

^{13}C NMR Study of Poly(propylene oxide) and Poly(1-butene oxide)

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ABSTRACT: ^{13}C NMR spectra of poly(propylene oxide) and its optically active derivative, prepared with typical anionic, cationic, and coordinated catalysts, were analyzed. The absorptions originating from the methine and methylene carbons of polymers were analyzed in terms of triad and dyad, respectively. ^{13}C NMR spectra of poly(1-butene oxide) were also analyzed in the same manner.

KEY WORDS ^{13}C NMR spectroscopy / Poly(propylene oxide) / Poly(1-butene oxide) /

In a preceding communication,¹ ^{13}C NMR spectra of poly(racemic propylene oxide), which consisted predominantly of head-to-tail linkages, were analyzed in terms of triads on the methine carbon and of dyads on the methylene carbon of the polymer main chain; this analysis disagreed with the one made by Schaefer.² Recently, Sigwalt *et al.*³ and Matsuzaki *et al.*⁴ reported the analysis of the ^{13}C NMR spectrum of optically active poly(D-(+)-propylene oxide); their results were in accord with ours.¹

This paper deals with the ^{13}C NMR spectra of poly(propylene oxide) and poly(1-butene oxide), which have either predominantly head-to-tail linkages or both head-to-tail and head-to-head (tail-to-tail) linkages.

EXPERIMENTAL

Materials

In general, purification of materials was carried out under a dry argon atmosphere. Racemic-propylene oxide and racemic-1-butene oxide were refluxed over potassium hydroxide pellets, distilled, and redistilled over calcium hydride; bp 34.0°C and 62.5°C, respectively. All solvents were purified by conventional methods, dried over calcium hydride, and distilled just before use. Diethylzinc and triethylaluminum were purified by distillation under reduced pressure.

(R)-(+) -Propylene Oxide

This compound was prepared by the method of Levene⁵; $[\alpha]_{\text{D}}^{20} + 15.6^\circ\text{C}$ (neat).

Polymerization Procedure

All the polymerization procedures were carried out under a dry argon atmosphere. The polymerizations of propylene oxide and 1-butene oxide were carried out using a $\text{ZnEt}_2\text{-H}_2\text{O}$ (molar ratio, 1 : 0.8) freeze-dried catalyst, $\text{AlEt}_3\text{-H}_2\text{O}$ (molar ratio, 1 : 1) catalyst, and potassium *tert*-butoxide catalyst. The procedures for the preparation of these catalysts were almost the same as these described in our ^1H NMR study on poly(propylene oxide- β - d_1).⁷ The monomer was charged by distillation over calcium hydride into the polymerization ampoule containing the catalyst solution. The ampoule was sealed and allowed to stand at 30°C for 48 h, except in the case of using potassium *tert*-butoxide catalyst (at 80°C for 120 h). Polymerization was terminated by adding a mixture of benzene and a small amount of methanol, and the latter is used in slight excess for precipitating the catalyst. Catalyst residue was removed by centrifugation, and the polymer was obtained from the supernatant clear solution by freeze-drying.

Fractionation of Raw Polymer

A Poly(propylene oxide) and its Deuterated Derivatives. The solution obtained by dissolving 0.05 g of the raw polymer in 100 cm³ of acetone at 60°C was allowed to stand at 0°C for 48 h. The

precipitated crystalline isotactic polymer was separated by centrifuging at 0°C. An acetone-soluble amorphous polymer was obtained by evaporating the acetone.

B. Poly(1-butene oxide). The raw polymer (0.5 g) was immersed in 100 cm³ of ethanol at 30°C for 48 h. The insoluble fraction was separated by filtration and the soluble fraction was isolated by evaporating the ethanol under reduced pressure.

Measurement of NMR spectrum

Natural abundance ¹³C NMR spectra at 25.1 MHz were measured in benzene-*d*₆ at 30°C with proton noise decoupling, using a Varian XL-100-15 spectrometer equipped with a standard VFT-100X Fourier transform system. Internal frequency stabilization of the spectrometer was provided by a lock signal from benzene-*d*₆ used as the solvent. The peak area ratio was determined by the use of a du Pont 310 curve resolver.

RESULTS AND DISCUSSION

We reported already that ¹H NMR spectra of poly(propylene oxide-*α-d*) showed dyad splitting about the methylene protons and we investigated microstructures of various samples of poly(propylene oxide) prepared with cationic, anionic, and coordinate catalysts.⁶ This research was extended to the more detailed microstructural analysis by ¹³C NMR spectroscopy.

The investigation of the ¹³C NMR spectra of various samples of poly(propylene oxide) and optically active polymers enabled us to analyze the splitting of absorptions originating from both methylene and methine carbons. Such results should be useful for the study of the polymerization mechanism of propylene oxide.

The ¹³C NMR spectrum of the isotactic poly(propylene oxide) in C₆D₆ solution is shown in Figure 1. There are three main peaks, at 17.33, 73.90, and 75.90 ppm, of almost equal intensity. The upfield peak at 17.33 ppm can be assigned to the methyl carbon, the center peak at 73.90 ppm to the methylene carbon, and the peak at 75.90 ppm to the methine carbon, from the comparison with the undecoupled spectrum of poly(propylene oxide). This assignment agrees with the one made by Schaefer.²

Schaefer found that the methine carbon peak split

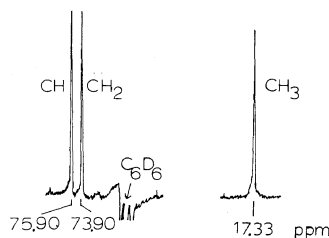


Figure 1. 25.1 MHz ¹³C{¹H} spectra of the main-chain carbons of crystalline poly(racemic propylene oxide). The instrument conditions were: spectrum width, 2500 Hz; acquisition time, 1.6 s; transients, 6000; temperature, 30°C. The numbers give the separation in Hz downfield from the proton decoupled line of tetramethylsilane. The magnetic field increases from left to right.

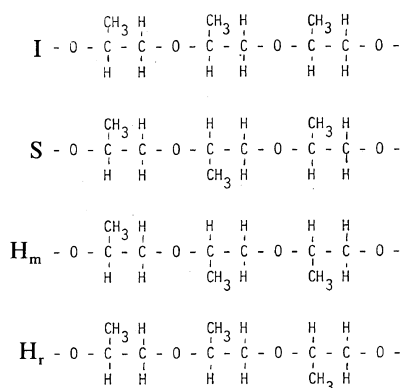
into three and methylene carbon peak into mainly two. These absorptions were analyzed based on the ¹³C NMR spectra of the various trimer glycols. However, his assignment had been faulted and corrected.⁷

In our reinvestigation of the ¹³C NMR spectra of poly(racemic propylene oxide), the analytical method used in the study of ¹H NMR spectra of poly(racemic propylene oxide-*α-d*) was applied: typical anionic (*tert*-BuOK), cationic (AlEt₃-H₂O, molar ratio 1 : 1), and coordinate (ZnEt₂-H₂O, molar ratio 1 : 0.8 freeze-dried system) catalysts were used to obtain four kinds of polymer samples.

Racemic propylene oxide is composed of an equimolar mixture of two enantiomers, (*R*) and (*S*). Since the ring opening is known to occur exclusively at the methylene carbon-oxygen bond in anionic polymerization,⁶ the resulting polymer consists of repeating units of the *R* and *S* configuration. Two successive (*R*) or (*S*) units form an isotactic dyad -(*R,S*)- or -(*S,S*)-, whereas the other sequences -(*R,S*)- or -(*S,R*)- form a syndiotactic dyad. For the triads, there should be four different triads for methine and methylene carbons, distinguishable at least in principle: one isotactic (*I*), one syndiotactic (*S*) and two heterotactic (*H_m* and *H_r*), where the subscripts *m* and *r* indicate meso and racemic, respectively.

The ¹³C NMR spectra of the methine and methylene regions in C₆D₆ of the crystalline (*I*) and amorphous (*II*) polymers prepared with ZnEt₂-H₂O freeze-dried catalyst, and of the amorphous polymer (*III*) prepared with *tert*-BuOK catalyst, are shown in Figures 2A, 2B, and 2C, respectively. There are three

¹³C NMR of Poly(propylene oxide) and Poly(1-butene oxide)



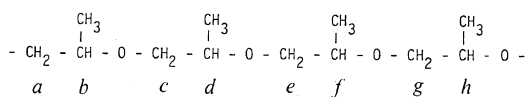
peaks in the methine carbon and two main peaks in the methylene carbon of the spectra of samples (II) and (III). Since samples (II) and (III) are atactic polymers which contain no head-to-head and tail-to-tail linkages in the polymer main chain,⁶ splitting of the absorptions must originate from different configurational isomeric units. In comparison with the spectrum of isotactic polymer, the two peaks at 73.90 and 73.71 ppm of the methylene carbon [observed peak area ratio 50:50 for the sample (III)] can readily be assigned to isotactic and syndiotactic dyads (m and r, respectively), and three methine carbon peaks at 75.90, 75.82, and 75.70 ppm [observed peak area ratio 25:50:25 for the sample (III)] to isotactic, heterotactic, and syndiotactic triads (I, H, and S, respectively). If sample (III) is a completely atactic polymer, the relative intensities of the three peaks on the methine carbon would be 0.25:0.50:0.25.

There are asymmetric carbon atoms in the polymer main chain of poly(propylene oxide), and there-

fore there should be two heterotactic triad sequences, distinguishable at least in principle: for example, RRS is not equivalent to SRR. Nevertheless, the spectra observed show only a singlet for the heterotactic triad, possibly because of the strong magnetic shielding effect of oxygen.

The relative intensities of triads and dyads on the four polymer samples prepared with potassium *tert*-butoxide and ZnEt₂-H₂O freeze-dried catalysts are summarized in Table I.

In the wide sweep spectrum of the amorphous polymers prepared with potassium *tert*-butoxide and with ZnEt₂-H₂O catalysts, splitting into 73.71 and 73.63 ppm of the upfield peak assigned to the syndiotactic dyad in the methylene carbon region was observed (Figure 2). Since these samples contain no head-to-head and tail-to-tail linkages in the polymer main chain, this splitting possibly originates from different triad sequences (S and H_r): one may expect four tetrad resonances: mrm, mrr, rrm, and rrr, for the methylene carbon *e* of syndiotactic dyad. The resonance of methylene carbon *e* will be more sensitive magnetically to the configuration of methine carbon *h* than to that of methine carbon *b*,



because the methylene carbon *e* is located at a distance farther from the carbon *b* than from the methine carbon *h*, and also the magnetic effect of the configuration of the carbon *b* on the carbon *e* is small because of the shielding effect of the two oxygen atoms. Therefore, the syndiotactic dyad, r, originating from the methylene carbon of poly(racemic propylene oxide) may be resolved into two frequen-

Table I. Tacticity of poly(propylene oxide) prepared with two kinds of catalysts

Polymerization catalyst	Fraction	Tacticity ^a				
		Dyad		Triad		
		<i>m</i>	<i>r</i>	<i>I</i>	<i>H</i>	<i>S</i>
<i>tert</i> -BuOK		0.50	0.50	0.25	0.50	0.25
ZnEt ₂ -H ₂ O	Whole	0.67	0.33	0.50	0.31	0.19
Freeze-dried	Crystalline	1.00	0	1.00	0	0
(mol ^a ratio 1:0.8)	Amorphous	0.60	0.40	0.38	0.43	0.19

^a Estimated accuracy is ±0.02.

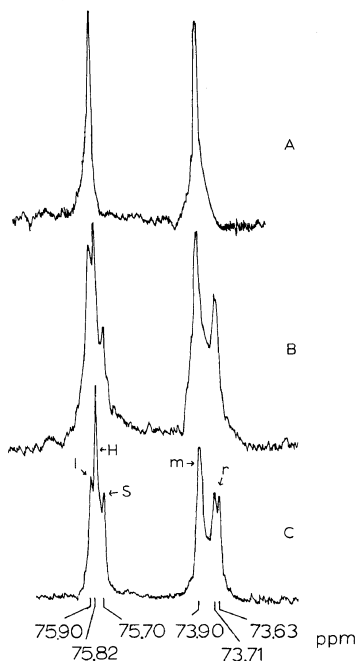


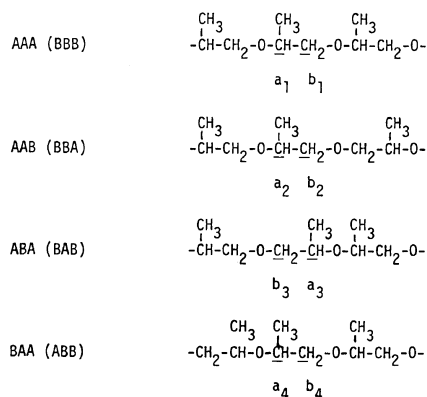
Figure 2. 25.1 MHz $^{13}\text{C}\{^1\text{H}\}$ spectra in the methylene and methine carbon region of the crystalline (A) and amorphous (B) poly(racemic propylene oxide) prepared with $\text{ZnEt}_2\text{-H}_2\text{O}$ (molar ratio, 1:0.8) freeze-dried catalyst and of the amorphous polymer (C) prepared with *tert*-BuOK catalyst. The instrument conditions were: spectrum width, 1000 Hz; acquisition time, 2.0 s; transients, 10000; temperature, 30°C.

cies of $\text{rm}(\text{mrm} + \text{rrm})$ and $\text{rr}(\text{rrr} + \text{mrr})$. On the other hand, splitting of the peak for the methylene carbon of the isotactic dyad was not observed. The characteristic conformation around -mm- units in solution may be responsible for very small chemical shifts.⁸

It is interesting to compare this result with that on the ^{13}C NMR spectrum of poly(propylene sulfide), in which the absorptions originating from the methine carbon split into two peaks assignable to isotactic and syndiotactic dyads.⁸

The ^1H NMR study of poly(racemic propylene oxide- α -*d*) studied by us⁶ and the chemical method applied to poly(racemic propylene oxide) by Price⁹ showed that the polymer obtained with $\text{AlEt}_3\text{-H}_2\text{O}$ catalyst contains a certain amount of head-to-head and tail-to-tail linkages in the polymer main chain. The occurrence of these abnormal linkages should produce a complicated NMR spectrum in which the presence of 4 (dyad) and 16 (triad) lines would be

expected corresponding to the structural and configurational isomeric units. Actually in the ^{13}C NMR spectrum of the polymer obtained with this catalyst, 13 peaks were visible, possibly due to the presence of these abnormal linkages (Figure 3A). The analysis of this complicated spectrum could be undertaken by the use of the polymer obtained from the optically active monomer. For poly(*(R)*-(+)-propylene oxide) containing these abnormal linkages, the whole polymer should consist of eight possible isomeric units: AAA, AAB, ABA, BAA, ABB, BAB, BBA, and BBB, where A is $\text{-CH}(\text{CH}_3)\text{CH}_2\text{O-}$, and B is $\text{-CH}_2\text{CH}(\text{CH}_3)\text{O-}$.



Now it can be assumed that the steric environment of AAA triad is nearly equivalent to that of BBB triad, and also AAB to BBA, ABA to BAB, and BAA to ABB. Moreover, this polymer contains 11% of head-to-head and tail-to-tail linkages, as was estimated from the optically rotatory power, $[\alpha]_D^{20} = -29.0^\circ$, of the polymer in benzene ($[\alpha]_D^{20} = -32.6^\circ$ in benzene for the optically active polymer consisting of only head-to-tail linkages). Based on these facts, the eight peaks observed in the spectrum of the optically active polymer could be analyzed in terms of the above four types of triad (Figure 3B). The environmental magnetic shielding effect on methine(a) and methylene(b) carbons may be expected to increase in the orders of $a_3, a_1, a_2, a_4,$ and b_2, b_1, b_3, b_4 ; these were obtained from empirical rules allowing for $\alpha, \beta, \gamma,$ and δ effects on the shielding effects of the nearest three methyl groups.¹¹ Thus all the peaks observed in the spectrum of the optically inactive polymer obtained with the aluminium catalyst contain the absorptions originating from configurational isomers, in addition to those of structural isomers. The presence of these configurational

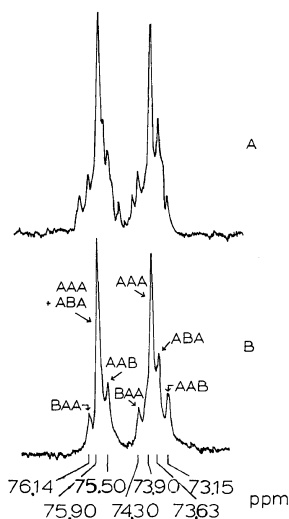


Figure 3. 25.1 MHz ¹³C{¹H} spectra in the methylene and methine carbon region of the amorphous poly(racemic propylene oxide) (A) and poly(*R*-(+)-propylene oxide) (B) (molar ratio, 1:1) catalyst. A is $-\text{CH}(\text{CH}_3)\text{CH}_2\text{O}-$ and B is $-\text{CH}_2\text{CH}(\text{CH}_3)\text{O}-$. The instrument conditions were the same as in Figure 2.

isomers makes the spectra complex. So the precise analysis of the ¹³C NMR spectrum of poly(propylene oxide) obtained with the aluminium catalyst remains to be performed.

These results indicate that the microstructure of the poly(racemic propylene oxide) containing head-to-head and tail-to-tail linkages cannot be determined quantitatively at present.

Application of the Analysis of ¹³C NMR Spectra of Poly(propylene oxide) to That of Poly(1-butene oxide)

In the ¹³C NMR analysis of poly(propylene oxide), the spectrum of the polymer containing a relatively large amount of head-to-head and tail-to-tail linkages is too complicated to be solved precisely. In order to acquire knowledge about the polymerization of a series of alkylene oxides, one should look for another alkylene oxide which affords a well resolvable ¹³C NMR spectrum. Therefore, the ¹³C NMR spectrum of poly(1-butene oxide), one of the higher homologues, was studied by a similar method.

The ¹³C NMR spectra of poly(1-butene oxides) prepared with potassium *tert*-butoxide (IV) and ZnEt₂-H₂O freeze-dried catalysts [the ethanol soluble fraction (V) and insoluble fraction (VI)], have a singlet peak for the methine carbon regardless of the kinds of samples, while they have three peaks at 73.30, 72.55, and 72.31 ppm in different intensities for the methylene carbons (Figures 4A, 4B, and 4C). Sample (VI), which is insoluble in ethanol and crystalline at low temperatures, may be a polymer

Table II. Line assignments for the main-chain ¹³C NMR Spectrum of poly(propylene oxide)

Carbon	Structural sequence ^a	Configurational sequence	Chemical shift ^b (Hz at 25.1 MHz)
Methine	*	*	1918
	BAA(a ₄) ^c	Isotactic	1911
	AAA(a ₁) + ABA(a ₃)	Isotactic(triad)	1905
	AAA(a ₁)	Heterotactic(triad)	1903
	AAA(a ₁)	Syndiotactic(triad)	1900
	AAB(a ₂) ^c	Isotactic	1895
	*	*	1884
Methylene	*	*	1869
	BAA(b ₄) ^c	Isotactic	1865
	AAA(b ₁)	Isotactic	1855
	AAA(b ₁)	Syndioactactic(dyad)	1848
	ABA(b ₃)	Isotactic	1841
	*	*	1841
	AAB(b ₂) ^c	Isotactic	1836

^a A = $-\text{CH} + \text{CH}_3\text{CH}_2\text{O}-$; B = $-\text{CH}_2\text{CH}(\text{CH}_3)\text{O}-$.

^b Tetramethylsilane was used as an internal standard.

^c The assignment was made by the use of the optically active polymer. Accuracy is ± 1 Hz. * Undetermined.

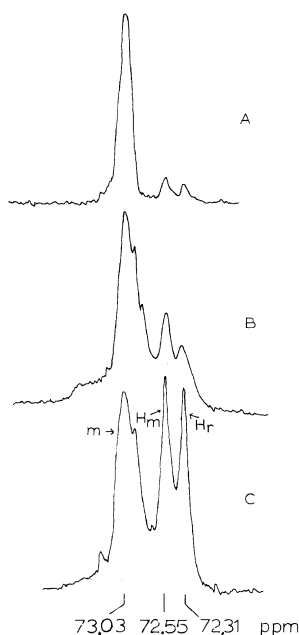


Figure 4. 25.1 MHz $^{13}\text{C}\{^1\text{H}\}$ spectra in the methylene carbon region of the crystalline (A) and amorphous (B) poly(1-butene oxide) prepared with $\text{ZnEt}_2\text{-H}_2\text{O}$ (molar ratio, 1:0.8) freeze-dried catalyst and of the amorphous polymer (C) prepared with *tert*-BuOK catalyst. The instrument conditions were: spectrum width, 1250 Hz; acquisition time, 1.6 s; transients, 8000; temperature, 30°C.

consisting predominantly of isotactic sequences, the absorption at 73.03 ppm being assignable to an isotactic dyad and those at 72.55 and 72.31 ppm to a syndiotactic dyad. The splitting into two peaks of the syndiotactic dyad could be explained by taking account of the environmental magnetic shielding effect on the methylene carbons. The peak at 72.55 ppm is assignable to $\text{rm}(\overline{\text{mrm}}+\overline{\text{rrm}})$ and the one at 72.31 ppm to $\text{rr}(\overline{\text{rrr}}+\overline{\text{mrr}})$. The relative intensity of these two peaks is equivalent in the spectrum of polymer (IV) prepared with *tert*-BuOK catalyst.

In the ^{13}C NMR spectrum of poly(1-butene oxide) prepared with $\text{AlEt}_3\text{-H}_2\text{O}$ (molar ratio, 1:1) catalyst system (VII), some new absorptions originating from head-to-head and tail-to-tail linkages were observed at the methylene and methine carbon regions (Figure 5A). The intensity of these new absorptions was enhanced on the sample prepared with $\text{AlEt}_3\text{-H}_2\text{O}$ catalyst under a molar ratio of 1:0.6 (Figure 5B).

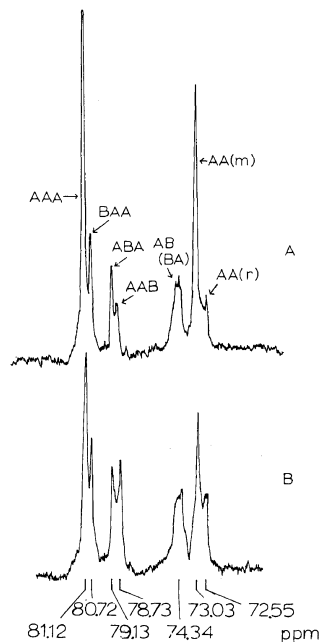


Figure 5. 25.1 MHz $^{13}\text{C}\{^1\text{H}\}$ spectra in the methylene and methine carbon region of the amorphous poly(1-butene oxide) prepared with $\text{AlEt}_3\text{-H}_2\text{O}$ catalyst in a molar ratio of AlEt_3 : water, 1:1 (A) and 1:0.6 (B). A is $-\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2\text{O}-$ and B is $-\text{CH}_2\text{CH}(\text{C}_2\text{H}_5)\text{O}-$. The instrument conditions were: spectrum width, 2500 Hz; acquisition time, 0.8 s; transients, 5000; temperature, 30°C.

The analysis of the spectrum was made by the method applied to that of poly(propylene oxide). The multiple peaks at 74.34 ppm may be assignable to the methylene carbon in tail-to-tail linkage, and the three peaks at 78.38, 79.12, and 80.72 ppm to the methine carbons of AAB, ABA, and BAA, respectively, in head-to-head linkages, where A is $-\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2\text{O}-$ and B is $-\text{CH}_2\text{CH}(\text{C}_2\text{H}_5)\text{O}-$. This assignment is supported by the following data: the total intensity of peaks at 80.72, 79.12, and 78.73 ppm is equivalent to that at 74.34 ppm, and ^{13}C NMR of methine carbon is not sensitive to changes in tacticity, as mentioned above. The results obtained are summarized in Table III.

In summary, we have confirmed that the ^{13}C NMR spectroscopy is the most useful for the study of the microstructure of poly(alkylene oxide). The triad for methine carbon and dyad for methylene carbon are quantitatively determined for poly(propylene oxide) containing no head-to-head and tail-to-tail

Table III. Line assignments for main-chain ^{13}C NMR spectrum of poly(1-butene oxide)

Carbon	Structural sequence ^a	Configurational sequence	Line position ^b (Hz at 25.1 MHz)
Methine	AAA	*	2036
	BAA	*	2026
	ABA	*	1986
	AAB	*	1976
Methylene	AB(BA)	*	1866 (multiplet)
	AA	Isotactic(dyad)	1833
	AA	Syndiotactic(H_m) ^c	1821
	AA	Syndiotactic(H_r) ^c	1815

^a A = $-\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2\text{O}-$; B = $-\text{CH}_2\text{CH}(\text{C}_2\text{H}_5)\text{O}-$. ^b Tetramethylsilane was used as an internal standard. ^c The splitting into two peaks of the syndiotactic dyad may be a split into H_m and H_r . Accuracy is ± 1 Hz.
* Undetermined.

linkages. The dyad for methylene carbon and the absorptions originating from head-to-head and tail-to-tail linkages are quantitatively determined for poly(1-butene oxide).

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