Structural characterization of 1,2-polybutadiene by ^{13}C n.m.r. spectroscopy: 1. Signal assignment in hydrogenated polybutadienes

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The configurational sequences of 1,2-unit in a series of hydrogenated syndiotactic 1,2-polybutadienes were investigated in relation to the sequence distribution of 1,2- and 1,4-units. The signals at 10.20–10.94 ppm were assigned to the methyl carbons in the isolated 1,2-unit, the 1,2–1,2 dyad sequence flanked by 1,4-unit, and the 1,2–1,2–1,2 triad sequence, in order of increasing magnetic field. The splittings due to the configurational sequences were observed in the signals, reflecting the dyad and triad sequences of the 1,2-unit, which were assigned by considering the relative intensity of the signals and also the chemical shifts of model polymers.

Keywords Characterization; spectroscopy; structure; 1,2-polybutadiene; nuclear magnetic resonance; hydrogenation

INTRODUCTION

^{13}C n.m.r. spectroscopy has been successfully applied to the investigation of the sequence distribution of isomeric units in polybutadiene such as *cis*-1,4 and *trans*-1,4[1–3], 1,4 and 1,2[4,5], *cis*-1,4 and 1,2[6,7], and *cis*-1,4, *trans*-1,4, and 1,2[4,8,9]. These studies took advantage of the sensitivity of ^{13}C chemical shifts to differences in structural environments. The ^{13}C n.m.r. spectra of polybutadiene and hydrogenated polybutadiene have been assigned to the carbons in various sequences of isomeric units, using the empirical equation of Paul and Grant derived for branched alkanes[10] or its modification for alkenes. This method has proved a powerful tool in the detailed assignment of the signals in hydrogenated polybutadiene. Clague *et al.*[4] and Randall[5] carried out the signal assignment of hydrogenated polybutadiene by considering only the monomer sequences of hydrogenated 1,2- and 1,4-units.

In the case of polybutadiene with a syndiotactic or isotactic configuration of 1,2-unit, it is reasonable to assume that the crystallinity of the polymers depends on the configurational sequence of 1,2-unit as well as the sequence distribution of 1,2- and 1,4-units. Therefore, it is necessary to take into consideration the tacticity of 1,2-unit for the assignment of the ^{13}C spectrum of polybutadiene. In small molecules, conformational terms were expected to have no substantial effect on the chemical shifts of alkanes[10]. However, the non-equivalence of isopropyl methyl and internal methylene carbons has been observed for long-chain branched molecules such as 2,4,6-trimethylheptane, 2,5,8-trimethylnonane, and 2,5,8,11-tetramethyldodecane[11], which was attributed to differences in rotational conformations in diastereomers. The tacticity of 3,4-units in polyisoprene was successfully determined from the methylene carbon signal in hydrogenated polyisoprene by preparing various types of 3,4-polyisoprene and model polymers[12].

We prepared a series of syndiotactic 1,2-polybutadienes with various degrees of crystallinity. The relationship between crystallinity and sequence structure of these polymers was investigated from the standpoint of the sequence length of syndiotactic 1,2-unit. The assignment of ^{13}C n.m.r. signals was carried out by considering the configurational sequences of 1,2-unit as well as the sequence of 1,2- and 1,4-units in hydrogenated 1,2-polybutadienes.

EXPERIMENTAL

Materials

Syndiotactic 1,2-polybutadienes were prepared with $CoBr_2[P(C_6H_5)_3]_2$-Al(i-Bu)$_3$-H_2O catalyst in methylene chloride at $-15°C$ to $30°C$[13]. Atactic 1,2-polybutadienes were prepared with $CoBr_2[P(C_2H_5)_3]_2$-Al(i-Bu)$_3$-H_2O catalyst in methylene chloride at $30°C$[13] and with n-butyllithium in tetrahydrofuran. Highly crystalline syndiotactic 1,2-polybutadiene was synthesized with Co(octate)$_2$-AlEt$_3$-CS_2 catalyst in benzene[14]. The isomeric structure of these polymers was determined by ^1H n.m.r. measurement[15]. The crystallinity of these polymers was determined for thin films prepared by pressing under 100 kg cm^{-2} at 130°C by a density gradient method, assuming a density of 0.963 for crystalline part[16] and 0.889 for the amorphous part.

These 1,2-polybutadienes were hydrogenated

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Table 1 Polymerization conditions and microstructure of 1,2-polybutadienes

Polymer	Catalyst	Polymerization temperature (°C)	Microstructure (%) 1,2	1,4	Crystallinity (%)	T_e[a] (°C)
A	$CoBr_2[P(C_2H_5)_3]_2$–$Al(i\text{-}Butyl)_3$–H_2O	30	75	25	0	79
B	$CoBr_2[P(C_6H_5)_3]_2$–$Al(i\text{-}Butyl)_3$–H_2O	30	82	18	18	116
C	"	10	84	16	25	132
D	"	0	85	15	29	142
E	"	–15	86	14	35	154
F	n-Butyllithium–THF	0	80	20	0	–
G	$Co(Octate)_2$–$Al(C_2H_5)_3$–CS_2	30	96	4	63[b]	210

[a] Determined from d.s.c.[19];
[b] Presumed from T_e

according to the method of Sanui *et al.*[17] with *p*-toluenesulphonylhydrazide in xylene at 135°–145°C for 2 h. The hydrogenated polymers were purified by reprecipitation from toluene solution with methanol. The absence of the residual unsaturation was confirmed by the disappearance of the characteristic infra-red bands at 967, 911, and 730–737 cm^{-1}.

Commercially obtained isotactic polybutene-1 (WITRON 0400) was extracted by refluxing with methylene chloride. The soluble polymer (~5%) was purified by reprecipitation.

Measurements

^{13}C n.m.r. spectra were obtained at 25.05 MHz, using a JEOL JNM-FX-100 spectrometer. Measurements were made at 60°C in $CDCl_3$ (~15 %w/v) with tetramethylsilane (TMS) as internal standard. All the spectra were proton noise decoupled and obtained with multiple scans at a pulse repetition time of 3.0 s. Spectrum accumulation was carried out using 8K computer locations for a spectral sweep width of 2000 Hz. The overlapped signals were separated by a Hewlett-Packard 9825 A calculator assuming a Lorentzian curve for each component.

RESULTS AND DISCUSSION

1,2-Polybutadienes with different degree of crystallinity

Syndiotactic 1,2-polybutadiene was synthesized with various catalysts. The tacticity of 1,2-polybutadiene could be controlled by polymerization of butadiene with $CoBr_2$ complex catalysts[13]. The crystallinity of the polymers increased with decreasing polymerization temperature without a large difference in isomeric structure of the resulting polymers. Atactic 1,2-polybutadiene was obtained using $CoBr_2[P(C_2H_5)_3]_2$ instead of $CoBr_2[P(C_6H_5)_3]_2$ in the syndiotactic catalyst system. The polymerization conditions, isomeric structure, degree of polymerization, and melting temperature of these 1,2-polybutadienes are tabulated in *Table 1*.

Assignment of ^{13}C n.m.r. signals in hydrogenated polybutadiene

The ^{13}C n.m.r. spectrum of polybutadiene containing *cis*-1,4-, *trans*-1,4-, and 1,2-units exhibits quite a complicated splitting, resulting from overlapping of the signals due to a variety of carbon atoms in various types of sequences. The hydrogenated polybutadienes are regarded as copolymers of the following isomeric units:

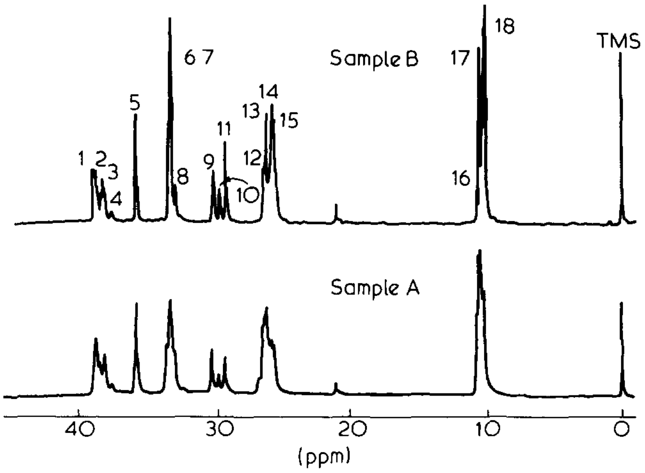
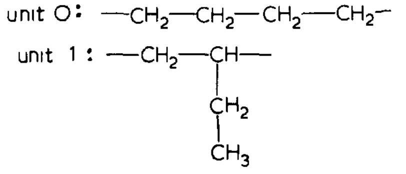


Figure 1 ^{13}C n.m.r. spectra of hydrogenated 1,2-polybutadienes



$$\text{unit 0: } -CH_2-CH_2-CH_2-CH_2-$$

$$\text{unit 1: } -CH_2-\underset{\underset{CH_3}{|}}{\underset{CH_2}{|}}{CH}-$$

The hydrogenated syndiotactic 1,2-polybutadienes showed a similar spectrum, on the whole, as that of atactic polymers as shown in *Figure 1*. The peaks are numbered in a similar manner to that of Randall[5]. Small splittings are observed in peaks 1–4 and 16–19, which were assigned to the methylene carbons flanked by tertiary carbons (except for peak 3) and to the methyl carbons in the substituent group, respectively, by Randall[5].

We call attention to the methyl carbon signals around 10 ppm, because these signals are isolated completely from the other carbon signals. Further details of the signals 16 to 19 are shown in *Figure 2*, which are composed of ten peaks. The signal at 10.94 ppm (16) is assigned to the methyl carbon in the isolated 1 unit as in the 010 sequence. The relative intensity of this signal against the total methyl carbon signals is close to zero with an increase of 1,2-unit content. The same signal was observed as a sharp singlet in the spectrum of hydrogenated *cis*-1,4 polybutadiene containing only 2% of 1,2-unit. In this polymer all of the 1,2-units were estimated to be flanked by 1,4-units (determined from the

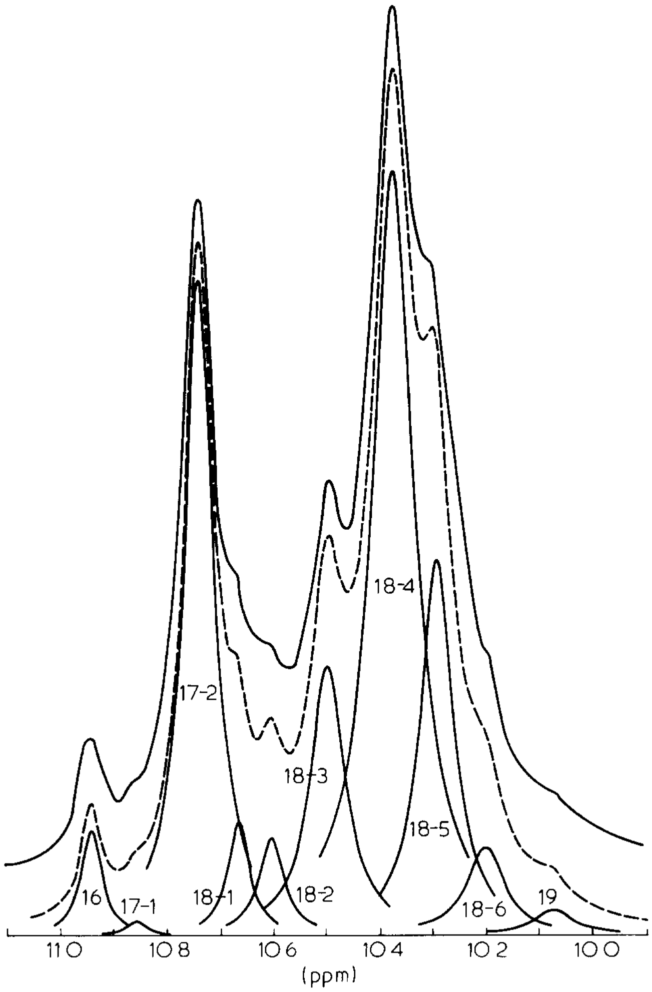


Figure 2 Methyl carbon signals in hydrogenated 1,2-polybutadiene (sample B). Broken line represents the spectrum from curve fitting

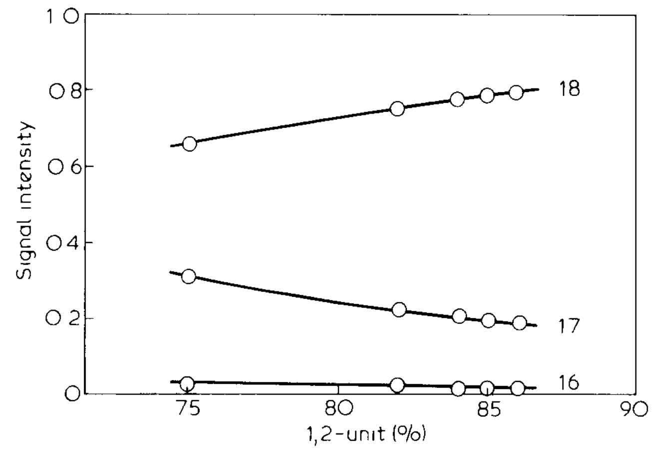


Figure 3 Relationship between signal intensities and crystallinity of starting polymers

result of thermal analysis of the hydrogenated polymer, which will be reported elsewhere).

The methyl carbon in the dyad sequences of 1 unit flanked by 0 unit such as 011 and 110 is expected to be shielded less than that in the triad sequence of 1 unit. In other words, 1 units in $0\underline{11}0$ and $0\underline{1}11$—$11\underline{1}0$ sequences are presumed to resonate in a lower magnetic field than those in $1\underline{1}1$ sequence and to give two signals reflecting a configurational dyad sequence of *m* and *r*. The signal at 10.74 ppm (17–2) shows a small shoulder at 10.86 ppm (17–1) in the spectrum of atactic and low crystallinity polymers. The relative intensity of the signals 17–1 and 17–2 decreased with increasing content of 1,2-unit in the starting polymer as shown in *Figure 3*. From these findings, the signals 17–1 and 17–2 are assigned to *m* and *r* dyads, respectively, in 011 and 110 sequences.

The methyl carbon in isotactic polybutene-1 resonated at 10.66 ppm and that in highly syndiotactic hydrogenated 1,2-polybutadiene (sample G) at 10.37 ppm as shown in *Figure 4*. In the spectrum of hydrogenated 1,2-polybutadienes the corresponding signals, 18–1 and 18–4, are assigned to the triad (111) or pentad (11111) sequences in *mm* (or *mmmm*) and *rr* (or *rrrr*) configurations, respectively. The other signals are tentatively assigned by considering the relative intensities of each signal.

The total intensity of the signals 18–1 to 18–6 increased with increasing content of 1,2-unit in the starting polymers (*Figure 3*). The relative intensity of the *rr* signals (18–4, 18–5, and 18–6) increased with an increase in crystallinity of starting polymers, while *mm* (18–1) and *mr* (18 2 and 18–3) signals varied inversely as shown in *Figure 5*. These facts support the assumption that the methyl carbon signals exhibit splitting, reflecting the sequences of 1,2- and 1,4-units as well as the configurational sequences of 1,2-unit. The assignment of the methyl carbon signals is tabulated in *Table 2*.

In the spectrum of sample G, a small signal was observed at 10.74 ppm, accompanied by the main peak at 10.37 ppm, which was assigned to $0\underline{1}1$ in *r* addition (signal 17 2). This indicates that the polymer is composed of

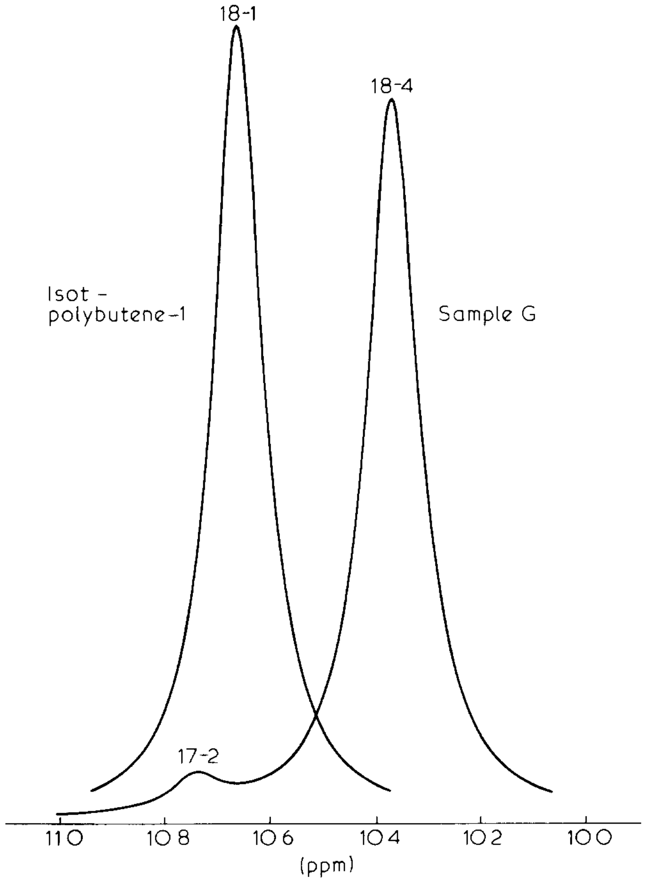


Figure 4 Methyl carbon signals in isotactic poly(butene-1) and hydrogenated syndiotactic 1,2-polybutadiene (sample G)

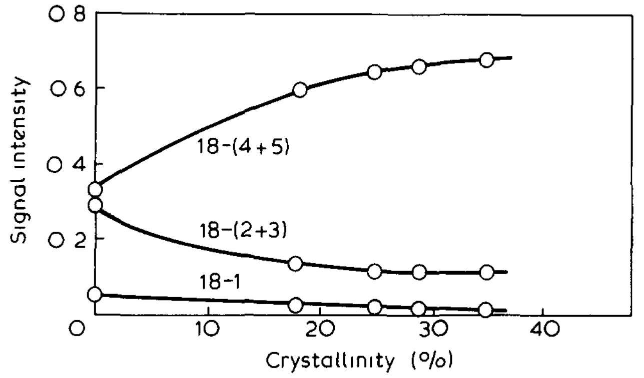


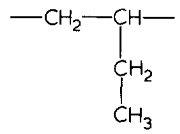
Figure 5 Relationship between signal intensities and crystallinity of starting polymers

Table 2 Assignment of methyl carbon signals

Signal No.	Chemical shift (ppm)	Monomer sequence[a]	Configurational sequence
16	10.94	010	–
17–1	10.86	011 (110)	*m*
17–2	10.74	011 (110)	*r*
18–1	10.64	111	*mm mmmm, mmmr, rmmr*
18–2	10.58	111	*mr* {*mmrm, rmrm, mmrr*
18–3	10.49	111	*rmrr*
18–4	10.37	111	*rr* {*rrrr*
18–5	10.27	111	*mrrr*
18–6	10.20	111	*mrrm*

[a] unit 0: $—CH_2—CH_2—CH_2—CH_2—$

unit 1 :



$—CH_2—CH(CH_2CH_3)—$

predominantly long sequences of racemic 1,2 units, flanked by 1,4 units.

Atactic polybutene-1, obtained by extraction from isotactic polybutene-1, exhibited a similar splitting corresponding to the signals 18–1 to 18–6 as shown in *Figure 6*. The signals corresponding to 16 and 17 were not detected as expected. The prominent signal at 10.13 ppm was thought to arise from a terminal unit or from an irregular addition of momomeric units, e.g. tail-to-tail linkage, which was also observed as a small signal in hydrogenated polybutadienes (signal 19).

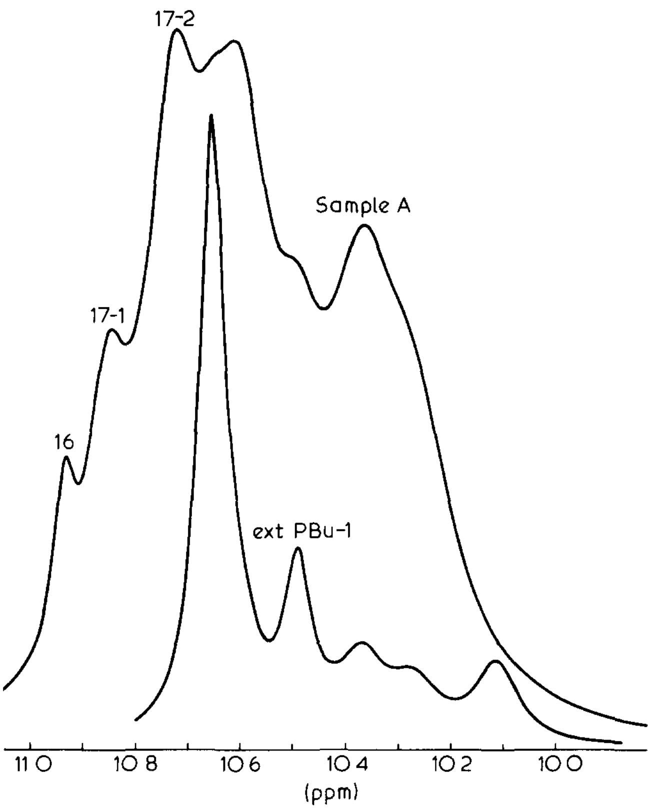


Figure 6 Methyl carbon signals in atatic poly(butene-1) and hydrogenated atactic 1,2-polybutadiene (sample A)

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