2D-INADEQUATE ^{13}C nuclear magnetic resonance assignment of regioirregular poly(1-butene)

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The ^{13}C nuclear magnetic resonance (n.m.r.) spectrum of regioirregular poly(1-butene) with a large number of chemical inversion units in the chain was observed. The assignments were performed by ^{13}C n.m.r. Lindeman–Adams empirical rules, the insensitive nuclei enhancement by polarization transfer (INEPT) and two-dimensional incredible natural abundance double quantum transfer experiment (2D-INADEQUATE) ^{13}C n.m.r. techniques. 2D-INADEQUATE was especially useful to assign each peak to carbon atoms located in several kinds of sequences in the chain.

(Keywords: ^{13}C n.m.r.; 2D-INADEQUATE; regioirregular poly(1-butene))

Introduction

The recently developed two-dimensional incredible natural abundance double quantum transfer experiment (2D-INADEQUATE) ^{13}C nuclear magnetic resonance (n.m.r.) technique[1,2] has been successfully used to assign the ^{13}C n.m.r. spectra of ethylene–propylene (E-P) copolymers[3,4], stereoirregular polypropylene (PP)[5] and regioirregular PP[6].

In this paper, we have used the 2D-INADEQUATE method in order to assign the ^{13}C n.m.r. spectrum of regioirregular poly(1-butene) (PB). Although there are many reports on the ^{13}C n.m.r. assignment of regioirregular PP[6–15], the assignment of regioirregular PB is limited[16]. Because of the coexistence of several kinds of sequences containing inverted monomer units and the splitting due to the tacticity[17,18], the spectra are extremely complex. This paper contains the first detailed assignment of regioirregular PB.

Experimental

The polymer solution was prepared at a concentration of 21 w/v% in an *o*-dichlorobenzene–deuteriobenzene (9:1 v/v) mixture. The 2D-INADEQUATE ^{13}C n.m.r. spectrum was measured at 100°C using a Jeol GX-270 n.m.r. spectrometer operating at 67.8 MHz. The standard pulse sequence, $90°\text{-}1/4J\text{-}180°\text{-}1/4J\text{-}90°\text{-}t_1\text{-}135°$-acquisition$(t_2)$, was used, where J is a constant of $^{13}C-^{13}C$ direct coupling. The delay time, $1/4J$, was set to be 7.11 ms corresponding to the $^{13}C-^{13}C$ coupling constant of 35.2 Hz. The data matrix size of the time domain was $4096(f_2) \times 128(f_1)$, and that of the frequency domain was expanded to $8192(F_2) \times 256(F_1)$. Hexamethyldisiloxane was used as the internal reference (2.03 ppm downfield from the peak of tetramethylsilane).

Results and discussion

Figure 1 shows the ^{13}C n.m.r. spectra of a regioirregular PB sample with a large number of chemical inversion units. The ^{13}C chemical shifts calculated according to ^{13}C n.m.r. Lindeman–Adams empirical rules[19] for the prediction of ^{13}C chemical shifts of alkanes are also shown as stick spectra by assuming the presence of several kinds of sequences containing the chemical inversion units[7]. This sample is atactic judging from the relative peak intensities of the carbons located at the regular head-to-tail (H–T) sequence of the chain[17,18]. From a comparison of the calculated and observed chemical shifts, it is clear that there are some sequences other than H–T and isolated H–H or T–T units. In order to separate the CH and CH_2 peaks in the spectrum, the insensitive nuclei enhancement by polarization transfer (INEPT) spectrum was observed[13]. The expanded spectra in the 34–45 ppm region are shown in *Figure 2*. Thus, the two peaks at 36 and 36.5 ppm, and the peaks at 24–34 ppm are assigned to the CH_2 carbons. The peak at 43 ppm, two peaks at ~38 ppm and the peak at 35 ppm are assigned to the CH carbons. The peaks at 39.5–40.5 ppm are a mixture of the CH and CH_2 carbons which are separated by the INEPT observation. The peaks at 11–13 ppm are assigned to the CH_3 carbons. In order to assign these peaks to carbons located in several kinds of sequences, the 2D-INADEQUATE spectrum was observed.

Figure 3 shows the 2D-INADEQUATE spectra of regioirregular PB. The region from 22 to 45 ppm was expanded and the $^{13}C-^{13}C$ connectivities of the carbons located at the sequences which contain the isolated H–H and T–T units are shown. Unassigned peaks still remain, indicating the presence of other sequences in the chain. Thus, the $^{13}C-^{13}C$ connectivities of the carbons located at three kinds of sequences other than the sequences of the isolated H–H and T–T units are also examined.

Figure 4 shows the $^{13}C-^{13}C$ connectivities of the sequence involving a single inverted unit in the H–T sequences, termed as 1-r. Thus, the peaks at 28.5, 33.2 and 43.2 ppm are now assigned. Similarly, other sequences, 2-r and 2U-r are taken into account and the $^{13}C-^{13}C$ connectivities are also made in the 2D-INADEQUATE spectrum (data not shown). Here, the sequence where inversion occurs followed by a second inversion is termed 2-r and the sequence where two

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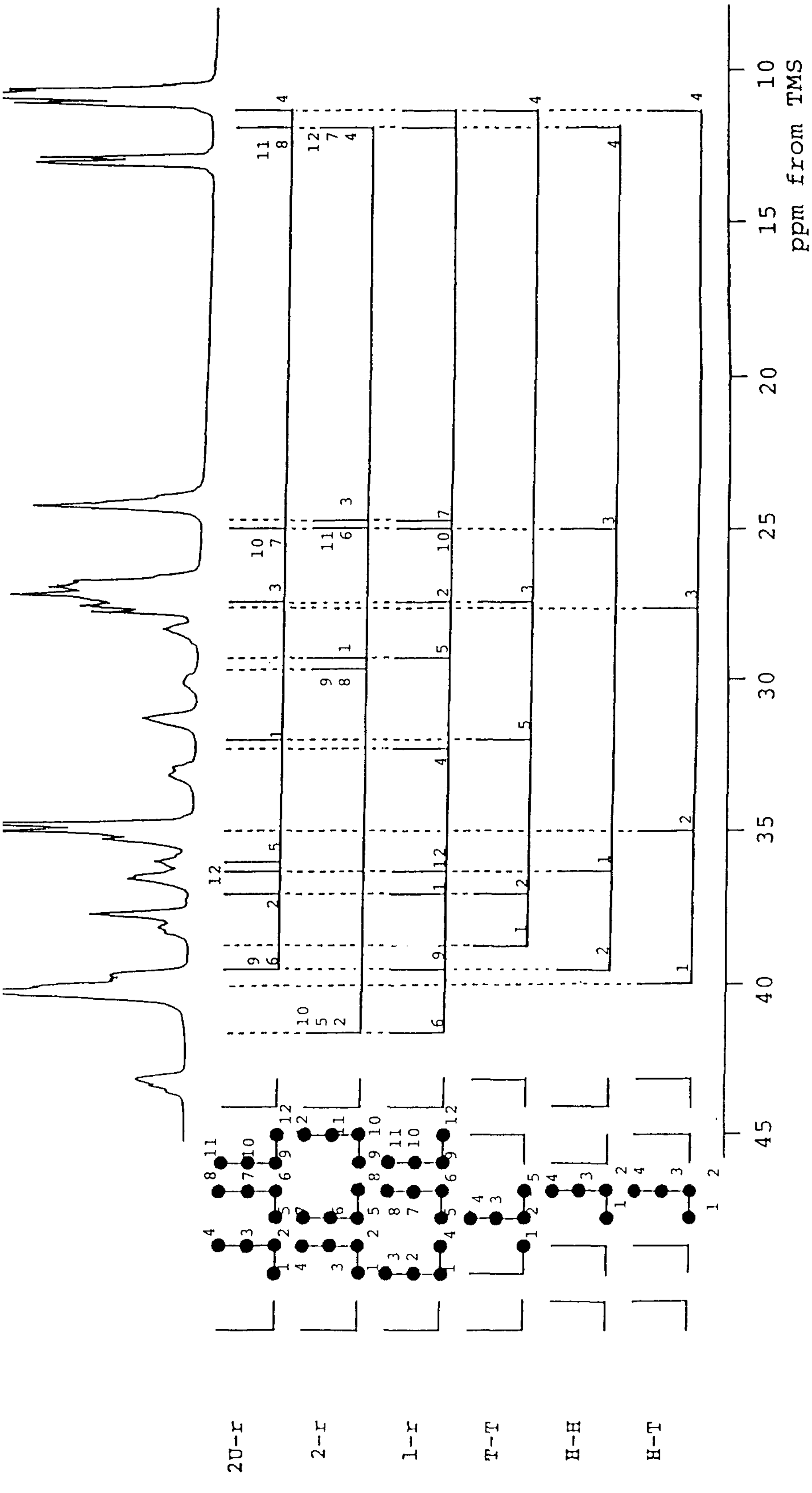
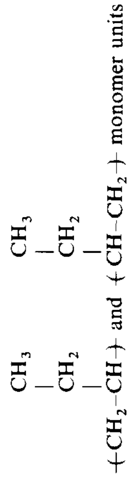


Figure 1 ^{13}C n.m.r. spectrum of regioirregular poly(1-butene). The stick spectra calculated using Lindeman–Adams ^{13}C n.m.r. chemical shift empirical rules by assuming the presence of several kinds of sequences in the chain are also shown. The notations ⏌ and ⎿ represent the



$$\underset{}{+CH_2-\overset{\overset{\displaystyle CH_3}{|}}{\overset{\displaystyle CH_2}{\underset{}{|}}}{CH}+}\text{ and }+\overset{\overset{\displaystyle CH_3}{|}}{\overset{\displaystyle CH_2}{|}}{CH}-CH_2+$$ monomer units

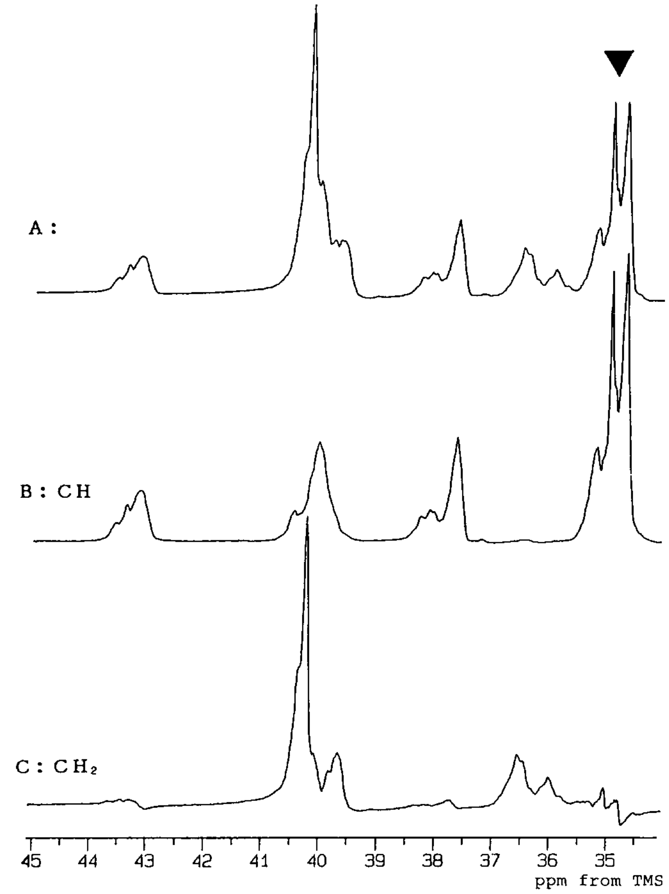
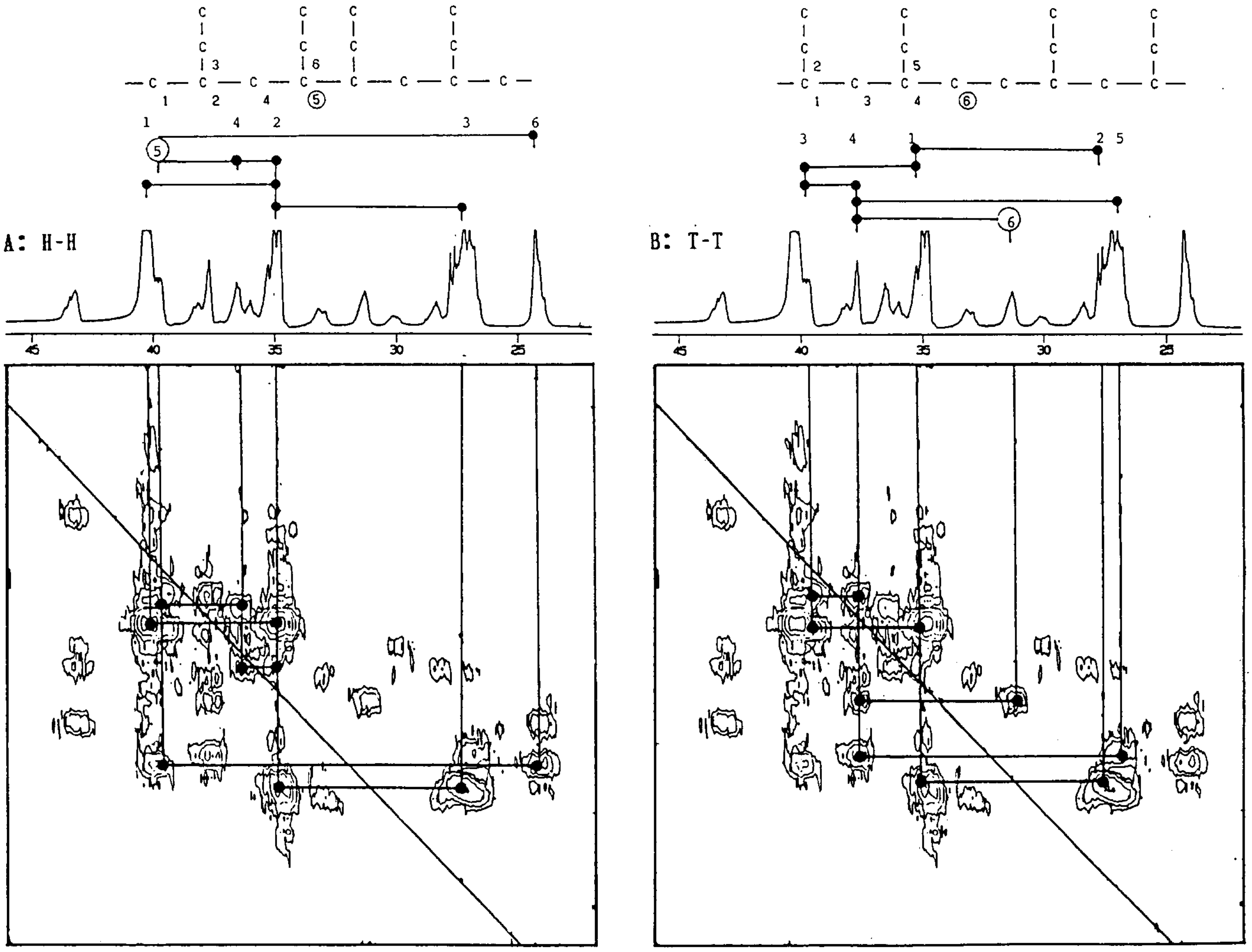


Figure 2 ^{13}C n.m.r. spectra of regioirregular poly(1-butene). The region 34–45 ppm was expanded: (A) ^{1}H completely decoupled; (B) INEPT ($\Delta = 2/4J$), methine only; (C) difference (A–B), methylene only; (▼) reference peak

Figure 3 2D-INADEQUATE ^{13}C n.m.r. spectra of regioirregular poly(1-butene). The region 22–45 ppm was expanded. The ^{13}C–^{13}C connectivities of the sequences containing isolated (A) head-to-head and (B) tail-to-tail units are shown as solid lines



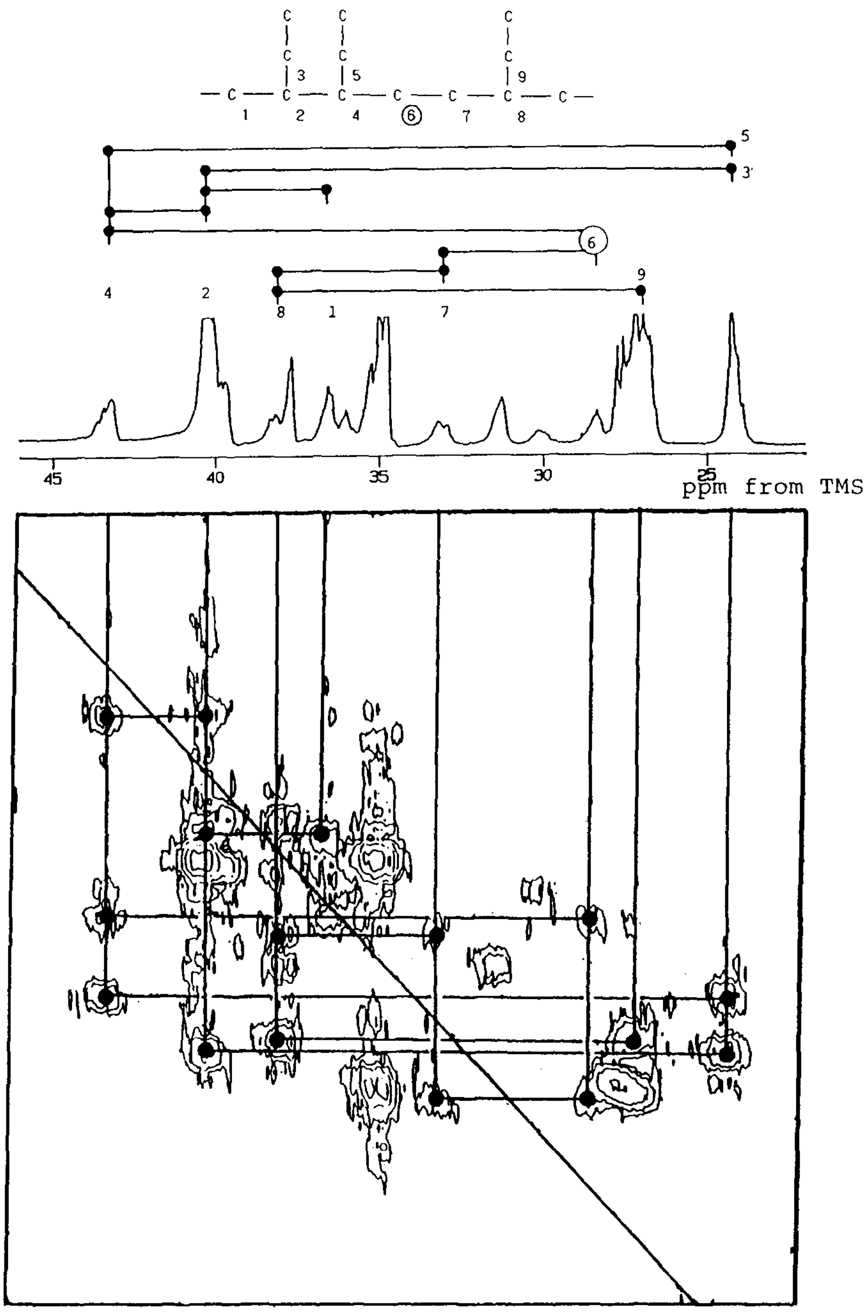


Figure 4 2D-INADEQUATE ^{13}C n.m.r. spectrum (22–45 ppm) of regioirregular poly(1-butene). The ^{13}C–^{13}C connectivities of the sequence 1-r where a single chemical inversion occurs in the H–T sequences are shown

Table 1 ^{13}C n.m.r. chemical shift assignment for regioirregular poly(1-butene)

Chemical shift (ppm)	H-T	H-H	T-T	1-r	2-r	2U-r
43.6–43.0	–	–	–	Tδγαγ	Tδαγδ	–
40.1–39.4	m-Sαα	Tδβαγ	m-Sγααδ	Tδαβδ	–	Tδ$^+$βαγ
38.2–37.5	–	–	Tδβγδ	–	–	Tδ$^+$γβγ
36.4	–	m-Sγααβ	–	–	–	–
35.9	–	–	–	–	–	m-Sδααβ
35.2–34.6	Tββ	Tδββγ	–	–	–	–
33.1–32.8	–	–	–	–	m-Sγαβγ	–
31.2	–	–	m-Sγαβδ	–	–	m-Sδβαγ
30.1–29.9	–	–	–	–	m-Sβαβγ	–
28.3	–	–	–	m-Sδβαβ	–	–
27.7–26.5	s-Sββ	–	s-Sδβγδ	–	–	s-Sδ$^+$δβγ
24.2–23.7	–	s-Sδβαγ	–	s-Sδγαγ	s-Sδαγδ	s-Sδ$^+$βαγ
13.0–12.8	–	Pδβαγ	–	Pδγαγ	Pδαγδ	Pδ$^+$βαγ
11.0–10.5	Pββ	–	Pδβγδ	–	–	Pδ$^+$γβγ

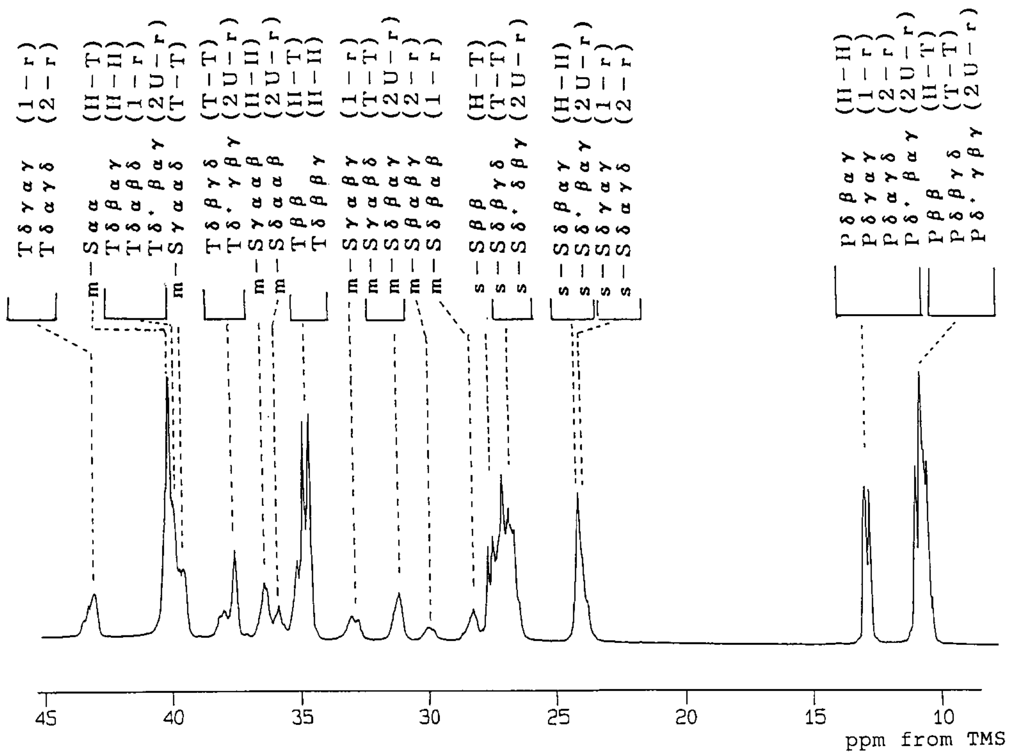


Figure 5 ^{13}C n.m.r. spectrum of regioirregular poly(1-butene). The nomenclature proposed by Carman and Wilkes[20] is used for the designation of the carbon types

successive inverted units occurs is 2U-r:

2-r └─ └─ └─ ─┘ └─ ─┘ └─ └─ └─
2U-r └─ └─ └─ ─┘ ─┘ └─ └─ └─ └─

Thus, all of the peaks are assigned to each carbon in the sequences considered here. This is similar to the case of the ^{13}C n.m.r. spectrum of regioirregular PP with a large amount of chemical inversion[6].

The final assignments including the CH_3 carbons are summarized in *Figure 5* and *Table 1*, where the nomenclature proposed by Carman and Wilkes[20] is used for the designation of carbon types. The side-chain secondary and primary carbons are designated by s-S and P, respectively, and the main chain secondary and tertiary carbons by m-S and T, respectively. The Greek subscripts indicate position relative to the nearest and/or the next nearest neighbour tertiary carbons in both directions along the polymer chain.

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