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

Kenya Makino, Masaru Ikeyama and Yasumasa Takeuchi
Development Research Laboratory, Japan Synthetic Rubber Co. Ltd., Kawajiri, Yokkaichi, 510, *Japan*
and Yasuyuki Tanaka
Department of Textiles and Polymer Science, Faculty of Technology, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184, *Japan*
(*Received* 14 *May* 1981)

The configurational sequences of 1,2-unit in a series of hydrogenated syndiotactic 1,2-polybutadienes were determined in relation to the sequence distribution of 1,2- and 1,4-units on the basis of the ^{13}C-n.m.r. signal assignment of the methyl carbons. The observed triad distributions of 1,2- and 1,4-units and configurational distributions of the 1,2-unit are in good agreement with the calculated distributions from transition probabilities. The number average sequence lengths of the 1,2-unit and the 1,2-unit in the racemic addition are 5.7 to 8.0 and 4.1 to 5.4, respectively. From the extrapolation of the plot of the number average sequence length against the crystallinity of the starting 1,2-polybutadienes, the minimum sequence length for crystallization is estimated to be 3.7 for the 1,2-unit in the racemic addition.

Keywords Characterization; structure; spectroscopy; nuclear magnetic resonance; sequence distribution; hydrogenation; polybutadienes

INTRODUCTION

A number of studies have been done on the tacticity of 1,2-polybutadiene by ^{13}C-n.m.r. spectroscopy. The triad and pentad tacticities of the 1,2-unit were obtained from vinyl carbon signals[1-3] and from methylene carbon signals[1,2,4]. In these studies the assignments were carried out without taking the 1,4-unit into account which was detected even in syndiotactic 1,2-polybutadiene. 1,2-Polybutadiene always gives a complicated ^{13}C-n.m.r. spectrum due to the splittings reflecting the tacticity of the 1,2-unit and also the sequence distribution of the 1,2- and 1,4-units. The ^{13}C-n.m.r. spectrum is simplified by the hydrogenation of the double bonds in the 1,2- and 1,4-units. Triad tacticity of the hydrogenated 1,2-unit has been determined by Mauzac[5] from methylene carbon signals in main chain. The sequence distribution of the 1,2- and 1,4-units has been determined in detail by Randall[6] by the use of methine and methylene carbon signals.

In the case of syndiotactic 1,2-polybutadiene which usually contains 5 to 30% of the 1,4-unit, the crystallinity of the polymer is expected to be governed by the amount of long sequences of the 1,2-unit in the racemic configuration. The average sequence length of the racemic addition is restricted by the distribution of the 1,4-unit as well as the configurational distribution of the 1,2-unit. In a previous paper, the methyl carbon signals in hydrogenated 1,2-polybutadiene were assigned to the triad sequences of the 1,4- and 1,2-units and to the triad and pentad of the configurational sequences of 1,2-unit[7].

Here, the distribution of the configurational sequences and the isomeric units is determined for a series of hydrogenated syndiotactic 1,2-polybutadienes. The crystallinity of these polybutadienes are discussed in relation to the number-average sequence lengths of racemic configuration and also to that of the total 1,2-units.

EXPERIMENTAL

The preparation of the hydrogenated 1,2-polybutadienes and ^{13}C-n.m.r. measurements were described in the previous paper[7]. The run numbers of the samples are identical with those in the previous paper.

RESULTS AND DISCUSSION

The methyl carbon signals in hydrogenated 1,2-polybutadienes are resolved into 10 peaks by curve resolving using Lorentzian peak shapes as shown in *Figure 1*. The fractions of 1,2-centred triads, F_{111}, $F_{011}+F_{110}$, and F_{010}, were determined from the relative intensities of the signals 16, 17, and 18 which were assigned to the methyl carbons in 111, 011 + 110, and 010 sequences, respectively[7]. Here, 0 stands for the hydrogenated 1,4-unit and 1 for the hydrogenated 1,2-unit.

The triad equations are given in terms of the transition probability P_{10} for a chain ending in 0 to add 1 on the assumption of a first-order Markov statistics:

0032-3861/82/030413-04$03.00

$$\left\{\begin{aligned} &F_{111}=(1-P_{10})^2\\ &F_{011}+F_{110}=2P_{10}(1-P_{10})\\ &F_{010}=P_{10}{}^2\end{aligned}\right. \tag{1}$$

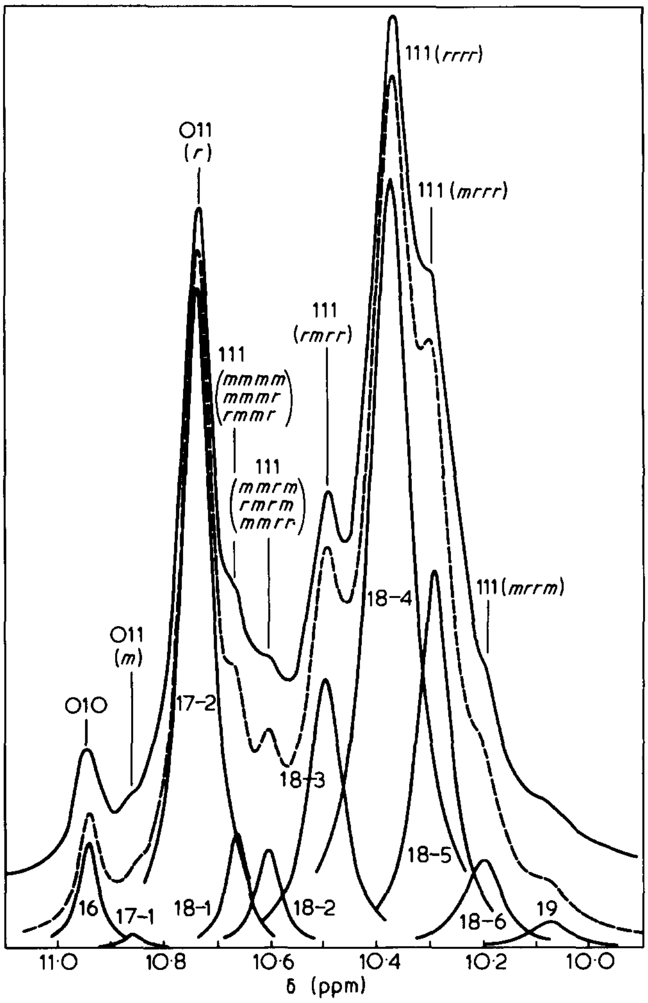

Figure 1 Curve resolution and assignment of methyl carbon signals in hydrogenated 1,2-polybutadiene

P_{10} were calculated directly from F_{111} values for a series of hydrogenated 1,2-polybutadienes. The other transition probabilities were obtained by the following relationships, where F_1 is the fraction of 1,2-unit. The result is shown in *Table 1*.

$$\left\{\begin{aligned} &P_{01}=P_{10}\cdot F_1/(1-F_1)\\ &P_{11}=1-P_{10}\\ &P_{00}=1-P_{01}\end{aligned}\right. \tag{2}$$

The number-average sequence length of the 1,2- and 1,4-units, $\bar{n}_1$ and $\bar{n}_0$, can be determined from the transition probabilities. The former is also determined from the numbers of 1 runs

$$\left\{\begin{aligned} &\bar{n}_1=1/P_{10}\\ &\bar{n}_0=1/P_{01}\end{aligned}\right. \tag{3}$$

according to the following equation. The results are

$$\bar{n}_{1'}=2F_1/F_{01}=2F_1/(2F_{010}+F_{110}+F_{011}) \tag{4}$$

shown in *Table 2*.

The triad fractions calculated from the P_{10} values are in good agreement with the observed values for all the samples. The first-order Markov-fits were also reported by Randall for alkyl-lithium initiated polybutadienes[6]. These facts suggest that the addition of the 1,2-unit is governed by the first-order Markov statistics regardless of the configurational sequence of the 1,2-unit.

1,2-Polybutadienes prepared with $CoBr_2$ complex catalysts (samples A to E) show a systematic change of transition probabilities, which are distinct from those of *n*-butyllithium catalysed polymer (sample F). The number-average sequence lengths of the 1,2-unit of the samples B to E are apparently longer than that of A. However, sample F showed $\bar{n}_1$ values close to B in spite of the non-crystallizability of the starting polymer. The crystallizability of the 1,2-polybutadienes can be interpreted by the sequence length of the racemic addition.

Table 1 Triad distribution of 1,2-unit

		F_{010}		$F_{110}+F_{011}$		F_{111}	
Sample	F_1	Observed	Calculated	Observed	Calculated	Observed	Calculated
F	0.80	0.027	0.025	0.266	0.268	0.707	0.707
A	0.75	0.024	0.036	0.317	0.306	0.659	0.659
B	0.82	0.026	0.020	0.236	0.242	0.738	0.738
C	0.84	0.019	0.016	0.215	0.219	0.766	0.766
D	0.85	0.017	0.015	0.216	0.217	0.767	0.767
E	0.87	0.014	0.012	0.190	0.193	0.796	0.796

Table 2 Transition probabilities and number-average sequence length

Sample	P_{10}	P_{11}	P_{01}	P_{00}	$\bar{n}_1$	$\bar{n}_0$	$\bar{n}_{1'}$
F	0.159	0.841	0.637	0.363	6.28	1.57	5.00
A	0.188	0.812	0.565	0.435	5.31	1.77	4.11
B	0.141	0.859	0.642	0.358	7.10	1.56	5.69
C	0.125	0.875	0.656	0.344	8.00	1.52	6.64
D	0.124	0.876	0.703	0.297	8.06	1.42	6.80
E	0.108	0.892	0.723	0.277	9.26	1.38	7.98

Table 3 Configurational triad and pentad distribution of the 1,2-unit

	Sample											
	F		A		B		C		D		E	
Triad and Pentad	Observed	Calculated	Observed	Calculated	Observed	Calculated	Observed	Calculated	Observed	Calculated	Observed	Calculated
mm	0.038	0.060	0.080	0.095	0.040	0.015	0.029	0.010	0.024	0.069	0.023	0.008
mmmm *mmmr* *rmmr*	0.038	0.060	0.080	0.095	0.040	0.015	0.029	0.010	0.024	0.023	0.023	0.008
mr	0.392	0.370	0.443	0.427	0.190	0.215	0.159	0.179	0.156	0.171	0.143	0.159
mmrm *rmrm* *mmrr*	0.240	0.159	0.297	0.223	0.039	0.050	0.027	0.034	0.023	0.031	0.022	0.027
rmrr	0.152	0.211	0.146	0.204	0.151	0.166	0.132	0.145	0.133	0.140	0.121	0.133
rr	0.571	0.571	0.477	0.478	0.769	0.770	0.812	0.812	0.821	0.820	0.833	0.833
rrrr	0.305	0.326	0.262	0.222	0.516	0.593	0.599	0.659	0.621	0.672	0.629	0.694
mrrr	0.223	0.211	0.189	0.204	0.199	0.166	0.176	0.145	0.174	0.140	0.166	0.133
mrrm	0.043	0.034	0.026	0.046	0.054	0.012	0.037	0.008	0.026	0.007	0.038	0.006

Table 4 Number-average sequence length of the 1,2-unit in racemic- and meso-additions

Sample	$\bar{n}_r$	$\bar{n}_m$
F	2.68	1.16
A	2.16	1.25
B	4.05	1.42
C	4.68	1.36
D	4.75	1.31
E	5.36	1.32

In these samples, the $\bar{n}_1$ value was always smaller than $\bar{n}_1$ by 1.0 to 1.3 for the 1,2-unit. This difference may be due to the experimental errors in the determination of the transition probabilities. In principle, $\bar{n}_1$ values determined from F_{010} and $F_{110}+F_{011}$ are expected to reflect directly the sequence lengths of the 1,2-unit.

The configurational triad sequences of the 1,2-unit were determined from the relative intensities of the signals 18–1, 18–2+18–3, and 18–4+18–5+18–6 by using the probability of finding the meso addition P_m according to the following equations. In a similar manner, the pentad distributions were

$$\begin{cases} mm = P_m^2 \\ mr + rm = 2(1-P_m)P_m \\ rr = (1-P_m)^2 \end{cases} \tag{5}$$

calculated and compared with the observed values. The results are shown in *Table 3*.

The calculated triad and pentad distributions were in good agreement with the observed distributions for all the samples. These Bernoullian fits for the configurational distributions demonstrate that the addition of the 1,2-unit is governed only by the configuration of the terminal unit, which is consistent with the first-order Markov fits observed for the distribution of the 1,2- and 1,4-units. Diad configurational sequences in the $0\underline{11}0$ and $0\underline{1}11$ sequences were observed from the signals 17–1 and 17–2. The observed *m* to *r* ratio is in accord with that estimated from the P_m value in the case of samples A to F, while the *m* sequence was not detected in the other samples. This may imply the presence of a penultimate effect of the 1,4-unit on the configurational sequence of the 1,2-unit in short sequences.

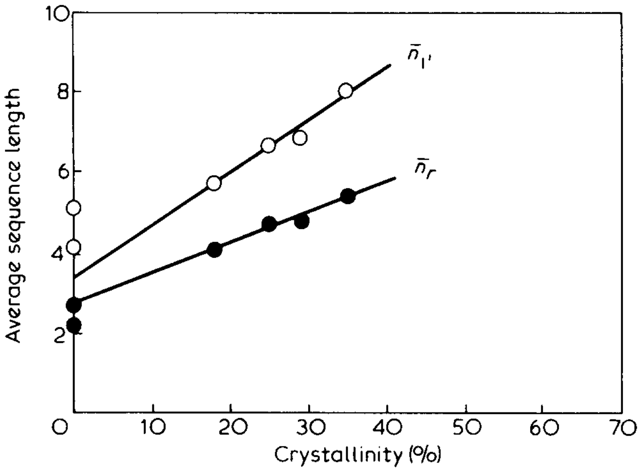

Figure 2 Relationship between the crystallinity and number-average sequence length of the 1,2-unit ($\bar{n}_l'$) and of the racemic addition ($\bar{n}_r$)

The number-average sequence lengths of the racemic and meso addition are calculated with the following equations on the assumption that the polymer is composed of *r*, *m*, and 0 units.

$$\begin{cases} \bar{n}_r = (2F_{rr} + F_{0r} + F_{rm})/F_{0r} + F_{rm}) \\ \bar{n}_m = (2F_{mm} + F_{0m} + F_{rm})/(F_{0m} + F_{rm}) \end{cases} \tag{6}$$

The diad fractions were obtained from the relative intensities of the signals 17–1 to 18–6 according to the assignment of the signals; F_{0m} and F_{0r} are from the signals 17–1 and 17–2, respectively. The result is shown in *Table 4*.

The crystallizability of 1,2-polybutadienes is checked in connection with the number-average sequence length of the 1,2-unit. In *Figure 2* the relationship between the crystallinity of the starting polymers and the number-average sequence lengths of 1,2-unit and racemic addition is shown. The minimum sequence length to crystallization estimated from the extrapolation of the plots is found to be 3.3 for the 1,2-unit and 2.7 for racemic addition which corresponds to 3.7 for the 1,2-unit in the racemic configuration. This clearly shows that about 3 to 4 of the 1,2-units in the racemic configuration are required in order to crystallize syndiotactic polybutadiene under our crystallization conditions.

It is worth noting that the number-average sequence lengths of racemic addition in samples A and F are shorter than the minimum sequence length required for the crystallization, while those for the total 1,2-unit are sufficient to crystallize the polymer chain. This indicates that the non-crystallizability of these 1,2-polybutadienes is ascribed to the short sequence length of the racemic configuration rather than a sequence length of the total 1,2-unit.

REFERENCES

1 Araki, Y., Yoshimoto, T., Imanari, T. and Takeuchi, M. *Kobunshi Kagaku* 1972, **29**, 397
2 Mochel, V. D. *J. Polym. Sci., A-1* 1972, **10**, 1009
3 Elgert, K. F., Quack, G. and Stützel, B. *Makromol. Chem.* 1974, **175**, 1955
4 Furukawa, J., Kobayashi, E., Katsuki, N. and Kawagoe, T. *Makromol. Chem.* 1974, **175**, 237
5 Mauzac, M., Vairon, J. P. and Sigwalt, P. *Polymer* 1977, **18**, 1193
6 Randall, J. C. *J. Polym. Sci., Polym. Phys. Edn.* 1975, **13**, 1975
7 Makino, K., Ikeyama, M., Takeuchi, Y. and Tanaka, Y. *Polymer* 1981, **22**, 000