

¹H and ¹³C NMR Assignment of Regioirregular Sequence in Poly((S)-(–)-propylene oxide) Prepared with Organotin-Alkyl Phosphate Condensate by 2D NMR Technique

Katsuhito MIURA,[†] Tatsuki KITAYAMA, Koichi HATADA,^{††}
and Tetsuya NAKATA*

Department of Chemistry, Faculty of Engineering Science, Osaka University,
Toyonaka, Osaka 560, Japan

* Research Laboratories, Daiso Co., Ltd.,
Amagasaki, Hyogo 660, Japan

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ABSTRACT: Structures of regioirregular sequence in poly((S)-(–)-propylene oxide) prepared with Bu₂SnO–Bu₃PO₄ (1:2) condensate were investigated extensively using 2D NMR technique. ¹³C NMR signals of regioirregular enchainment of triad and ¹H NMR signals of head-to-tail (H-T), tail-to-tail (T-T), and head-to-head (H-H) were assigned by 2D NMR spectroscopy. Assignments of ¹³C NMR spectra are scarcely consistent with the assignments from the calculations of chemical shift based on shielding effect or on γ -*gauche* effect and rotational isomeric model.

KEY WORDS Propylene Oxide / Organotin-Alkyl Phosphate Condensate / Irregular Linkage / ¹H NMR / ¹³C NMR / 2D NMR / ¹³C–¹H COSY / ¹H COSY/

Organozinc and organoaluminium compounds are highly reactive initiators for ring opening polymerization of oxirane compounds. The structural analyses of the polymers, in particular poly(propylene oxide), obtained with these initiators have been previously reported.^{1–10}

Ramey *et al.*¹¹ studied 100 MHz ¹H NMR spectra of poly(propylene oxide) by decoupling experiment to elucidate its tacticity, but the decoupled spectra were still too complex to be interpreted reasonably. Oguni *et al.*⁶ reported that the tacticity and the fraction of the tail-to-tail linkage could be determined by 100 MHz ¹H NMR spectroscopy using α -deuterated poly(propylene oxide), although peak separation seems not to be good enough to evaluate quantitative data. Recently, Bruch

*et al.*¹² applied two-dimensional *J*-resolved 500 MHz ¹H NMR spectroscopy to the analysis of undeuterated poly(propylene oxide), and assigned isotactic and syndiotactic signals. However, the quantitative values of tacticity as well as the assignments for the irregular linkage were not reported.

The assignments of the ¹³C NMR spectra of poly((R)-(+)–propylene oxide) and poly((RS)-propylene oxide) with irregular sequences have been reported by Oguni *et al.*⁹ and by Schilling *et al.*,¹³ which are partly inconsistent with each other. The assignments by Oguni were based on magnetic shielding effects from the neighboring units, and those by Schilling were made from the chemical shift calculation based on γ -*gauche* effect and rotational isomeric (RIS) model.

[†] On leave from Daiso Co., Ltd.

^{††} To whom correspondence should be addressed.

We have reported that condensation products of organotin and alkyl phosphate functioned as efficient initiators for the polymerization of oxirane compounds,¹⁴⁻¹⁶ and these have been used for the industrial production of epichlorohydrin-ethylene oxide rubber.¹⁷ In the present work, polymers of (*S*)-propylene oxide prepared with the organotin-alkyl phosphate condensate were analyzed in regard of regioirregular sequence by ¹H and ¹³C NMR spectroscopy using 2D NMR technique. The polymers were found to contain unique irregular sequences that supported the present NMR assignments.

EXPERIMENTAL

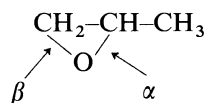
Preparation of the dibutyltin oxide(Bu₂-SnO)-tributyl phosphate(Bu₃PO₄) (1:2) condensate¹⁴ and polymerization of (*S*)-(-)-propylene oxide¹⁶ were carried out as described in the previous papers.

¹H NMR spectra were measured in benzene-*d*₆ at 50°C on a JNM-GX 500 or a JNM-GSX 270 spectrometers (JEOL) at 500 and 270 MHz, respectively. Chemical shifts of ¹H NMR spectra were referred to tetramethylsilane as an internal standard. ¹³C NMR spectra were measured under the same conditions on the JNM-GX 500 spectrometer at 125 MHz. Chemical shifts of ¹³C NMR spectra were referred to the central peak of benzene-*d*₆ as 128.0 ppm. The ¹³C-¹H COSY and long range ¹³C-¹H COSY(COLOC) experiments employed a recycle time of 1.5 s, with 128 transients being collected for each *t*₁ value. A total of 256 spectra, each consisting of 4096 data points, were accumulated with a frequency range of 18000 Hz and column frequency range of 4000 Hz in both dimensions. τ_1 of ¹³C-¹H COSY and long range ¹³C-¹H COSY were set at 3.7 ms and 60 ms, respectively. The ¹H COSY experiment employed a recycle time of 1.4 s, with 16 transients being collected for each *t*₁ value. A total of 256 spectra, each consisting of 2048 data points, were accumu-

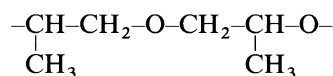
lated with a frequency range of 2360 Hz in both dimensions.

RESULTS AND DISCUSSION

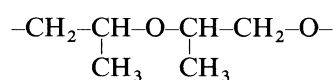
The characteristics of poly((*S*)-(-)-propylene oxide)s used in the present work are listed in Table I. Propylene oxide may undergo ring-opening reactions in both α - and β -positions;



and the polymer may contain irregular enchainments (head-to-head (H-H) and tail-to-tail (T-T)) as well as regular head-to-tail (H-T) sequence. The



(T-T)



(H-H)

polymers derived from the optically active monomer are expected to be almost devoid of irregularity of stereochemistry, and thus are suited for NMR studies on these irregular sequences. The soluble fractions contain larger amounts of these irregular linkages than the insoluble one, and thus were subjected to NMR analyses. The soluble fraction of polymer (A) was used for ¹³C NMR, ¹H NMR,

Table I. Characterization of poly((*S*)-(-)-propylene oxide)

Fraction ^a	mp/°C	$[\alpha]_D^{20}$	\bar{M}_w^b
Insoluble	69	+31.5°	1.4×10^5
Soluble (A)	—	+19.2°	5.8×10^4
Soluble (B)	—	+23.4°	7.2×10^4

^a Benzene-hexane insoluble or soluble fraction.

^b Determined by viscometry using following equation; $[\eta] = 0.81 \times 10^{-4} \bar{M}_w^{0.85}$ in benzene at 25°C.¹⁸

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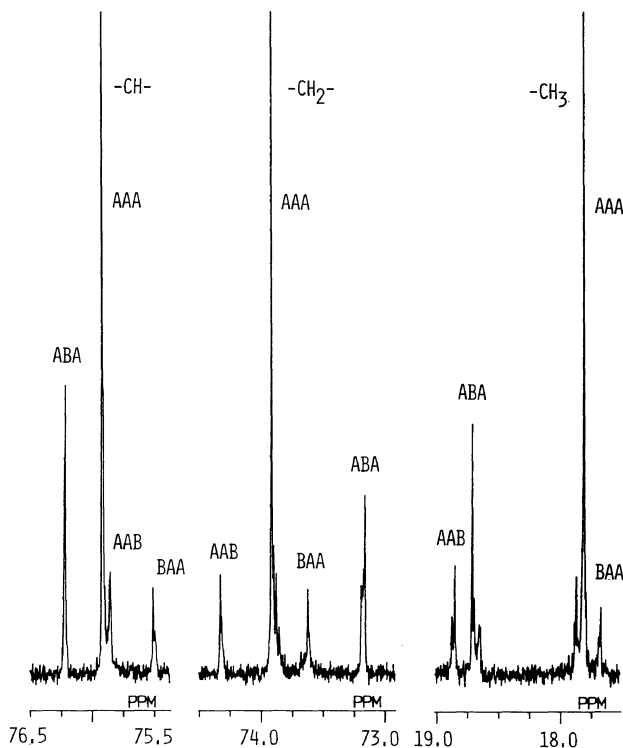
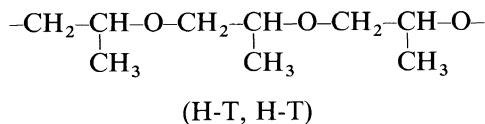


Figure 1. 125 MHz ¹³C NMR spectrum measured in benzene-d₆ at 50°C of benzene-hexane soluble fraction of poly((S)-(-)-propylene oxide) prepared with Bu₂SnO-Bu₃PO₄ (1:2) condensate.

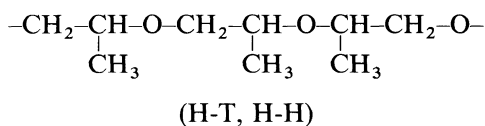
and ¹H COSY and that of polymer (B) was used for ¹³C-¹H COSY and long range ¹³C-¹H COSY.

Figure 1 shows the ¹³C NMR spectrum of benzene-hexane soluble fraction of the poly((S)-(-)-propylene oxide) prepared with Bu₂SnO-Bu₃PO₄ (1:2) condensate. For poly((S)-(-)-propylene oxide) eight isomeric triads are possible; AAA, AAB, ABA, BAA, ABB, BAB, BBA, and BBB, where A is -CH₂CH(CH₃)O- (β-cleavage), and B is -CH(CH₃)CH₂O- (α-cleavage) according to Oguni's definition.⁹ However, the following four types of triads are distinguishable by ¹³C NMR spectroscopy:

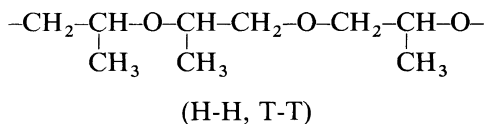
AAA(BBB)



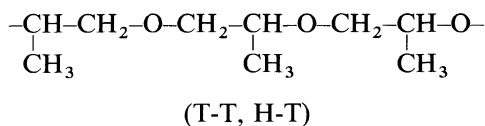
AAB(BBA)



ABA(BAB)



BAA(ABB)



It is self-evident to assign the highest signals to AAA triad from Figure 1. Since the probabilities of AAB and BAA triads are

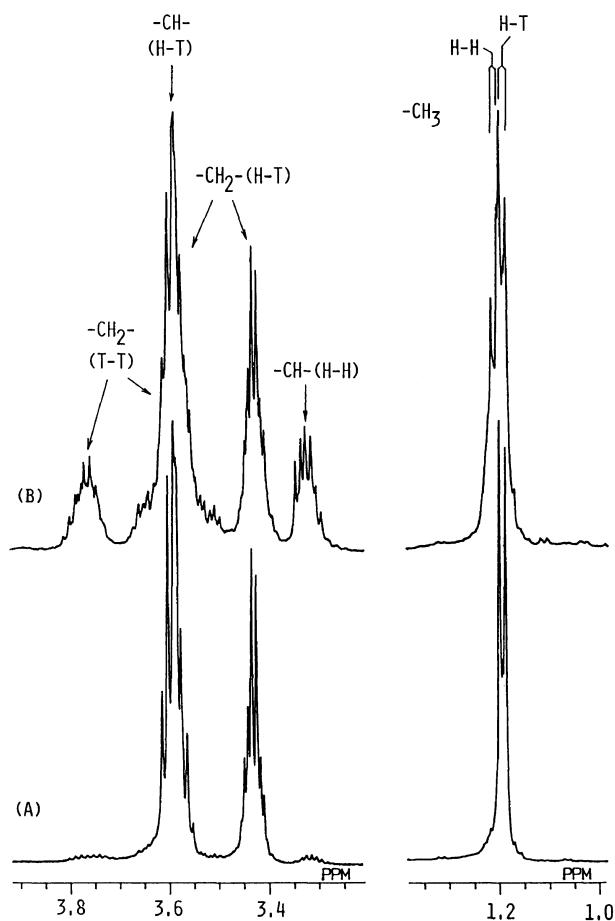


Figure 2. 500 MHz ^1H NMR spectra of poly((*S*)-(-)-propylene oxide) prepared with $\text{Bu}_2\text{SnO}-\text{Bu}_3\text{PO}_4$ (1:2) condensate measured in benzene- d_6 at 50°C . (A) Benzene-hexane insoluble fraction. (B) Benzene-hexane soluble fraction.

statistically the same, peaks or groups of peaks in each carbon signals with equal intensities could be assigned to either AAB or BAA triad. Then the remaining peak or group of peaks was assigned to ABA triad. It is evident from the spectrum that the fraction of ABA triad is larger than that of AAB or BAA triad. In the poly((*S*)-(-)-propylene oxide) formed with $\text{AlEt}_3-\text{H}_2\text{O}-\text{AcAc}$ (1:0.5:0.5) or $\text{ZnEt}_2-\text{H}_2\text{O}$ (1:1), the fractions of ABA, AAB, and BAA triads were almost equal to each other. Thus, the assignments for ABA based on the statistical consideration would not be possible for the spectra of these poly-

mers. The difference in irregular sequence distribution between the polymers formed with $\text{Bu}_2\text{SnO}-\text{Bu}_3\text{PO}_4$ (1:2) and with $\text{AlEt}_3-\text{H}_2\text{O}$ (1:0.5:0.5) or $\text{ZnEt}_2-\text{H}_2\text{O}$ (1:1) initiator was discussed in a separate paper.¹⁶ The assignments for AAB and BAA triads were made by $^{13}\text{C}-^1\text{H}$ COSY and long range $^{13}\text{C}-^1\text{H}$ COSY as described later.

Figure 2 shows the ^1H NMR spectra of benzene-hexane insoluble and soluble fractions of poly((*S*)-(-)-propylene oxide) prepared with $\text{Bu}_2\text{SnO}-\text{Bu}_3\text{PO}_4$ (1:2) condensate. The insoluble fraction (Figure 2A) was almost devoid of irregular enchainments and showed

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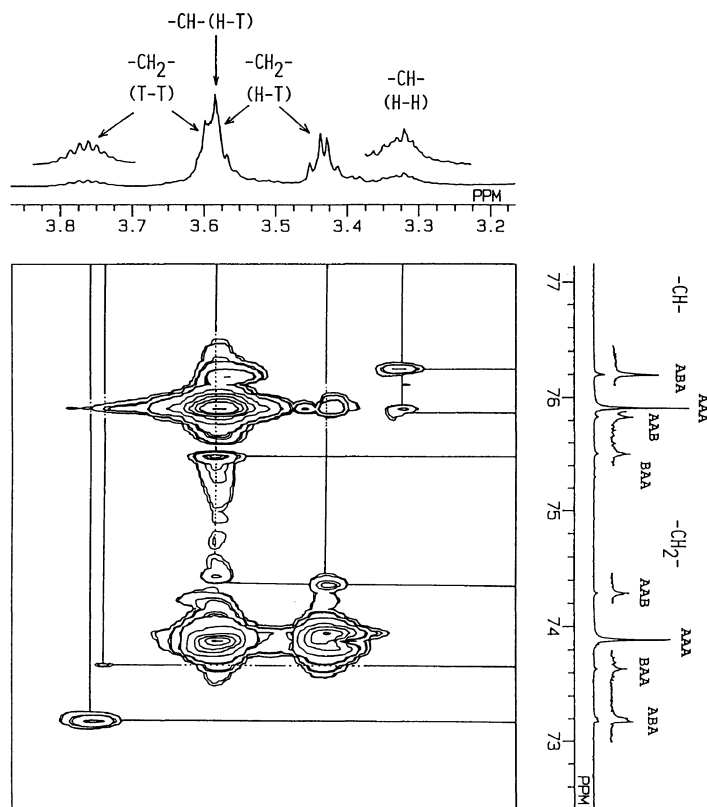


Figure 3. ^{13}C - ^1H COSY spectrum measured in benzene- d_6 at 50°C of benzene-hexane soluble fraction of poly(*S*)-(-)-propylene oxide prepared with $\text{Bu}_2\text{SnO}-\text{Bu}_3\text{PO}_4$ (1:2) condensate. The correlations between off-diagonal signals due to irregular sequence (ABA, AAB, and BAA) are indicated with solid lines.

the nonequivalent methylene proton signals in H-T linkage as multiplets centered at 3.43 and 3.59 ppm. The latter signal was further complicated by the overlapping signals of methine proton. The methyl protons in H-T linkage showed a doublet signal at 1.190 ppm ($J=6.2$ Hz). The spectrum of the benzene-hexane soluble fraction showed additional two multiplet signals with the same intensity centered at 3.32 ppm due to methine proton in H-H linkage and at 3.78 ppm due to one of the methylene protons in T-T linkage (Figure 2B). The methyl protons also showed an additional doublet signal ($J=6.4$ Hz) at 1.208 ppm, assignable to H-H sequence, as a shouldered peak of the main peak. The assignments shown in Figure 2 were made by ^{13}C - ^1H

COSY and ^1H COSY as described in the following.

Methylene groups in the centered units in AAA and AAB triads are located in H-T linkage and those in ABA and BAA triads in T-T linkage. On the other hand, methine groups in the centered units in AAA and BAA are included in H-T linkage and those in ABA and AAB triads in H-H linkage. Thus, the connectivities between diads (H-T, H-H, T-T) and triads listed in Table II are expected in 2D NMR.

From ^{13}C - ^1H COSY spectrum shown in Figure 3, it is evident that the ^1H NMR signals centered at 3.32 and 3.78 ppm could be assigned to methine proton in H-H linkage and methylene protons in T-T linkage, respec-

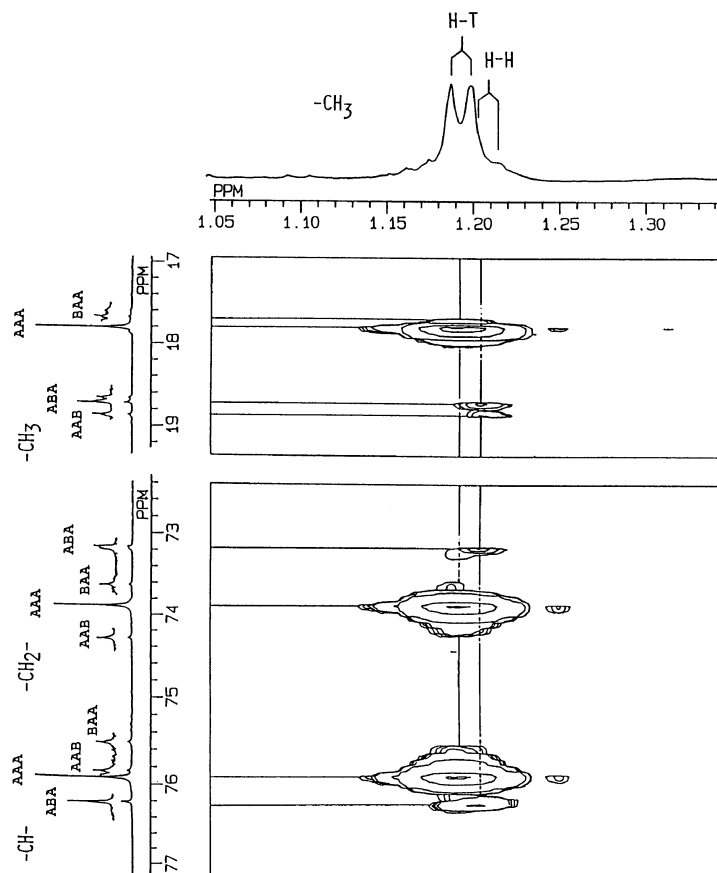


Figure 4. Long range ^{13}C - ^1H COSY(COLOC) spectrum measured in benzene- d_6 at 50°C of benzene-hexane soluble fraction of poly(*S*)-(-)-propylene oxide prepared with $\text{Bu}_2\text{SnO}-\text{Bu}_3\text{PO}_4$ (1:2) condensate.

Table II. Diad-triad relationship which would be observed for ^{13}C - ^1H COSY spectrum of regioirregular poly(propylene oxide)

Triad (^{13}C)	Diad (^1H)		
	CH_2	CH	CH_3
AAA	H-T	H-T	H-T
AAB	H-T	H-H	H-H
ABA	T-T	H-H	H-H
BAA	T-T	H-T	H-T

tively; the signals showed correlation peaks with respective carbon signals due to ABA triad. These two multiplet proton signals had

equal intensity to each other. The results are quite consistent with the fact that the proportions of H-H and T-T linkages are equivalent statistically. Methine proton in H-H linkage is expected to correlate with AAB triad signals as well as ABA ones (Table II). Thus, methine carbon signal at 75.85 ppm should be assigned to AAB triad, and then the signal at 75.51 ppm could be assigned to BAA triad. On the other hand, methylene protons in T-T linkage are expected to show correlation peak with BAA and ABA triad signals. Thus, the methylene carbon signal at 73.62 ppm was assigned to BAA triad.

Figure 4 illustrates a part of the long range

^{13}C - ^1H COSY spectrum, exhibiting correlations between methyl protons and methyl, methylene or methine carbon. From the diad-triad correlations shown in Table II, methyl protons in H-H linkage are expected to correlate with carbon signals due to AAB and ABA triads. Although methine (75.85 ppm) and methylene (74.33 ppm) carbon signals due

to AAB triad did not show cross peaks with methyl proton signals owing to lower signal intensities, ABA triad signals of methine and methylene carbons showed cross peaks with methyl proton signals at 1.208 ppm, which could be assigned to H-H diad as shown in Figure 2. The methyl proton signal clearly showed cross peaks with methyl carbon signals

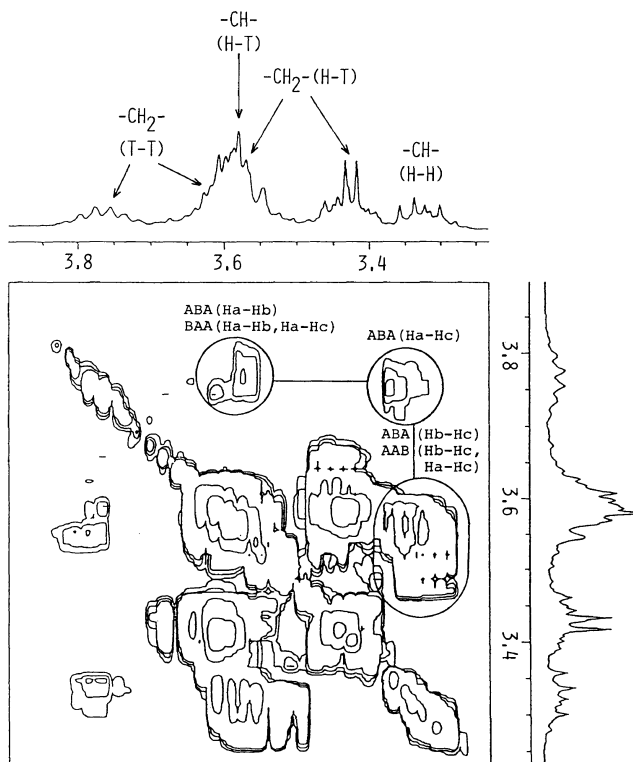


Figure 5. 270 MHz ^1H COSY spectrum measured in benzene- d_6 at 50°C of benzene-hexane soluble fraction of poly(*S*)-(-)-propylene oxide) prepared with $\text{Bu}_2\text{SnO}-\text{Bu}_3\text{PO}_4$ (1:2) condensate. The correlations among off-diagonal signals due to the irregular sequence (ABA, BAA, AAB) are indicated with solid lines. H_a , H_b , and H_c represent hydrogens in the following structures:

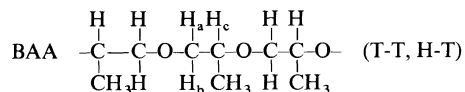
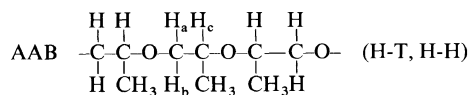
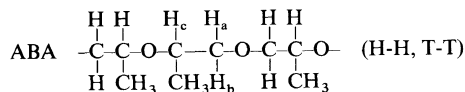


Table III. ^{13}C NMR chemical shift (ppm) of poly((S)-(-)-propylene oxide) at 50°C in benzene- d_6

	-CH	-CH ₂ -	-CH ₃
AAA	75.92	73.92	17.80
AAB	75.85	74.33	18.85
ABA	76.21	73.16	18.71
BAA	75.51	73.62	17.67

at 18.71 and 18.85 ppm. Since the former was assigned to ABA triad, the latter should be assigned to AAB triad. Thus, the last methyl signal at 17.67 ppm could be assigned to BAA, although the expected cross peak with H-T ethyl protons (1.190 ppm) was not clearly distinguished from the strong cross peak between methyl carbon in AAA triad and methyl protons in H-T diad.

From the above results, ^{13}C NMR spectrum of poly((S)-(-)-propylene oxide) could be assigned completely by ^{13}C - ^1H COSY and long range ^{13}C - ^1H COSY (Table III). The present assignments differ from those reported by Oguni⁹ and Schilling.¹³ Consequently, the chemical shift prediction from simple shielding effect or more elaborated combination of γ -effect and rotational isomeric (RIS) model is not sufficiently applicable to the present case.

The detailed assignments for ^1H NMR spectrum in the methylene and methine proton regions were made possible from ^1H COSY spectrum (Figure 5). One of the methylene protons in T-T linkage (3.78 ppm) showed two cross peaks with the signals at 3.59 and 3.32 ppm. The latter peak (3.32 ppm) was already assigned to methine proton in H-H linkage, and the cross peak is due to the sequence (H-H)-(T-T), that is, ABA triad. Thus the former peak (3.59 ppm) can be assigned to the geminal methylene proton in T-T diad. The peak intensities also proved these assignments. The methylene proton signal at 3.78 ppm may exhibit cross peak with methine proton signal due to H-T linkage as shown in

Table IV. ^1H NMR chemical shift (ppm) of poly((S)-(-)-propylene oxide) at 50°C in benzene- d_6

	-CH-	-CH ₂ -	-CH ₃
H-T	3.59	3.43	3.59
H-H	3.32	—	1.208
T-T	—	3.59	3.78

the figure. The results of the ^1H NMR assignments are summarized in Table IV.

In our previous paper¹⁵ the multiplet of 3.32 ppm was erroneously assigned to one of the methylene protons in T-T linkage. However, the calculation of the number of T-T linkage in the polymer chain is not affected at all by the correction of assignment, because the number of H-H and T-T linkages in the polymer chain is the same. Thus the conclusion drawn in the previous paper should be kept valid.

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