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Carbon-13 Nuclear Magnetic Resonance Analysis of Inverted Monomeric Units in Regioirregular Poly(1-butene)

Yoshiharu Doi*[1] and Tetsuo Asakura[2]

Departments of Chemical Engineering and Polymer Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan. *Received April 4, 1980*

ABSTRACT: ^{13}C NMR resonances arising from 1-butene unit inversion have been observed in the spectrum of poly(1-butene) obtained with a soluble $Ti(OC_4H_9)_4/Al_2(C_2H_5)_3Cl_3/C_2H_5OH$ catalyst system. ^{13}C spin–lattice relaxation times have been measured at 25.14 MHz and 98 °C. Chemical shift assignments are given and compared with those predicted with the Lindeman and Adams parameters. The dyad and triad sequence distributions of inverted 1-butene units are determined from ^{13}C NMR peak areas and compared with those calculated from first-order Markov statistics. The mechanism of 1-butene polymerization is discussed.

It has been demonstrated[3-7] that ^{13}C NMR is sensitive to the specific sequence structure of propylene units resulting from propylene unit inversion along the polypropylene chain. Chemical shift assignments of ^{13}C resonances in the spectra of regioirregular polypropylenes were made by using the Lindeman and Adams relationship[8] and alkane model compounds.[9] Recently, the chain dynamics of a polypropylene containing inverted monomeric units was examined by ^{13}C relaxation measurements.[10] The ^{13}C spin–lattice relaxation times revealed that a tail-to-tail sequence (---●— —●---) is more mobile than a regular head-to-tail sequence (---●—●—---), while a head-to-head sequence (---—●●—---) is less mobile. Here, —● and ●— indicate the propylene units in the orientation $-CH_2CH(CH_3)-$ and $-CH(CH_3)CH_2-$, respectively.

The dyad and triad sequence distributions of inverted propylene units were determined from ^{13}C NMR peak areas of polypropylenes obtained with different Ziegler-type catalysts. When soluble vanadium-based catalysts were employed for polymerization of propylene, the resulting polymer contained sequence blocks of head-to-tail units and of tail-to-head units, i.e., isolated tail-to-tail and head-to-head units in the chain, as represented by[3-5]

---●—●— —●—●---—●—●●—●—---

In contrast, the polypropylene obtained with titanium-based catalyst contained some isolated inversions of single propylene units in long sequences of head-to-tail or tail-to-head units:[6]

---●—●—●—●— —●●—●—●—---

The above results gave us some important information concerning the mechanism of propylene polymerization.[3-6]

To extend our study of monomer unit inversion, we have prepared a regioirregular poly(1-butene) with a soluble titanium-based catalyst, $Ti(OC_4H_9)_4/Al_2(C_2H_5)_3Cl_3/C_2H_5OH$, and attempted to assign to ^{13}C NMR resonances arising from 1-butene unit inversion. We have also carried out ^{13}C spin–lattice relaxation measurements. The sequence distribution of inverted monomeric units has been determined from ^{13}C NMR peak areas.

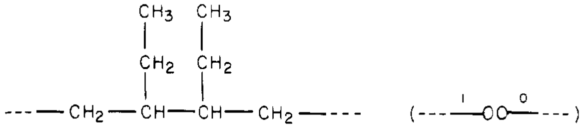
Experimental Section

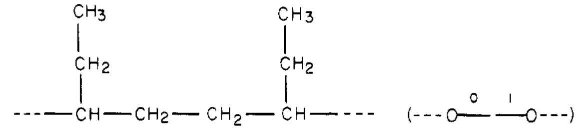
Poly(1-butene) was prepared by polymerization of 1-butene (6 g) in the presence of a catalyst system consisting of 2.4 mmol of $Ti(OC_4H_9)_4$, 4.0 mmol of C_2H_5OH, and 7.5 mmol of $Al_2(C_2H_5)_3Cl_3$. The polymerization was carried out for 6 h at 20 °C in 20 mL of heptane solution. The resulting polymer (0.45 g) had $\bar{M}_n = 3500$ and $\bar{M}_w = 5600$.

^{13}C NMR spectra of the polymer were recorded at 98 °C with a JEOL PS-100 spectrometer operating at 25.14 MHz in the PFT mode. ^{13}C NMR spin–lattice relaxation time measurements were made by using a 180°–τ–90° pulse sequence. Six τ values were used in the measurement, and the peak areas of each resonance were used in T_1 determinations. The number of transients accumulated for each τ value was 1500. The solution was made up in o-dichlorobenzene to 14% (w/v) (0.14 g of polymer/1 mL of solution) without degassing.

Results and Discussion

Figure 1 shows a ^{13}C NMR spectrum of the poly(1-butene) obtained in the presence of the soluble catalyst system $Ti(OC_4H_9)_4/Al_2(C_2H_5)_3Cl_3/C_2H_5OH$.[11] Some small peaks are observed other than the four major peaks assigned to main-chain $S_{\gamma\alpha\alpha\gamma}$, $T_{\beta\beta}$, side-chain $S_{\beta\beta}$, and $P_{\beta\beta}$ species in the head-to-tail sequence of 1-butene units. These ^{13}C resonances may arise from a specific sequence structure of 1-butene units containing irregular head-to-head and tail-to-tail units:





The ^{13}C chemical shift assignments, made using the Lindeman and Adams relationship,[8] are given in Table I. Here, we denote each tertiary carbon as T with two Greek subscripts indicating its position relative to the nearest tertiary carbons along the polymer chain, as used in a previous paper.[12] The side-chain secondary and primary carbons are designated by sc-S and P with the same Greek subscripts as used for the attached tertiary carbon. Each main-chain secondary carbon is designated by mc-S with four Greek subscripts, which indicate its position with respect to the nearest- and the next-neighbor tertiary carbons in both directions along the polymer chain. For simplification, the 1-butene units in the orientations ○— and —○ are represented, respectively, by "0" and "1". As shown in Table I, the observed chemical shifts are in relative agreement with the calculated ones obtained with the Lindeman and Adams parameter values, though a tendency may be noted for all resonances of main-chain secondary carbons to be shifted toward low field. The resonances at 37.0–37.5 and 33.6–33.8 ppm appear to be composed of two overlapping tetrads, mc-$S_{\beta\alpha\alpha\gamma}$ and mc-$S_{\beta\alpha\alpha\delta}$, mc-$S_{\gamma\alpha\beta\gamma}$ and mc-$S_{\gamma\alpha\beta\delta}$, respectively. Unfortunately, we could not detect ^{13}C resonances of mc-$S_{\gamma\alpha\alpha\delta}$, sc-$S_{\beta\gamma}$, $P_{\beta\gamma}$, $P_{\alpha\beta}$, and $P_{\alpha\gamma}$, which are most likely to overlap with the major ^{13}C resonances arising from triad or tetrad sequences of connecting regular head-to-tail units. The two major ^{13}C resonances of $T_{\beta\beta}$ and sc-$S_{\beta\beta}$ are obviously split into two or three components, resulting from the tacticity of poly(1-butene).[13]

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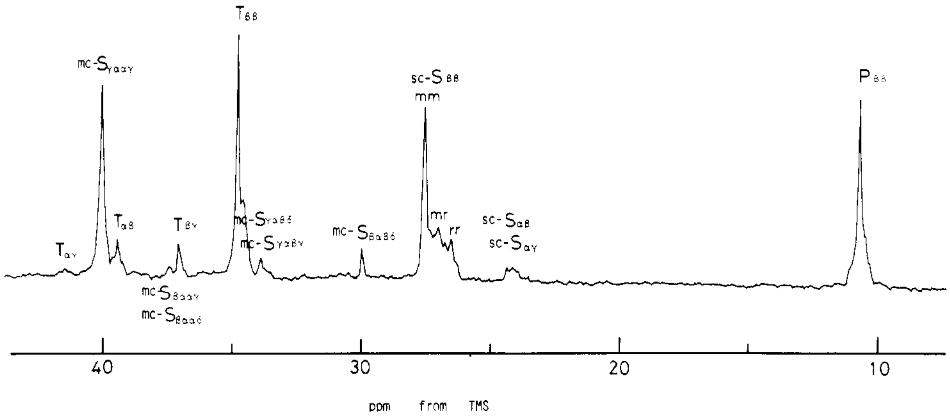

Figure 1. ^{13}C NMR spectrum of poly(1-butene) at 98 °C in *o*-dichlorobenzene. The spectrum represents 1500 transients accumulated with a repetition time of 2.5 s.

Table I
Observed Chemical Shifts of ^{13}C Resonances in Poly(1-butene) and Corresponding Chemical Shifts Calculated with the Lindeman and Adams Parameters

species	sequence assignment	obsd,[a] ppm	calcd, ppm	T_1,[b] s
mc-$S_{\gamma\alpha\alpha\gamma}$	○—○—○—○— (0000) and —○—○—○—○ (1111)	39.9	38.98	0.28
mc-$S_{\gamma\alpha\alpha\delta}$	○—○—○——○ (0001) and ○——○—○—○ (0111)	(39.5)[c]	38.73	
mc-$S_{\beta\alpha\alpha\gamma}$	—○ ○—○—○— (1000) and —○—○—○ ○— (1110)	37.0-37.5	36.29	
mc-$S_{\beta\alpha\alpha\delta}$	—○ ○—○——○ (1001) and ○——○—○ ○— (0110)		36.04	
mc-$S_{\gamma\alpha\beta\gamma}$	○—○——○ ○— (0010) and —○ ○——○—○ (1011)	33.6-33.8	32.28	
mc-$S_{\gamma\alpha\beta\delta}$	two for ○—○——○—○ (0011)		32.03	
mc-$S_{\beta\alpha\beta\gamma}$	two for —○ ○——○ ○— (1010)	(—)	29.59	
mc-$S_{\beta\alpha\beta\delta}$	—○ ○——○—○ (1011) and ○—○——○ ○— (0010)	29.8	29.34	0.82
$T_{\beta\beta}$	○—○—○— (000) and —○—○—○ (111)	34.4-34.7	34.98	0.49
$T_{\beta\gamma}$	○—○——○ (001) and ○——○—○ (011)	36.8	37.05	0.58
$T_{\alpha\beta}$	—○ ○—○— (100) and —○—○ ○— (110)	39.2	39.52	
$T_{\alpha\gamma}$	—○ ○——○ (101) and ○——○ ○— (010)	41.3	41.59	
sc-$S_{\beta\beta}$	○—○—○— (000) and —○—○—○ (111)	26.4-27.4	27.66	0.38 for mm
sc-$S_{\beta\gamma}$	○—○——○ (001) and ○——○—○ (011)	(—)	27.41	
sc-$S_{\alpha\beta}$	—○ ○—○— (100) and —○—○ ○— (110)	23.8-24.3	24.97	
sc-$S_{\alpha\gamma}$	—○ ○——○ (101) and ○——○ ○— (010)		24.72	
$P_{\beta\beta}$	○—○—○— (000) and —○—○—○ (111)	10.7	11.36	
$P_{\beta\gamma}$	○—○——○ (001) and ○——○—○ (011)	(—)	11.36	
$P_{\alpha\beta}$	—○ ○—○— (100) and —○—○ ○— (110)	(—)	11.85	
$P_{\alpha\gamma}$	—○ ○——○ (101) and ○——○ ○— (010)	(—)	11.85	

[a] Downfield from internal Me_4Si at 98 °C in *o*-dichlorobenzene. [b] ^{13}C NMR spin-lattice relaxation times at 98 °C. [c] Chemical shift is shown in parentheses because of the uncertainty of assignment.

^{13}C NMR spin-lattice relaxation times (T_1's) were determined at 98 °C for the five well-resolved resonances 39.9, 36.8, 34.7, 29.8, and 27.4 ppm. The T_1 values are given in Table I. The T_1 values of mc-$S_{\beta\alpha\beta\delta}$ and $T_{\beta\gamma}$ in tail-to-tail units are longer than those of the corresponding carbons mc-$S_{\gamma\alpha\alpha\gamma}$ and $T_{\beta\beta}$ in head-to-tail units, indicating that the tail-to-tail units are more mobile (longer NT_1) than the head-to-tail units. This motional behavior is easily understandable by taking into account the number of carbon atoms participating in the steric repulsion restricting chain rotation.[10]

The sequence distribution of inverted monomeric units in poly(1-butene) was determined from ^{13}C NMR peak areas. The relative intensities *I* of each tertiary and side-chain secondary ^{13}C resonance can be related to the following mole fractions of the different triads of connecting 1-butene units "0" and "1":

$$I(T_{\beta\beta}) = I(\text{sc-}S_{\beta\beta}) = F_{000} + F_{111} \quad (1)$$

$$I(T_{\beta\gamma}) = I(\text{sc-}S_{\beta\gamma}) = F_{001} + F_{011} \quad (2)$$

$$I(T_{\alpha\beta}) = I(\text{sc-}S_{\alpha\beta}) = F_{100} + F_{110} \quad (3)$$

$$I(T_{\alpha\gamma}) = I(\text{sc-}S_{\alpha\gamma}) = F_{010} + F_{101} \quad (4)$$

where F_{iji} represents the mole fraction of *iji* units sequence.

Table II
Dyad and Triad Sequence Distributions of 1-Butene Units

	dyad fractions		triad fractions			
	$F_{00} + F_{11}$	$F_{01} + F_{10}$	$F_{000} + F_{111}$	$F_{001} + F_{011}$	$F_{100} + F_{110}$	$F_{010} + F_{101}$
CH[a]			0.84	0.06	0.06	0.04
sc-CH_2 [b]			0.91		0.09	
mc-CH_2 [c]	0.90	0.10				
calcd[d]	0.90	0.10	0.84	0.06	0.06	0.04

[a] From tertiary carbon resonance areas. [b] From side-chain secondary carbon resonance areas. [c] From main-chain secondary carbon resonance areas. [d] Calculated with the values of p_{ij} in Table III.

The triad fractions of connecting 1-butene units were determined from the peak areas of both tertiary and side-chain secondary carbon resonances. The result is shown in Table II. The peak deconvolution of the side-chain secondary carbon resonances, sc-$S_{\beta\beta}$ and sc-$S_{\beta\gamma}$, sc-$S_{\alpha\beta}$ and sc-$S_{\alpha\gamma}$, was not carried out because of its difficulty. The triad sequence distributions determined from the specific tertiary and side-chain secondary carbon peak areas show good agreement, confirming the ^{13}C chemical shift assignment in Table I. Conversely, the relative intensities of main-chain secondary carbons were used to determine the mole fractions of different dyads of connecting 1-butene units by the following relations, since some tetrad resonances overlapped each other:

$$I(\text{mc-S}_{\alpha\alpha}) = I(\text{mc-S}_{\gamma\alpha\alpha\gamma}) + I(\text{mc-S}_{\gamma\alpha\alpha\delta}) + I(\text{mc-S}_{\beta\alpha\alpha\gamma}) + I(\text{mc-S}_{\beta\alpha\alpha\delta}) \quad (5)$$

$$I(\text{mc-S}_{\alpha\beta}) = I(\text{mc-S}_{\gamma\alpha\beta\gamma}) + I(\text{mc-S}_{\gamma\alpha\beta\delta}) + I(\text{mc-S}_{\beta\alpha\beta\gamma}) + I(\text{mc-S}_{\beta\alpha\beta\delta}) \quad (6)$$

$$I(\text{mc-S}_{\alpha\alpha}) = F_{00} + F_{11} \quad (7)$$

$$I(\text{mc-S}_{\alpha\beta}) = F_{01} + F_{10} \quad (8)$$

where F_{ij} is the mole fraction of ij units sequence. The dyad fractions determined from the peak areas of main-chain secondary carbon resonances are given in Table II.

As we showed in a previous paper,[4] the observed sequence distribution of inverted monomeric units can be interpreted in terms of the statistics of a binary copolymerization involving the following propagation steps:

$$\cdots\circ\text{—}\mathrm{Mt} + C_4H_8 \xrightarrow{p_{00}} \cdots\circ\text{—}\circ\text{—}\mathrm{Mt} \quad (9)$$

$$\cdots\circ\text{—}\mathrm{Mt} + C_4H_8 \xrightarrow{p_{01}} \cdots\circ\text{——}\circ\,\mathrm{Mt} \quad (10)$$

$$\cdots\text{—}\circ\,\mathrm{Mt} + C_4H_8 \xrightarrow{p_{10}} \cdots\text{—}\circ\;\circ\text{—}\mathrm{Mt} \quad (11)$$

$$\cdots\text{—}\circ\,\mathrm{Mt} + C_4H_8 \xrightarrow{p_{11}} \cdots\text{—}\circ\text{—}\circ\,\mathrm{Mt} \quad (12)$$

Here p_{ij} is the conditional probability of step ij with the relations that $p_{00} + p_{01} = 1$ and $p_{11} + p_{10} = 1$. In the above scheme, a 1-butene unit is designated by a "0" when a 1-butene molecule adds by primary insertion or by a "1" when a 1-butene molecule adds by secondary insertion. In first-order Markov statistics, one can express the different dyad and triad fractions of 1-butene units "0" and "1" with four conditional probabilities:[14-16]

$$F_{00} + F_{11} = \frac{p_{10}p_{00} + p_{01}p_{11}}{p_{01} + p_{10}} \quad (13)$$

$$F_{01} + F_{10} = \frac{2p_{01}p_{10}}{p_{01} + p_{10}} \quad (14)$$

$$F_{000} + F_{111} = \frac{p_{10}p_{00}p_{00} + p_{01}p_{11}p_{11}}{p_{01} + p_{10}} \quad (15)$$

$$F_{001} + F_{011} = F_{100} + F_{110} = \frac{p_{01}p_{10}(p_{00} + p_{11})}{p_{01} + p_{10}} \quad (16)$$

$$F_{010} + F_{101} = p_{01}p_{10} \quad (17)$$

Combining eq 13 and 14 with eq 15, 16, or 17, we calculated the four conditional probabilities, p_{ij}, using the observed dyad and triad sequence distributions (Table II). The result is given in Table III. For comparison, the dyad and triad distributions calculated with the values of p_{ij} are shown in Table II. The calculated dyad and triad sequence distributions are consistent with the observed distributions, confirming that the sequence distributions of connecting two different types of 1-butene units "0" and "1" are accounted for in terms of first-order Markov statistics.

Table III
Four Conditional Probabilities and Number-Average Sequence Lengths of 1-Butene Units "0" and "1"

p_{ii} (p_{00})	p_{ij} (p_{01})	p_{ji} (p_{10})	p_{jj} (p_{11})	$\bar{n}_i$ ($\bar{n}_0$)	$\bar{n}_j$ ($\bar{n}_1$)
0.95	0.05	0.75	0.25	20	1.3

The number-average sequence lengths of 1-butene units "0" and "1" can be determined from two conditional probabilities by the following relationships:

$$\bar{n}_0 = 1/p_{01} \quad (18)$$

$$\bar{n}_1 = 1/p_{10} \quad (19)$$

However, we could not distinguish "0" units from "1" units by ^{13}C NMR analysis of dead polymer. As a result, we could not distinguish p_{00} from p_{11}, p_{01} from p_{10}, or $\bar{n}_0$ from $\bar{n}_1$ by calculation. From Table III, we have a relation

$$\bar{n}_i\ (=20) >> \bar{n}_j\ (=1.3) \quad (20)$$

indicating that one type of insertion of 1-butene molecule (either the primary or the secondary) is always favored in the catalyst system of $Ti(OC_4H_9)_4/Al_2(C_2H_5)_3Cl_3/C_2H_5OH$.

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