appreciably more reactive with ethyllithium-d_5 in toluene-d_8 than either 1,3-pentadiene or 2-methyl-1,3-pentadiene, the reaction at 23° being complete within 24 hr, compared to two or more days for the latter. However, no chain-end absorptions could be detected in the nmr spectrum because of an unfavorable initiation to propagation ratio. The microstructure of the polymer produced was 80 ± 5% 1,4 and 20 ± 5% 1,2. Using isopropyllithium-d_7 as an initiator in benzene-d_6 the reaction was complete in less than two hours and the solution had a deep red color, indicating a delocalized carbon-lithium bond. However, no absorptions from γ hydrogens could be seen in the nmr spectrum (there would be no β protons in a 1,4 chain end).

Furthermore, this spectrum contained a broad resonance peak from the in-chain units centered around 2.8 ppm. This peak could easily mask a small γ-hydrogen resonance peak. Upon pseudotermination of this species the ratio of the areas of the two methyl group resonance peaks at 1.6 and 1.1 ppm decreased from approximately 2.3 to 1.5. This shows that part of the resonance peak at 1.6 ppm was due to the α-methyl group of the 1,4 chain end. This result is analogous with that found for the 1,3-pentadiene (see Figure 3) and confirms the presence of the delocalized 1,4 chain end.

It is not surprising that the chain-end is exclusively 1,4 in the case of this monomer, since the inductive effect of the methyl group on the 3 carbon would make attack at the 1 carbon more favorable than in the 1,3-pentadiene case. The delocalized bond, with a high charge density on the γ carbon, explains the relatively high amount (~20%) of 1,2 microstructure formed in this polymerization in hydrocarbon media. Also the high amount of 1,2 microstructure indicates that methyl groups on the β carbon, unlike methyl groups on the δ carbon, do not prevent monomer attack at the γ carbon. The high reactivity of the secondary carbon-lithium bond also explains the high reactivity of this monomer compared to the other 1,3-pentadienes.

Another monomer studied was 4-methyl-1,3-pentadiene. The reaction of a 0.5 M solution of ethyllithium-d_5 in toluene-d_8 with an equimolar amount of monomer was very slow, with only 40-45% conversion after 11 days at 23°. Using *sec*-butyllithium as an initiator in benzene-d_6, the reaction was complete in 24 hr. However, in both cases no active absorptions from the chain end unit could be observed in the nmr spectrum because of an unfavorable initiation to propagation ratio. The solution of the *sec*-butyllithium initiated species had a deep red color, again indicating a delocalized carbon-lithium bond. It is very likely that steric and inductive effects of the two methyl groups on the 4 carbon cause exclusive attack on the 1 carbon. Such attack would produce a 1,4 chain end that would possess a tertiary carbon-lithium bond. The instability of such a bond again should lead to a delocalized species, even in hydrocarbons. Also such a species should be very reactive and would account for the high propagation to initiation ratio found for this monomer.

The microstructure of the poly(4-methyl-1,3-pentadiene) polymers formed was about 83% 1,4 and 17% 1,2. These results agree with those of Cuzin *et al.*[13] who further determined by ir that the 1,4 structure was all trans.

These results thus show that delocalized carbon-lithium bonds can exist in hydrocarbon media, and thus support the previously proposed theory that the 1,2 and 3,4 polymer microstructures formed in polybutadiene and polyisoprene, respectively, is due to a small, undetectable amount of delocalized chain ends in equilibrium with the covalent species detected in the nmr spectrum.

Acknowledgments. We acknowledge the kind assistance of Mr. E. R. Santee in obtaining the 100-MHz data, as well as in their interpretation. This research was supported by a grant from The General Tire & Rubber Co.

Structure Analysis of Poly(propylene-α-d oxide) by High-Resolution Nuclear Magnetic Resonance Spectroscopy

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ABSTRACT: Nmr spectra of poly(propylene-α-d oxide) prepared using several types of catalyst were taken and analyzed. Nmr spectra of methylene protons were resolved as dyads arising from the difference in steric environment in the contiguous two monomeric units. Nmr spectra in deuteriochloroform solution showed two pairs of quartets, one of which on downfield was assigned to the methylene protons of head-to-tail linkages, the other on upfield to tail-to-tail linkages. On the other hand, nmr spectra of methylene protons in benzene solution showed splitting into isotactic and syndiotactic dyads of absorption assigned to head-to-tail methylene protons. According to these assignments, microstructure of poly(propylene-α-d oxide) prepared with several types of catalyst could be determined.

Information concerning the microstructure of the polymer is an essential prerequisite for the elucidation of the polymerization mechanism and for the characterization of the polymer samples. The use of nmr spectra in the determination of the tacticity of vinyl polymers has been developed, but the application of this valuable technique to the polymer in which the repeating monomeric unit has three backbone atoms, has not been made so extensively. In a preliminary report,[1] we described the nmr analysis of poly(propylene-α-d oxide) briefly and more recently the nmr spectra of poly(propylene-α-d sulfide) were analyzed in terms of dyads of methylene protons.[2]

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(1) H. Tani, N. Oguni, and S. Watanabe, *J. Polym. Sci., Part B*, 6, 577 (1968).

(2) K. J. Ivin and M. Navratil, *J. Polym. Sci., Part B*, 8, 51 (1970).

Table I
Polymerization Results of Poly(propylene-*α*-*d*-oxide)[a]

						[η]	
Catalyst	Polymerization Temp (°C)	Solvent	Polymer Yield (%)	Crystalline Fraction[b] (%)	Crystalline Fraction	Crystalline Fraction	Amorphous Fraction
KOH	80	None	100	0			0.87
$Et_2AlOAlEt_2$	30	Toluene	91	6	68	1.62	0.88
Et_2Zn-H_2O[c] (*in situ*)	30	Benzene	85	27	69	3.87	2.10
Et_2Zn-H_2O[c] (freeze-dried)	30	Benzene	96	38	73	5.72	3.34

[a] Polymerization was carried out in benzene or toluene solution (except for KOH catalyst) for 120 hr. The concentration of propylene-*α*-*d* oxide was 1.14×10^{-2} mol/l. The amount of catalyst was 0.7 mol % of monomer. [b] Fractionation was done in acetone solution by the method mentioned in the Experimental Section. Percentage value of the crystalline fraction is based on the total polymer. [c] The reaction of diethylzinc and water (molar ratio, 1:0.7) was done in benzene at 30° for 1 hr and then at 60° for 3 hr.

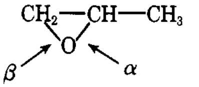

Figure 1. Bond scission of propylene oxide.

Very recently the ^{13}C nmr study of poly(propylene oxide) made by us afforded the dyad for methylene carbons and triad for methine carbons,[3] so the dyad spectrum for methylene protons of poly(propylene-*α*-*d* oxide) could be observed. This paper describes the method and some applications of the microstructure analysis of poly(propylene-*α*-*d* oxide).

Experimental Section

Materials. In general, purification of materials was carried out under a dry argon atmosphere. All solvents were purified by conventional methods, dried over calcium hydride, and then distilled just before use. Diethylzinc and triethylaluminum were purified by distillation under reduced pressure.

Preparation of Propylene-*α*-*d* Oxide. a. 1-Chloro-2-deuteriopropane-2-ol. A solution of 5.6 g (0.145 mol) of lithium aluminum deuteride (Merck Co., deuterium content 99%) in 400 ml of dry ether was placed in a three-necked flask equipped with a separatory funnel, a mechanical stirrer, and a reflux condenser. The solution was cooled to −78° in Dry-Ice–methanol bath, and a cold solution of 56 g (0.61 mol) of anhydrous monochloroacetone[4] in 100 ml of dry ether was added, with vigorous stirring, from the separatory funnel at a fast rate. Stirring was continued at −78° for 0.5 hr after the addition was complete. The reaction mixture was poured into 200 ml of 10% aqueous sulfuric acid at 0°, and the aqueous layer was extracted three times with 50-ml portions of ether. The combined ether solution was washed with water, dried over sodium sulfate, and evaporated. The residual liquid was distilled, and the fraction boiling at 126–127.5° was collected: yield, 40 g (71% based on lithium aluminum deuteride). The purity of the product was 98% by glpc analysis.

b. Propylene-*α*-*d* Oxide. Epoxidation of 1-chloro-1-deuteriopropan-2-ol with potassium hydroxide at 90° gave propylene-*α*-*d* oxide in 90% yield, bp 34.5°. The product was dried over calcium hydride and distilled. The purity of the product determined by glpc analysis was higher than 99%, and the deuterium content estimated by mass spectroscopic analysis was 99%. The nmr spectrum has a singlet at τ 8.68 and a quartet at τ 7.34 in the peak intensity ratio of 3:2, arising from methyl and methylene protons, respectively.

D-(+)-Propylene Oxide. This compound was prepared by the method reported by Levene:[5] $[\alpha]^{20}D$ +15.6° (neat).

Polymerization Procedure. Propylene-*α*-*d* oxide 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° for 24 hr, except for KOH catalyst (at 80° for 120 hr). Polymerization was terminated by adding a mixture of benzene and a small amount of methanol, the quantity of the latter is slightly over that required to precipitate the catalyst. Catalyst residue was removed by centrifugation, and the raw polymer was obtained from the supernatant clear solution by freeze-drying. The crystalline polymer was separated as a precipitate when the solution prepared by dissolving 0.5 g of the raw polymer in 100 ml of acetone at 60° was allowed to stand at 0° for 2 days, and was isolated by centrifugation at 0°. Acetone-soluble polymer was isolated by evaporating the mother liquor. Intrinsic viscosity, [η], was measured at 25 ± 0.1° in benzene solution. The results of polymerization are shown in Table I.

Preparation of Catalyst. a. Diethylzinc-Water Catalyst System. A tube connected to a vacuum line was flushed several times with dry argon. A solution of diethylzinc (0.53×10^{-1} g, 4.35×10^{-4} mol) in 2.0 ml of benzene was charged in the tube by using a syringe, and 5.5 μl of water was added with stirring by a microsyringe. Stirring was continued at room temperature for 0.5 hr and then at 60° for 3 hr. In this reaction, *ca.* 2 mol of ethane gas was evolved per mol of water. The resulting yellow slurry was used as a catalyst (*in situ* catalyst). The slurry was freeze-dried under vacuum to remove unreacted diethylzinc.[6] The residue obtained was also used as a catalyst (freeze-dried catalyst).

b. Bis(diethylaluminum)oxide Catalyst. This catalyst, $Et_2AlOAlEt_2$, was prepared by the equimolar reaction of Et_2AlOLi and Et_2AlCl according to the procedure developed in this laboratory.[7]

c. KOH Catalyst. Freshly fused potassium hydroxide hydroxide was ground under a dry argon atmosphere.

Measurement of Nmr Spectrum. Nmr spectra of the polymers were taken with JNM-4H 100 spectrometer at 100 MHz in 3–5% deuteriochloroform solution at 55° and deuteriobenzene solution at 70°. Tetramethylsilane was used as the internal standard. Relative intensities (peak areas) of three kinds of quartets were determined using a curve resolver, Du Pont 310. These values correspond to the relative contents of three different kinds of dyads in the polymer.

Results and Discussion

Analysis of Nmr Spectrum of Poly(propylene-*α*-*d* oxide). Since propylene oxide has an asymmetric carbon atom, two kinds of ring openings, *α* and *β* openings, are possible depending on the nature of attacking reagent (see Figure 1). If both types of ring openings take place in the propagation reaction, head-to-tail, head-to-head, and tail-to-tail linkages result in the polymer chain. In addition to this structural problem, a configurational problem also arises in the course of the propagation reaction. Therefore, the possibility of the presence of four different linkages should be kept in mind in considering the main-chain structure of a poly(propylene oxide) sample (Figure 2).

Nmr spectroscopy is expected to be a most powerful tool for analyzing exactly the microstructure of poly(propylene oxide), but unfortunately the spectrum is too complex to be analyzed exactly. Ramey *et al.* interpreted the difference observed between the spectra obtained by decoupling from the methyl protons of the crystalline and the amorphous fractions due to the difference in the tacti-

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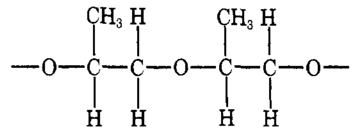
(3) N. Oguni, K. Lee, and H. Tani, *Macromolecules*, **5**, 816 (1972).

(4) This compound was prepared by chlorination of acetone according to the procedure reported by Frisch (*Ber.*, **26**, 597 (1893)).

(5) P. A. Levene and A. Walti, *J. Biol. Chem.*, **68**, 415 (1926).

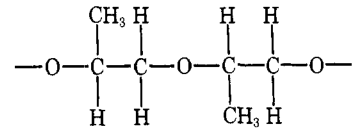
(6) This technique was described in K. Aryluk, M.S. Theses, Manchester University (1966).

(7) H. Tani, T. Araki, N. Oguni, and N. Ueyama, *J. Amer. Chem. Soc.*, **89**, 173 (1967).



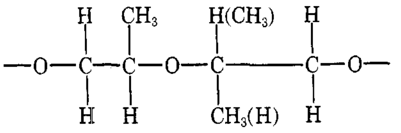
$$\begin{array}{ccccccccc} & CH_3 & & H & & CH_3 & & H & \\ & | & & | & & | & & | & \\ -O- & C & - & C & -O- & C & - & C & -O- \\ & | & & | & & | & & | & \\ & H & & H & & H & & H & \end{array}$$

isotactic unit (DD and LL)
(head-to-tail)



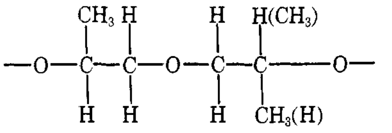
$$\begin{array}{ccccccccc} & CH_3 & & H & & H & & H & \\ & | & & | & & | & & | & \\ -O- & C & - & C & -O- & C & - & C & -O- \\ & | & & | & & | & & | & \\ & H & & H & & CH_3 & & H & \end{array}$$

syndiotactic unit (DL and LD)
(head-to-tail)



$$\begin{array}{ccccccccc} & H & & CH_3 & & H(CH_3) & & H & \\ & | & & | & & | & & | & \\ -O- & C & - & C & -O- & C & - & C & -O- \\ & | & & | & & | & & | & \\ & H & & H & & CH_3(H) & & H & \end{array}$$

head-to-head unit



$$\begin{array}{ccccccccc} & CH_3 & & H & & H & & H(CH_3) & \\ & | & & | & & | & & | & \\ -O- & C & - & C & -O- & C & - & C & -O- \\ & | & & | & & | & & | & \\ & H & & H & & H & & CH_3(H) & \end{array}$$

tail-to-tail unit

Figure 2. Four kinds of linkages in poly(propylene oxide).

city.[8] The nmr spectrum of poly(propylene oxide) decoupled from methylene protons is in any event too complex to determine the tacticity, because of the overlap of the absorptions arising from three backbone protons in the monomeric unit. The spectrum, therefore, should be simplified by substituting the methine hydrogen atom by a deuterium atom, since the magnitude of H-D coupling constant is too small to introduce any detectable splitting in the absorption bands. The nmr spectrum of poly(propylene-α-d oxide) was simplified expectedly by deuteration of the methine proton at lower field, as shown in Figure 3. The absorption at higher field arises from methyl protons and that at lower field from methylene protons.

The spectrum of poly(propylene-α-d oxide) was analyzed by referring to the following experimental results already known. The first is that the crystalline polymer has an isotactic configuration.[9] The second is that the amorphous polymer obtained with KOH catalyst is a random atactic polymer containing no tail-to-tail or head-to-head linkages.[1,10] The third is that the content of tail-to-tail or head-to-head linkages varies rather widely depending on the nature of catalyst used for the polymerization.[10]

The practical process we adopted for the assignment of three kinds of structures observed in the nmr spectrum of poly(propylene-α-d oxide) is explained most conveniently by referring to typical examples. Four different polymer samples used as examples are amorphous and crystalline polymers obtained with $ZnEt_2$-H_2O (1:0.7) freeze-dried catalyst system, the amorphous polymer with KOH catalyst, and the amorphous polymer with $AlEt_2OAlEt_2$ catalyst.

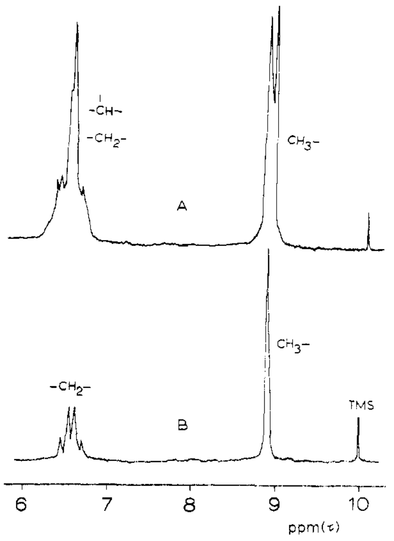


Figure 3. Nmr spectra of poly(propylene oxide) (A) and its α-deuterated derivative (B) in $CDCl_3$ solution at 100 MHz.

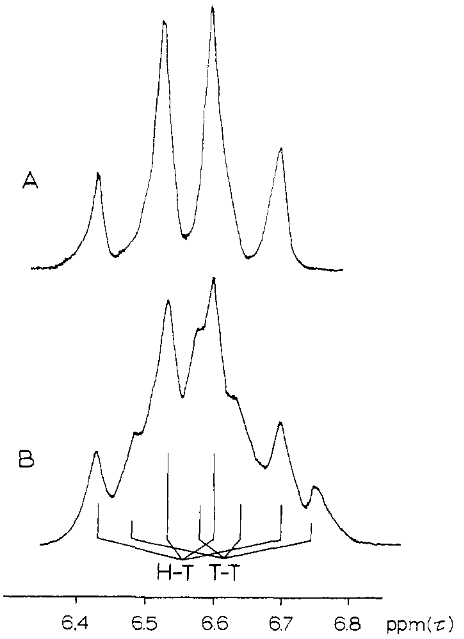


Figure 4. Methylene proton resonance spectra of poly(propylene-α-d oxide) in $CDCl_3$ solution: (A) crystalline polymer prepared with the freeze-dried $ZnEt_2$-H_2O catalyst; (B) amorphous polymer prepared with $Et_2AlOAlEt_2$ catalyst.

The spectrum taken in deuteriochloroform solution of the isotactic polymer prepared with $ZnEt_2$-H_2O catalyst system is shown in Figure 4A. The spectrum of the methylene protons has a symmetrical sharp quartet, whose parameters are ν_A = 6.50 ppm, ν_B = 6.63 ppm, and J_{AB} = 10 Hz. The atactic polymer obtained with KOH catalyst gives a spectrum almost identical with that of the isotactic polymer. Therefore, this absorption can be assigned to that originated from head-to-tail linkages, because it is known that the amorphous polymer prepared with KOH catalyst has an atactic structure containing no tail-to-tail linkages.[10] It can be concluded, therefore, that the absorptions originated from isotactic and syndiotactic dyads overlap in the spectrum measured in deuteriochloroform solution.

The spectrum taken in deuteriochloroform solution of the atactic polymer prepared with $Et_2AlOAlEt_2$ catalyst has an additional quartet at a slightly higher field, whose

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(8) K. C. Ramey and N. D. Field, *J. Polym. Sci., Part B,* 2, 461 (1964).
(9) M. Cesari, G. Perego, and W. Marconi, *Makromol. Chem.,* 94, 194 (1966).
(10) C. C. Price, R. Spectro, and A. L. Tumolo, *J. Polym. Sci., Part A-1,* 5, 407 (1967).

Table II
Microstructure of Poly(propylene-α-*d* oxide) Obtained with Various Types of Catalyst[a]

		By Nmr Spectra			By Ozonolysis Method
		Tacticity in Head-to-Tail Unit			
Catalyst	Nature of Sample	*I* (%)	*S* (%)	Tail-to-Tail Unit (%)	Tail-to-Tail Unit (%)
KOH	Amorphous	50	50	5	10
$ZnEt_2$-H_2O (*in situ*)	Crystalline	97	3	5	1
	Amorphous	65	35	17	25
$ZnEt_2$-H_2O (freeze-dried)	Crystalline	97	3	Trace	
	Amorphous	55	45	3	
$Et_2AlOAlEt_2$	Crystalline	97	3	5	
	Amorphous	75	25	32	25

[a] Experimental errors in peak area determination are ±1 to ~2%.

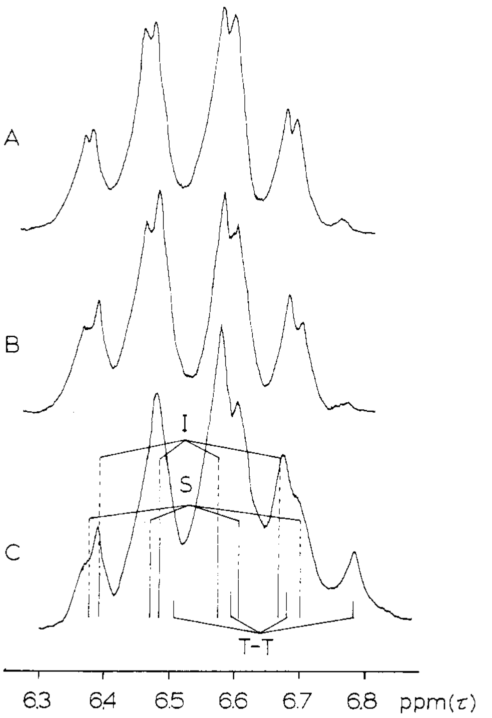

Figure 5. Methylene proton resonance spectra of poly(propylene-α-*d* oxide) in C_6D_6 solution: (A) amorphous polymer prepared with KOH catalyst; (B) amorphous polymer prepared with the freeze-dried $ZnEt_2$-H_2O catalyst; (C) amorphous polymer prepared with $Et_2AlOAlEt_2$ catalyst.

parameters are ν_A = 6.55 ppm, ν_B = 6.67 ppm, and J_{AB} = 10 Hz (see Figure 4B). This new absorption can be assigned to the methylene protons in tail-to-tail linkages, because the intensity of the quartet observed in the spectra of several kinds of catalyst roughly parallel the content of tail-to-tail and head-to-head linkages estimated chemically by Price *et al.*[10] (see Table II).

The spectra taken in deuteriobenzene solution afford additional information. A quartet assigned to head-to-tail linkage in nmr spectra taken in deuteriochloroform solution splits into a pair of quartets (see Figure 5A). Intensities of these two kinds of absorption are nearly equal to each other in the spectrum of the amorphous polymer prepared with KOH catalyst. The spectrum of the polymer containing no tail-to-tail linkages prepared with freeze-dried $ZnEt_2$-H_2O catalyst system also shows similar splitting (see Figure 5B). These results lead us to a reasonable conclusion that the quartet at ν_A = 6.43 ppm, ν_B = 6.61 ppm, and J_{AB} = 9 Hz is assigned to the methylene protons in isotactic dyads and that at ν_A = 6.41 ppm, ν_B = 6.65 ppm, and J_{AB} = 9 Hz to those in syndiotactic dyads. The methylene proton spectrum of the atactic polymer prepared with $Et_2AlOAlEt_2$ catalyst is apparently very complex, because the contents of all three kinds of quartets are relatively high (see Figure 5C). The nmr data of methylene protons in tail-to-tail linkage are found to be ν_A = 6.52 ppm, ν = 6.72 ppm, and J_{AB} = 10 Hz by the analysis of the spectrum with a curve resolver Du Pont 310. These results are summarized in Table III.

The effect of the nature of the solvent used for nmr measurement on the chemical shift between the absorption bands assigned to isotactic and syndiotactic dyads was examined. Splitting is observed in benzene and pyridine, but not in cyclohexane, toluene, chlorobenzene, and nitrobenzene.

Some Applications of Microstructure Determination. a. Effect of Free Diethylzinc on the Polymerization of Propylene Oxide with the $ZnEt_2$-H_2O Catalyst. Propylene-α-*d* oxide was polymerized with the *in situ* and freeze-dried $ZnEt_2$-H_2O (1:0.7) catalyst systems. The yield of the acetone-insoluble crystalline fraction increased by freeze-drying treatment of the *in situ* catalyst system. In addition, the amorphous fractions obtained with the above two catalyst systems differ in their microstructure and molecular weight. The amorphous polymer obtained with the *in situ* catalyst has a lower molecular weight and a higher content of tail-to-tail linkages than that with the freeze-dried catalyst (see Tables I and II). The difference observed in the structure of the polymers may be ascribed to some volatile components contaminating the *in situ* catalyst system which are removed in the course of the freeze-drying process. In fact, diethylzinc, one of the most plausible contaminants, was identified in the distillate obtained during the freeze-drying treatment. The assumption that the formation of tail-to-tail linkages is due to the presence of diethylzinc in the in situ catalyst system was supported positively by adding diethylzinc to the freeze-dried catalyst system. Addition of diethylzinc decreased the polymer yield and the amount of crystalline fraction, and increased the content of tail-to-tail linkages (see Table IV).

The amorphous fraction of the polymer obtained with $Et_2AlOAlEt_2$ catalyst contains a relatively large amount of tail-to-tail linkages, as already mentioned. The formation of this abnormal linkage may be ascribed to the action of triethylaluminum liberated by disproportionation of $Et_2AlOAlEt_2$ to give triethylaluminum and $Et(EtAlO)_nAlEt_2$.

Although diethylzinc and triethylaluminum have no catalytic activity for the polymerization of propylene oxide, these compounds play an important role in the polymerization to disturb the stereospecificity, as evidenced in the above-mentioned examples. Two possibilities can

Table III
Nmr Data of AB-Type Methylene Protons on Poly(propylene-α-d oxide)[a]

Solvent	Structure: Constitutional	Structure: Configurational	Chemical Shift, (ppm)		Coupling Constant, $J_{\text{gem H-H}}$ (Hz)
C_6D_6	Head-to-tail	Isotactic dyad	6.43	6.61	9[a]
		Syndiotactic dyad	6.41	6.65	9[a]
	Tail-to-tail		6.54	6.72	10
$CDCl_3$	Head-to-tail		6.50	6.63	10
	Tail-to-tail		6.55[a]	6.67	10

[a] These values were corrected by examining 220-MHz nmr spectra.

Table IV
Effect of Addition of Diethylzinc to the Freeze-Dried Residue of $ZnEt_2$-H_2O Catalyst on the Polymerization of Poly(propylene-α-d oxide)[a]

Zn ($ZnEt_2$)/Zn ($ZnEt_2$-H_2O)	Yield (%)	Insoluble Fraction in Acetone (%)	Tail-to-Tail Content in the Total Polymer (%)
0.0	88	38	2
0.1	83	33	2
0.2	59	27	5
0.4	29	20	30
0.6	11	Trace	48

[a] Polymerization condition: temperature, 30°; time, 24 hr; catalyst, 1.85 mol % of monomer; poly(propylene-α-d oxide), 1.0 ml; solvent, n-heptane, 1.0 ml.

be discussed for the action of these organometallics: one is the interaction of organometallics with the catalyst, and the other is that with the monomer. The fact that the formation of tail-to-tail linkage is observed for various types of catalysts seems to support the latter possibility. This interpretation is supported also by complex formation between diethylzinc and propylene oxide reported by Thiele,[11] ir shift of ethyl group of diethylzinc observed in various ethereal solvents by Ishimori and Tsuruta,[12] and chemical shift observed in nmr spectrum of methyl protons of dimethylzinc in ethereal solvents as reported by Allen *et al.*[13] The complex formation of triethylaluminum with various ethers is well known until now. The mechanistic aspect of the action of these free organometallics will be clarified by further experiment.

The existence of tail-to-tail linkage in the polymers has a marked effect on the melting points of the polymers. The crystalline polymers obtained using the $ZnEt_2$-H_2O (*in situ*) and $Et_2AlOAlEt_2$ catalysts have the same microstructure; the proportions of *I*, *S*, and tail-to-tail linkages are same (see Table II). This result is reflected in the nearly equal melting points of both polymers (see Table I). However, the crystalline polymer obtained using the $ZnEt_2$-H_2O freeze-dried catalyst, which contains no tail-to-tail linkage and has the same values of *I* and *S*, has a melting point higher than those of the polymers obtained using the $ZnEt_2$-H_2O (*in situ*) and $Et_2AlOAlEt_2$ catalysts. Aggarwal *et al.* pointed out that the melting point of the crystalline poly(propylene oxide) could be related to the sequence length of isotactic units in the polymer.[14] In addition, as mentioned above, the existence of tail-to-tail linkage may contribute to disturbing the crystallization of the polymer to depress the melting point.

b. Relation between Optical Rotatory Power and Content of Tail-to-tail Linkage. Price *et al.* pointed out that the decrease in specific rotation of the poly(propylene oxide) samples prepared from optically active monomer with various kinds of catalyst is due to the presence of tail-to-tail and head-to-head linkages in the polymers and not to partial racemization in the course of polymerization.[10] Their conclusion can be tested quantitatively using the nmr technique for determining microstructure and the catalyst systems composed of the $ZnEt_2$-H_2O freeze-dried catalyst and varied amounts of diethylzinc were used.

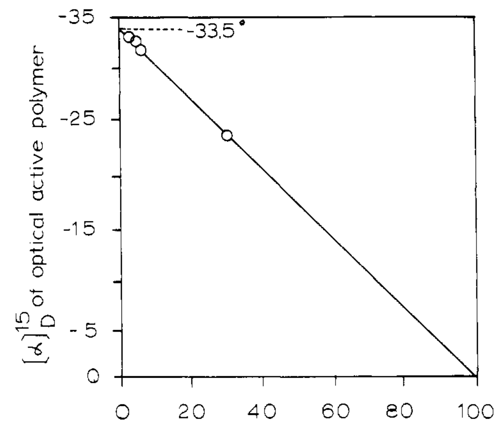

Figure 6. Relation between the specific rotatory power of optically active poly(propylene oxide) in benzene and tail-to-tail content (%) of poly(propylene-α-d oxide) by nmr spectra.

D,L-Propylene-α-d oxide and D-(+)-propylene oxide were polymerized in identical conditions. A linear relationship was observed between specific rotation of the optically active polymer and content of tail-to-tail linkage in the poly(propylene-α-d oxide) (see Figure 6). From the linear relationship, specific rotation of the polymer containing no tail-to-tail linkage is expected to be *ca.* −33.5°. This result not only confirms unambiguously Price's conclusion, but also strongly supports the validity of our microstructure analysis method by nmr spectroscopy.

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