	1.51
38.05	C	
37.72	C	
37.51	C	
37.00	C	
32.44	C	
32.38	CH <sub>3</sub>	0.99
32.27	CH <sub>3</sub>	1.50
31.16	CH <sub>3</sub>	1.11
30.73	CH <sub>3</sub>	1.11
28.37	CH <sub>3</sub>	1.66
18.93	CH <sub>3</sub>	1.70

<sup>a</sup> ppm downfield from TMS internal standard. <sup>b</sup> Obtained from DEPT and APT experiments. <sup>c</sup> Obtained from HETCOR experiment.

*gem*-dimethyl group at  $\delta$  32.27 that interferes with the *tert*-butyl integration. The two methyl carbons at  $\delta$  25.77 were not used as a measure for the isopropyl group region because of overlap with a methyl carbon ( $\delta$  25.63) in isomer **2** that was sometimes present.

In addition, we were able to estimate the quantity of individual double bond isomers as a percentage of the total olefin area. This is shown in Table 4.

Examination of the <sup>13</sup>C NMR spectrum of 0.5 M chromium (acac)<sub>3</sub> in chloroform-*d* alone showed the presence of a broad peak that extended from about  $\delta$  50 to 110 due to the chromium (acac)<sub>3</sub>. This peak was sufficiently removed from the peaks of interest that it did not interfere in the integration.

The data in Table 4 show that the Ultravis 10 contained 80% of the methylvinylidene isomer **1** and 8% of the trisubstituted isomer **2**. Small amounts of isomer **3** (1%) and isomer **5** (3%) accounted for all but about 9% of the total olefin area. At the other end of the polybutene chain, Ultravis 10 contained 96% *tert*-butyl group and 3% isopropyl group. The experimental uncertainty for this data was measured by averaging four separate integrations for the Ultravis 10 sample. The standard deviation ( $\sigma_{n-1}$ ) for the peaks that were integrated in the Ultravis 10 sample are shown in Table 4.

The analysis for the Glissopal 1000 was similar to the Ultravis 10 (see Table 4).

In contrast, the Parapol 950 contained 37% of the trisubstituted isomer **3** and smaller amounts of isomers **4** (13%) and **5** (11%). Unassigned double bond isomers accounted for 38% of the total olefin area. The Parapol 950 contained 40% isopropyl end groups, which was approximately equal to the sum of the area of isomer **3** and **4** (50%). A small amount of *tert*-butyl end group (14%) was detected in the sample of Parapol 950. The *tert*-butyl end group in Parapol 950 was due to the presence of isomers **1** and **5** in the sample. The sum of the areas for isomers **1** and **5** was 12% in the Parapol 950.

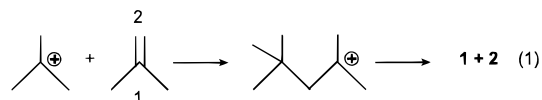
Separate experiments on samples with varying amounts of end group structures **1**–**5**<sup>11</sup> established that the *tert*-butyl area resulted mainly from contributions of isomer **1**, **2**, and **5** and the isopropyl area from contributions of isomer **3** and **4**.

The sum of the isopropyl and *tert*-butyl end groups in Parapol 950 equaled only 54% of the total expected. The

remaining end groups, whose area corresponds to the area of unassigned double bonds in the mixture, have not yet been determined.

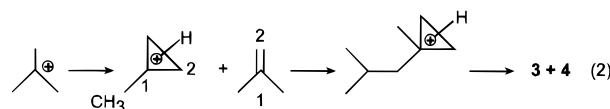
Other samples of AlCl<sub>3</sub>- and BF<sub>3</sub>-catalyzed polybutenes were also examined. These included Indopol H100H, AlCl<sub>3</sub>-catalyzed polybutene from AMOCO, Glissopal 1000, BF<sub>3</sub>-catalyzed polybutene from BASF, and PB 24, AlCl<sub>3</sub>-catalyzed polybutene from the Chevron Chemical Co. process. The PB 24, which was produced using a process patented in 1949,<sup>16</sup> was included to show historical changes in polybutene structure over the years. These data are also included in Table 4.

**Mechanistic Considerations.** The structure of a polymer is a primary source of information about the mechanism of polymer formation. The observed structure for the major isomer of the BF<sub>3</sub>-catalyzed polybutene is good evidence for the presence of the *tert*-butyl carbenium ion as the initiating species. Propagation proceeds by attack of the less hindered 2-position of isobutylene at the *tert*-butyl carbenium ion, followed by proton transfer without rearrangement to give isomers **1** and **2** (eq 1).



The situation is different for AlCl<sub>3</sub>-catalyzed polybutene. The presence of both *tert*-butyl and isopropyl end groups indicates that the mechanism is more complicated. One way to explain the isopropyl end group in structure **3** from the AlCl<sub>3</sub>-catalyzed polybutene is that the mechanism may proceed through a primary carbenium ion. Poorly understood effects such as ion pairing, steric/electronic requirements of the counterion, or solvent effects may stabilize such a high energy intermediate.<sup>17</sup>

An energetically more likely explanation is that a protonated cyclopropane intermediate may be formed from rearrangement of the *tert*-butyl carbenium ion. This intermediate has been estimated to be no greater than about 22 kcal/mol higher in energy than the *tert*-butyl carbenium ion and no greater than about 7.5 kcal/mol higher in energy than the 2-butyl carbenium ion.<sup>18</sup> The more hindered 1-position of the isobutylene then may react with the less hindered 2-position of the protonated cyclopropane intermediate in the propagation step (eq 2).



The importance of the 2-butylcarbenium ion in the polymerization of isobutylene, the involvement of 1-butene and 2-butene, which are present in the isobutylene feed, the effect of reaction conditions, and the presence of carbenium ion rearrangements in the AlCl<sub>3</sub>-catalyzed

(16) Levine, I. E.; Folsom, L. T. US Patent No. 2,484,384, Oct 11, 1949.

(17) The primary carbenium ion is estimated to be about 30 kcal/mol higher in energy than the tertiary carbenium ion: Vogel, P. *Carbocation Chemistry*; Elsevier: New York, 1985; p 337.

(18) Reference 17, 342.

**Table 4. Quantitative Integration of the  $^{13}\text{C}$  NMR Spectrum of Polybutenes<sup>a</sup>**

sample	isomer area, <sup>b</sup> %						end group area, <sup>c</sup> %		
	1	2	3	4	5	other	<i>tert</i> -butyl	isopropyl	other
Ultravis 10	80	8	2	0	3	9	96	3	3
(standard deviation) <sup>d</sup>	4.4	0.5	0.6	0	0.5	4.9	8.2	1.9	5.5
Glissopal 1000	82	9	0	0	2	7	98	1	1
Parapol 950	1	0	37	13	11	38	14	40	47
Indopol H100 H	1	0	29	10	12	48	9	35	56
PB 24	3	1	24	10	12	51	27	38	36

<sup>a</sup> Obtained at 75 MHz using 0.05 M Cr(acac)<sub>3</sub>. <sup>b</sup> Obtained by integration of the double bond carbons and divided by the total olefin area. <sup>c</sup> Obtained by the integration of the end groups and divided by the total olefin area. <sup>d</sup> Average of four determinations.

polymerization of isobutylene are all questions that await a more detailed study.

### Conclusions

Several significant conclusions can be reached from this study. First, for the AlCl<sub>3</sub>-catalyzed polybutene, the major isomer **3** contains an isopropyl group at the beginning of the polybutene chain. This was unexpected.

Second, the minor isomer **4** also contains an isopropyl group; but the minor isomer **5** contains a *tert*-butyl group at the beginning of the chain.

Third, for the AlCl<sub>3</sub>-catalyzed polybutene, isomers **1–5** account for only about half of the total double bond isomer area. Also, the *tert*-butyl and isopropyl end group area account for only about half of the end groups that were

expected. About 50% of the polybutene isomers remain unassigned.

Fourth, the BF<sub>3</sub>-catalyzed polybutene consists primarily of only isomers **1** and **2**, which both begin with a *tert*-butyl group. In the BF<sub>3</sub>-catalyzed polybutene, almost all of the double bond isomers and the end groups have been identified.

It is obvious that our understanding of the mechanism of polymerization of isobutylene is inadequate. It is hoped that these results may stimulate renewed interest in this important area and that a better understanding of the nature of the cationic polymerization of isobutylene in particular and of olefins in general will result.

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