Stereospecific Polymerization of Propylene Oxide and Its α-Deuterated Derivative by *N,N*-Bis(ethylzinc)-*tert*-butylamine

Nobuki Oguni, Takeshi Fujita, and Hisaya Tani*

Department of Polymer Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan. *Received November 21, 1972*

ABSTRACT: Stereospecific polymerization of propylene oxide to give isotactic polymer was investigated by using an excellent catalyst, EtZnNBu^{t}ZnEt. This crystalline organozinc compound was effective as a catalyst even in a minute amount for the polymerization of propylene oxide. In an extremely dry system, the catalyst gives no polymer, but recovers its catalytic activity by the addition of a small amount of water. The role of water was examined using propylene-α-*d* oxide as monomer in respect to the microstructure of the polymer produced and to the rate of polymerization. The addition of water enhances the rate of polymerization and also increases the yield of isotactic polymer.

A great number of papers have been published on the stereospecific polymerization of propylene oxide. Especially the catalyst systems of $ZnEt_2$-H_2O[1] and $AlEt_3$-H_2O[2] have been extensively investigated. These catalysts are insoluble in common organic solvents and/or give the crystalline polymer in a rather low yield. In order to obtain information about the mechanism of the stereospecific polymerization of this monomer, we should have a catalyst which gives crystalline polymer in high yield, dissolves in common organic solvents and can be isolated in crystalline form. One approach to satisfy these requirements was made by finding an excellent catalyst, EtZnNBu^{t}ZnEt, which is prepared by the reaction of diethylzinc with *tert*-butylamine (molar ratio, 2:1).[3] This catalyst forms the 1:1 complexes with electron donors, and the 1:1 complex with propylene oxide decomposes at temperatures above room temperature to give poly(propylene oxide) without any side reaction.[4] On the other hand, the successful development of nmr analysis of the microstructure of poly(propylene-α-*d* oxide) enables us to determine the content of isotactic and syndiotactic dyad units in head-to-tail linkage, and of tail-to-tail linkage in the polymer.[5] This paper describes the careful investigation carried out under high vacuum conditions which revealed that the polymerization, especially the stereospecific polymerization, required the cocatalyst. Also the role of the cocatalyst with respect to the microstructure of polymer and the rate of polymerization was studied.

Experimental Section

All experiments were carried out under a dry argon atmosphere.

Reagents. All reagents were of reagent grade purity, purified by conventional methods and dried over metallic sodium or calcium hydride.

Propylene-α-*d* Oxide. This compound was prepared by hydrogenation of menochloroacetone with lithium aluminum deuteride, followed by epoxidation of the resulting chlorohydrin with aqueous KOH.[5] The deuterium content in the product determined by nmr and mass spectra was above 99%.

EtZnNBu^{t}ZnEt. This compound was prepared by the reaction of diethylzinc with *tert*-butylamine (molar ratio, 2:1) in toluene at 80°: yield, 35%; mp 67-69°. *Anal.* Calcd for $C_8H_{19}NZn_2$: Zn, 50.27. Found: Zn, 51.7. This compound was hydrolyzed under acidic conditions and the evolved ethane was determined by the standard volumetric procedure; *Anal.* Calcd: C_2H_5-Zn, 1. Found: C_2H_5-Zn, 0.84.

Preparation of Catalyst. The apparatus consists of a manifold consisting of a length of wide bore tubing (22-mm i.d.) having four side tubes which are attached to the reaction vessels (see Figure 1-(I)). One of the end of the manifold leads to an efficient high vacuum pump system through a liquid nitrogen cooled trap, and the other end leads to a dry argon reservior through a tap.

Removal of moisture and oxygen from the glass ampoules and the lines were conducted under high vacuum (1×10^{-6} mm) by baking with a red flame for several hours. After thoroughly dried, the ampoules and the reaction vessel were filled with dry argon through a tap.

The reaction of *tert*-butylamine with diethylzinc was carried out in flask E (see Figure 1-(I)). Each of three ampoules F, G, and H attached through a breakable seal to the flask E contains purified diethylzinc (0.12 mol), *tert*-butylamine (0.05 mol), and toluene (15 ml), respectively. Tap A was closed and tap B closed, and then flask E was cooled to −78°. Tap C was closed, the breakable seals leading to F, G, and H were broken, and the reaction components and the solvent were transferred into flask E. After sealing off the ampoules F and G from the flask E, the flask was heated at 80° by stirring with magnetic stirrer under a dry argon atmosphere for 10 hr. The reflux condenser D was cooled by a mixture of Dry-Ice and methanol. When the reaction was completed, toluene and unreacted diethylzinc were evaporated under vacuum to the ampoule H, and the ampoule H was sealed off from the flask E. A crystalline residue was obtained. One-third of hexane was distilled into the flask E by breaking a breakable seal from the vessel I in which hexane was dried over a sodium mirror. The crystalline residue was recrystallized from hexane in E. After tap A was closed, taps B and C were opened slowly in order to fill the manifold with dry argon. The clear supernatant liquid was removed by a syringe under a dry argon stream from the top of L opened, and then the top of L was sealed and tap B was closed. After the ampoule I was cooled to −78°, the manifold was evacuated. This recrystallization procedure was repeated more twice. The crystalline product was identified as EtZnNBu^{t}ZnEt by nmr spectrum and zinc analysis.

Polymerization Procedure. The polymerizations were carried out in the manifold shown in Figure 1-(II). Propylene oxide which had been purified by conventional methods and dried over calcium hydride was charged into an ampoule J by using a syringe. After sealing the ampoule J, propylene oxide was distilled under vacuum into the ampoule K which contains crystalline *N*-ethylzinc diphenylamine ($EtZnNPh_2$) as drying agent. Propylene oxide was redistilled by breaking a breakable seal into the polymerization ampoule M in which the catalyst was placed beforehand. The ampoule M was sealed off from the ampoule K and the high vacuum line, and was allowed to stand at the specified temperature for the specified time.

Procedure for Isolation of Polymer. A large-scale polymerization was carried out under the above-described polymerization conditions. Polymerizations were terminated by adding a mixture of benzene and a small amount of methanol; the quantity of the

---

(1) J. Furukawa, T. Tsuruta, R. Sakata, T. Saegusa, and A. Kawasaki, *Makromol. Chem.*, 32, 90 (1959); R. Sakata, T. Tsuruta, T. Saegusa, and J. Furukawa, *Kogyo Kagaku Zashi*, 63, 1817 (1960).

(2) E. J. Vandenberg, *J. Polym. Sci.*, 47, 486 (1960); R. O. Colclough, G. Gee, C. E. Higginson, J. B. Jackson, and M. Litt, *J. Polym. Sci.*, 34, 171 (1959).

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

(4) H. Tani and N. Oguni, *J. Polym. Sci., Part B*, 3, 123 (1965); *J. Polym. Sci., Part A*, in press.

(5) H. Tani, N. Oguni, and S. Watanabe, *J. Polym. Sci., Part B-1*, 6, 577 (1968); N. Oguni, S. Watanabe, M. Maki, and H. Tani, *Macromolecules*, 6, 195 (1973).

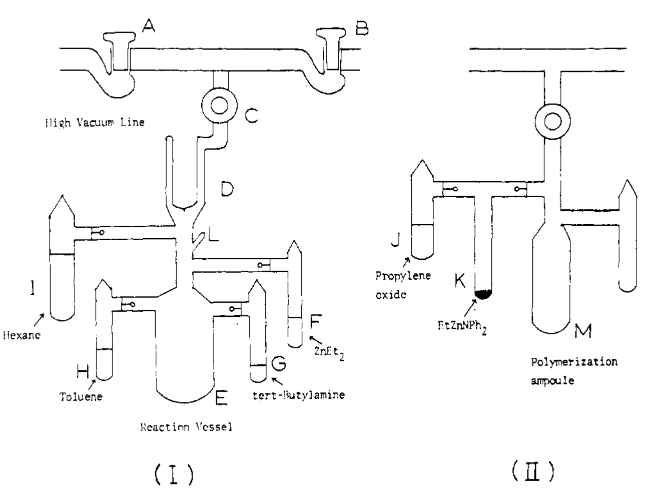

Figure 1. Apparatus for the preparation of catalyst (I) and the polymerization of propylene oxide (II) under high vacuum condition.

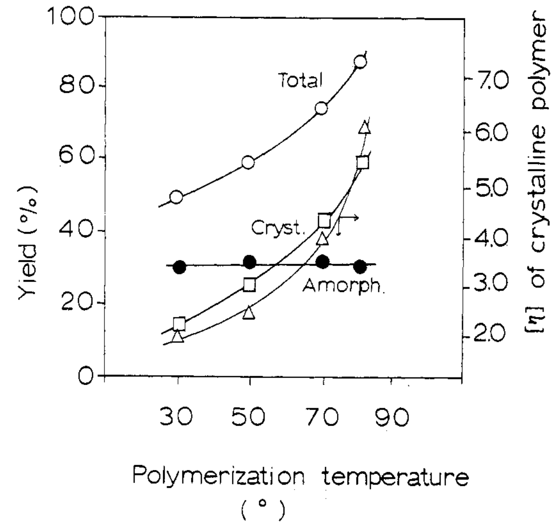

Figure 2. Effect of polymerization temperature on bulk polymerization of propylene oxide catalyzed by EtZnNBu^{t}ZnEt, (catalyst, 1 mol % of monomer; timer, 96 hr).

latter is slightly larger than that required to precipitate the catalyst residue completely. The catalyst residue was removed by centrifugation, and the raw polymer was obtained from the supernatant clear solution by freeze-drying. The crystalline isotactic 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°.

Polymerization Procedure Used for *in Situ* Nmr Measurement. 1. "Water-Addition Procedure." Propylene-α-d oxide (0.20 ml at 15°, 2.8×10^{-3} mol), containing a specified amount of water in benzene (0.40 ml), was distilled completely under reduced pressure into a nmr tube connected to a vacuum line, followed by the addition of the catalyst solution (1 mol % of monomer) at −78°. The nmr tube was sealed off, and kept in a constant-temperature bath maintained at 70°.

2. "Water-Pretreatment Procedure." Catalyst was allowed to react with a specified amount of water in benzene solution at 60° for 1 hr in a nmr tube. Pure propylene-α-d oxide (0.2 ml at 15°) was distilled into this reaction product. The nmr tube was sealed off, and kept in a constant-temperature bath maintained at 70°.

Measurement of Nmr Spectra. Nmr spectra of the benzene solution of the isolated poly(propylene-α-d oxide) and of the *in situ* polymerization system were recorded with a J. N. M. 4H 100 spectrometer (Japan Electron Optics Laboratory Co., Ltd) at 100 MHz at 70°. Relative intensities (peak areas) of the three kinds of quartet (isotactic, syndiotactic, and tail-to-tail dyad) were determined by using the curve resolver (Du Pont 310).

Table I
Bulk Polymerization of Propylene Oxide by EtZnNBu^{t}ZnEt Catalyst[a]

Catalyst Amount (mol/mol of Monomer)	Time (hr)	Yield (%) Total	Yield (%) Crystalline Fraction	Yield (%) Amorphous Fraction	$[\eta]^b$ of Crystalline Fraction
1×10^{-2}	96	46	17	29	8.4
1×10^{-3}	96	19	8	11	5.4
1×10^{-4}	168	17	7	10	2.7
1×10^{-5}	168	13	1	12	1.1

[a] Polymerization temperature, 80°. [b] Intrinsic viscosity was determined in benzene at 25 ± 0.1° using Ubbelohde viscometer.

Results and Discussion

Polymerization of Propylene Oxide by EtZnNBu^{t}ZnEt Catalyst. Catalyst-propylene oxide (PO) complex, EtZnNBu^{t}ZnEt·PO, transforms in solution at temperatures above room temperature to give a mixture of poly(propylene oxide) and the catalyst, at a rate depending upon the nature of the solvent and upon temperature.[4] On the other hand, the polymerization of propylene oxide by this catalyst is considered to proceed through the coordination of propylene oxide monomer to the catalyst, as evidenced by the inactivity of the pyridine complex for the polymerization.[4] These experimental results led us to bulk polymerization studies because the absence of any solvent simplifies the polymerization system.

Results obtained on the effect of temperature on the polymerization revealed very characteristic phenomena (see Figure 2). When the temperature was increased from 30 to 80°, the amount of the crystalline polymer increased steadily, while that of the amorphous polymer remained almost constant. In addition, a nearly parallel relationship was observed between the yield and the molecular weight of the crystalline polymer (see Figure 2). These experimental results seem to be explained by the three factors. First, at least two different kinds of active species, one for the crystalline and the other for the amorphous polymer, exist in the polymerizing system. Second, the rate of formation of the crystalline polymer depends on the polymerization temperature, while that of amorphous polymer not. Third, the molecular weight and the yield of the crystalline polymer increase with increasing polymerization temperature. This phenomenon may be explained by the reasoning that the rate of propagation is very slow and/or the termination reaction is suppressed progressively with an increase in the temperature.

The effect of the amount of catalyst on the polymerization was studied at 80° (Table I). In the range of catalyst concentrations of 10^{-2} to 10^{-5} mol/mol of the monomer, the following results were obtained. First, the molecular weight of the crystalline polymer increased with the increase in the amount of catalyst. Second, the catalyst is effective even when it was used in only a minute amount, for example, one molecule of the catalyst can polymerize about 1300 molecules of the monomer when the molar ratio of the monomer to the catalyst is about 100,000. To explain the seemingly curious result that an increase in the amount of the catalyst increases the yield and the molecular weight of the crystalline polymer, it seems reasonable to assume the existence of a contaminant playing a role as a cocatalyst in the polymerizing system. In addition, the possibility is considered that the catalyst may effectively suppress a chain termination and/or a chain-transfer reaction. If these assumptions are correct, some

Table II
Effect of the Dehydrating Agent on the Bulk Polymerization of Propylene Oxide by EtZnNBu^{t}ZnEt Catalyst[a]

Dehydrating Agent	Yield (%) Total	Yield (%) Crystalline Fraction	Yield (%) Amorphous Fraction	[η][c] of Crystalline Fraction
None[b]	36	19	17	3.7
Zeolite	25	10	15	3.2
K_2CO_3	15	6	9	3.4
CaH_2	9	3	6	1.7
$EtZnNPh_2$	7	2	5	1.5

[a] Polymerization condition: monomer was charged by distillation; catalyst, 1 mol % of monomer; temperature, 80°; time, 48 hr. [b] Propylene oxide was once dried over calcium hydride. [c] Refer to Table I.

Table III
Effect of Addition of Water on the Bulk Polymerization of Propylene Oxide[a]

Amount of Added Water[b] mol/mol of Catalyst	Amount of Added Water[b] mol/mol of Monomer	Yield Total (%)	Yield Crystalline Fraction (%)	Yield Amorphous Fraction (%)
		17	6	11
0.5×10^{-1}	0.25×10^{-3}	78	59	19
1.0×10^{-1}	0.5×10^{-3}	82	65	17
2.0×10^{-1}	1.0×10^{-3}	98	77	21
5.0×10^{-1}	2.5×10^{-3}	79	9	70

[a] Polymerization condition: temperature, 80°; time, 72 hr; catalyst, EtZnNBu^{t}ZnEt, 0.5 mol % of monomer. [b] Water was charged to monomer before catalyst was added.

correlation should exist between the amount of catalyst and that of cocatalyst.

In order to answer the problem whether any cocatalyst is required or not, the monomer and the catalyst were purified more rigorously than before. In previous experiments, propylene oxide used for polymerization experiment was dried by refluxing over calcium hydride. The monomer thus obtained was purified further by treating it with several kinds of drying agents. In addition, the catalyst was prepared and recrystallized under high vacuum condition. In the polymerization experiments in which the monomer and the catalyst were treated in these manner, the polymerization was almost completely suppressed (see Table II).

The catalyst inactivated by these treatments was activated again by adding a small amount of water to the monomer (see Table III). The yield of crystalline polymer increased remarkably by adding a small amount of water, but decreased again with a large amount of water. Thus, a relatively small amount of water acts as an activator, but a relatively large amount of water acts as an inhibitor for the stereospecific polymerization.

Polymerization of Propylene-α-d Oxide by EtZnNBu^t-ZnEt Catalyst in the Presence of Water. In order to examine the role of water in the polymerization of propylene oxide with this catalyst, the microstructure of polymer produced in the process of polymerization was determined by the *in situ* nmr spectra in the existence of catalyst and monomer. The analytical method of proton nmr spectra of dyad of methylene protons was already reported by us.[5]

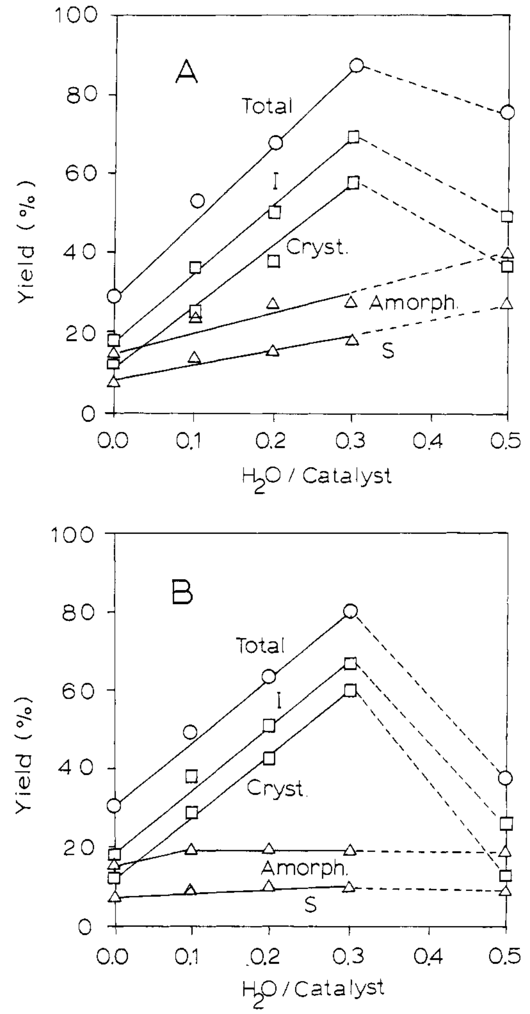

Figure 3. Polymerization of propylene-α-d oxide by EtZnNBu^{t}ZnEt-H_2O catalyst system in benzene at 70° for 8 days: (A) water-pretreatment procedure; (B) water-addition procedure.

Two different procedures were applied to the polymerization of propylene-α-d oxide. In one procedure, "water-addition procedure," water was added to the monomer, and then mixed with the catalyst solution. In another procedure, "water-pretreatment procedure," the monomer was added to the benzene solution of the reaction mixture of the catalyst and water. In the latter procedure, the polymerization system becomes heterogeneous when a molar ratio of water to catalyst is above 0.5. Therefore, the study was performed in molar ratios below 0.5.

Polymerization of propylene-α-d oxide was carried out in the presence of varying amount of water in benzene solution at 70° for 8 days by both procedures. Results obtained by these experiments revealed several characteristics of the polymerization reaction (see Figure 3 and Table IV). First, the increase in the amount of water up to a molar ratio of water to catalyst of 0.3 increases the yield of the total polymer and of the crystalline polymer in both procedures. Second, the yield of the amorphous polymer increases with the increase in the amount of water used in the water-pretreatment procedure, and remains almost constant, independent of the amount of added water, in the water-addition procedure. Third, the amount of the isotactic dyad unit nearly parallels that of the crystalline polymer, while the amount of the syndiotactic dyad unit also parallels that of the amorphous polymer. Fourth, the molecular weight of the polymer increases with the increase in the amount of added water in both cases. These

Table IV
Effect of Addition of Water on the Microstructure of Poly(propylene-α-*d* oxide)[a]

H_2O-Catalyst (Molar Ratio)	Water-Pretreatment Procedure				Water-Addition Procedure			
	Y (%)[b]	$[\eta]$[c]	T-T (%)[d]	I:S[e]	*Y* (%)[b]	$[\eta]$[c]	T-T (%)[d]	I:S[e]
0.0	28 (48)	3.4	6	2.5	28 (48)	3.4	6	2.5
0.1	52 (50)	4.9	3	2.7	50 (60)	4.7	2	4.0
0.2	67 (58)	6.0	1	3.1	64 (67)	5.8	2	4.5
0.3	88 (67)	7.8	1	4.0	80 (75)	6.3	1	5.6
0.5	76 (48)	5.7	1	1.8	37 (34)	4.1	1	2.3

[a] Polymerization condition: catalyst, EtZnNBu^{t}ZnEt, 1 mol % of monomer; solvent, benzene 2.0 ml; temperature, 70°; time, 8 days. [b] *Y* is the yield of polymer: the values in parentheses are percent of acetone-insoluble polymer to total polymer. [c] $[\eta]$ is intrinsic viscosity of total polymer. [d] T-T is the tail-to-tail content. [e] I:S is the ratio of isotactic dyad to syndiotactic one.

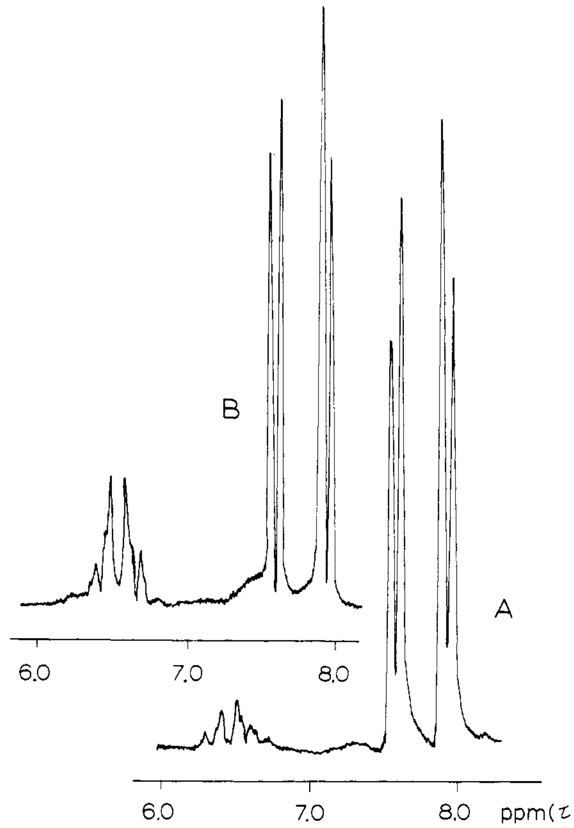

Figure 4. The *in situ* nmr spectra of methylene protons of the monomer and of the polymer in the polymerizing system at 100 MHz at 70°. Molar ratio of water to catalyst is 0.2: (A) the spectrum after 2 days; (B) one after 4 days.

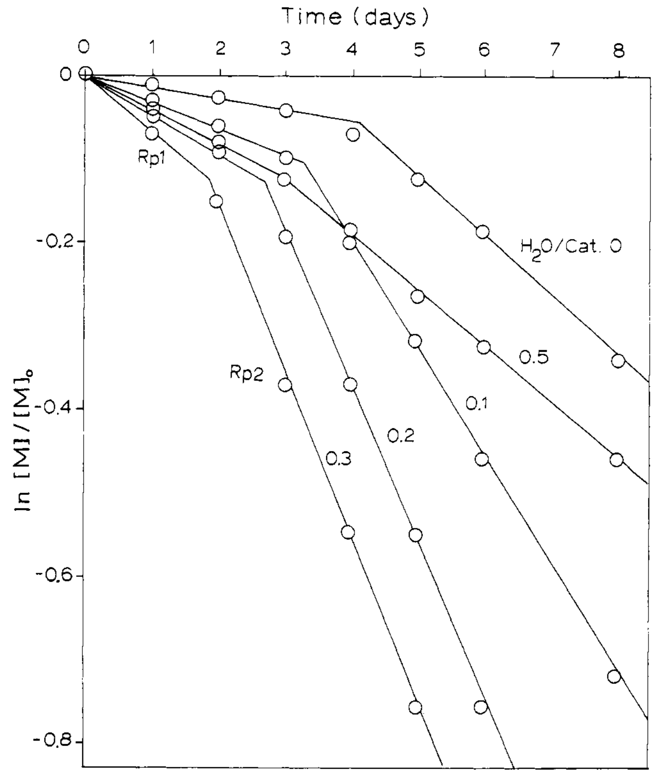

Figure 5. First-order plot of the polymerization of propylene-α-*d* oxide at 70° by EtZnNBu^{t}ZnEt-H_2O catalyst system in water-addition procedure. $[M]_0$ = 4.6 mol l.$^{-1}$, $[C]_0$ = 4.6 × 10^{-2} mol l.$^{-1}$.

results suggest that water contributes to the formation of the isotactic dyad unit in the polymer and to the increase in the molecular weight of the polymer, as observed in the water-addition procedure. The increase in the amount of water decreases the amount of the tail-to-tail linkage; this decrease may be attributed to the decrease in the Lewis acidity of the catalyst, because the Friedel-Craft-type catalyst gives the polymer containing a large amount of tail-to-tail linkage.[5]

The Course of the Polymerization Reaction of Propylene-α-*d* Oxide with EtZnNBu^{t}ZnEt Catalyst Followed with the *in Situ* Nmr Technique. The effect of water on the yield and the microstructure of the polymer can be followed simultaneously with the *in situ* nmr technique in benzene solution at 70°. The *in situ* nmr spectra of methylene protons of the monomer and of the polymer in polymerizing system taken at 100 MHz at 70° are illustrated in Figure 4. The intensity of the quartet at about τ 6.5 arising from the methylene protons of the polymer increased, while that of the quartet at τ 7.8 arising from those of the monomer decreased with the increase in polymerization time. Thus, the yield of polymer can be calculated from the intensity ratio of these two absorptions.

A first-order plot of the rate of polymerization calculated with the above technique are shown in Figures 5 and 6. In the case of water-addition procedure, the plot can be approximated by two straight lines. The first stage is a slow reaction which continues up to the conversion of about 10% and the second one is a faster reaction. In the case of water-pretreatment procedure, the initial slow reaction stage disappears almost completely as the amount of added water increased. In both procedures, the increase in the amount of added water increased the rate of polymerization up to a molar ratio of water to catalyst of about 0.3 (see Figure 7).

First-order plots of the rate of polymerization and of formation of three kinds of dyad units were analyzed in detail for the results obtained by water-addition procedure. The microstructure of polymer, *i.e.*, the content (%) of the three dyads, was analyzed by peak area ratios of

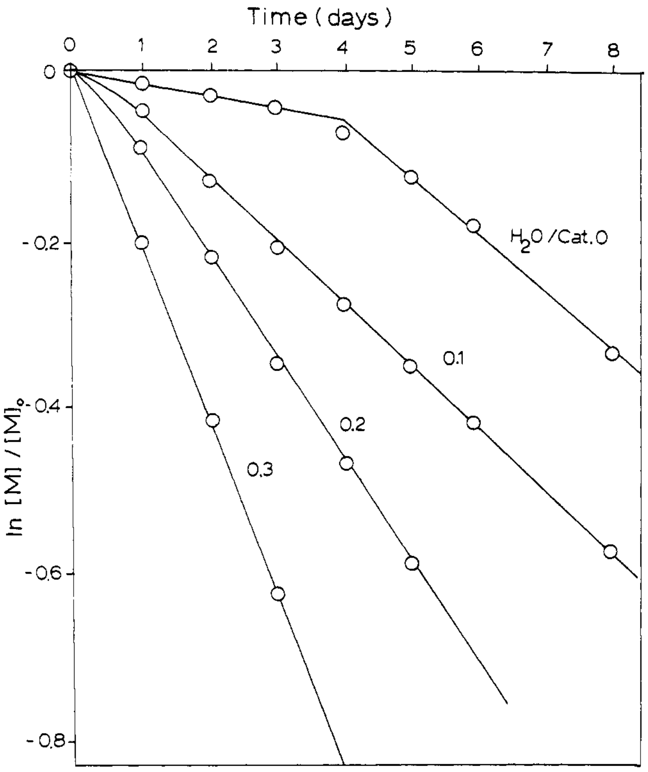

Figure 6. First-order plot of the polymerization of propylene-α-*d* oxide at 70° by EtZnNBu^{t}ZnEt-H_2O catalyst system in water-pretreatment procedure. $[M]_0$ = 4.6 mol l.$^{-1}$, $[C]_0$ = 4.6 × 10^{-2} mol l.$^{-1}$.

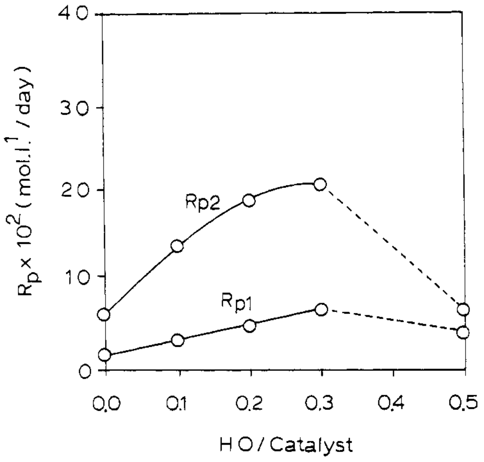

Figure 7. Effect of the addition of water on the polymerization rate in water-addition procedure.

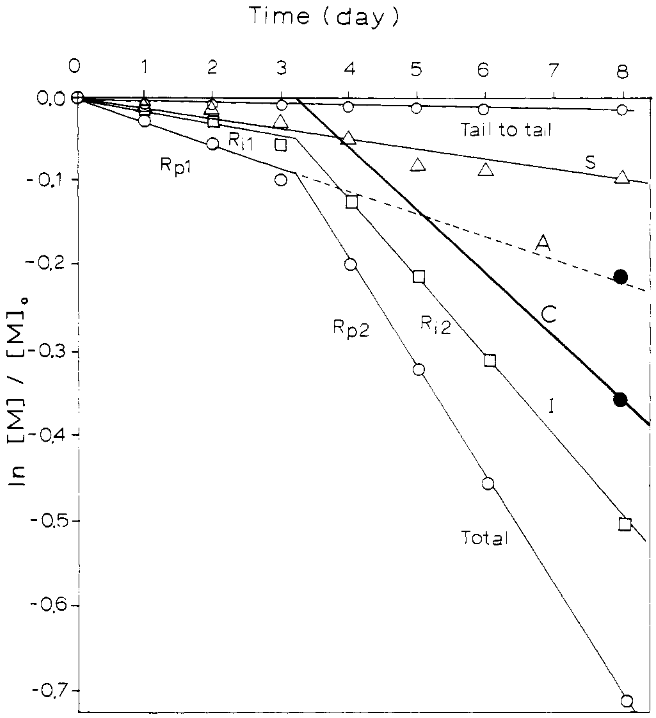

Figure 8. First-order plot of the microstructure of poly(propylene-α-*d* oxide) produced in the water-addition procedure. Molar ratio of water to catalyst is 0.1.

three kinds of quartets assigned to isotactic, syndiotactic, and tail-to-tail dyad units, respectively.[5] Amounts of the three kinds of dyad units of the polymers which are present in the polymerizing system at specified polymerization times can be calculated by multiplying the total polymer yield by the content of each dyad unit. These values are plotted against polymerization time, an example of which is shown in Figure 8. The plots of the rate of polymerization and that of formation of isotactic dyad unit against polymerization time can be approximated by two straight lines and the intersecting points in these two plots lie at about the same time scale. In sharp contrast to these plots, the plots of the yields of syndiotactic and tail-to-tail dyad unit against polymerization time can be approximated by single straight lines. These experimental results are most simply interpreted by the assumption that the polymerizing system contains two kinds of propagating species, one of which leads to the atactic polymer and another to the isotactic one. The atactic polymer is formed at a constant rate throughout the polymerization time observed, while the isotactic polymer begins to form after a definite induction period and is formed at a constant rate which is higher than that for the atactic polymer. If these assumptions are true, only the atactic polymer should be produced in the first stage (R_p1), and the extrapolated straight line of R_p1 (dotted line A) should represent the rate of formation of the atactic polymer. Also a bold line C which is drawn from the difference between R_p2 and extrapolated R_p1 should represent the rate of formation of the isotactic polymer (see Figure 8). Yields and microstructures of the isotactic and atactic polymers obtained in 8-days polymerization are estimated from these two straight lines C and A. These estimated values are in excellent agreement with corresponding values obtained by the fractionation of the polymer prepared independently under an identical polymerization condition (see Table IV). The very satisfactory degree of coincidence observed these two independently obtained values (see Figure 8) affords a very strong supporting evidence for our interpretation of these phenomena.

Booth *et al.* made kinetic studies on the polymerization of propylene oxide with $ZnEt_2$-H_2O (1:0.4) catalyst system which showed a period of fast rate in the 5-10% conversion region and a slow second stage of first order.[6] They interpreted these results by assuming that the low molecular weight amorphous polymer is produced in the first stage and the crystalline polymer in the latter stage. Our experimental results obtained with the *in situ* nmr technique prove unequivocally that the stereospecific polymerization with EtZnNBu^{t}ZnEt-H_2O catalyst system proceeds in the second stage of fast rate. Booth *et al.* assumed a cationic mechanism for their fast initial reaction,

---

(6) C. Booth, W. C. Higginson, and E. Powell, *Polymer*, 5, 479 (1964).

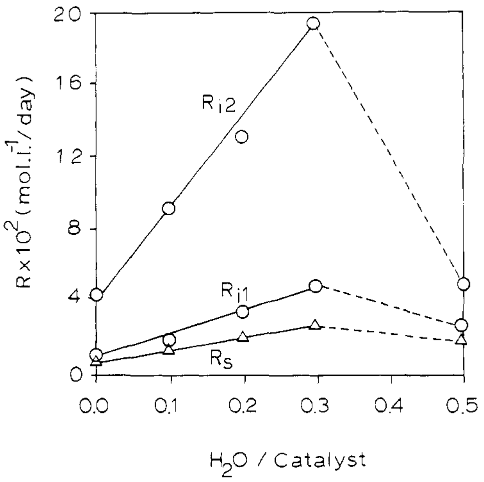

Figure 9. Effect of the addition of water on the rate of formation of isotactic and syndiotactic dyad units in water-addition procedure.

but we propose a anionic mechanism for the initial slow reaction observed in this work, in referring to the rate constant of the reaction of propylene oxide with alcohols which is larger with cationic catalyst than with anionic one.[7]

The rate of formation of isotactic dyad units in the first stage (R_i1), that in the second stage (R_i2) and that of the syndiotactic dyad unit (R_S) are plotted against the molar ratio of water to catalyst (see Figure 9). These values increases with the increase in the ratio of water to catalyst.

Thus, at least two kinds of active species, one for isotactic and the other for atactic polymer, are considered to exist in the polymerization system. According to the nmr and ir spectroscopic data on the reaction of the catalyst and water (molar ratio, 1:0.5), the main reaction is written as

$$2\text{EtZnNBu}^t\text{ZnEt} + \text{H}_2\text{O} \longrightarrow \underset{\text{I}}{2\text{EtZnNHBu}^t} + \underset{\text{II}}{(\text{EtZn})_2\text{O}}$$

The presence of I in the products was identified by comparing the nmr spectrum with that of the authentic sample[8] prepared by the reaction of diethylzinc and *tert*-butylamine (molar ratio, 1:1). The presence of II could not be identified for reasons pointed out by other workers.[9] Nevertheless, II was assumed by them to be an active catalyst for the polymerization of propylene oxide.[9] While the reaction product of diethylzinc and water is insoluble in common organic solvents, the reaction products of EtZnNBu^{t}ZnEt and water are soluble in organic solvents such as benzene, hexane, and toluene. This phenomenon suggests complex formation between I and II. The nature of the stereospecifically active catalyst species and the mechanism of stereoselection of the enantiomeric monomers remains to be determined.

(7) R. E. Parker and N. S. Isaacs, *Chem. Rev.*, **59**, 737 (1959).

(8) N. Oguni and H. Tani, *J. Polym. Sci.*, in press.

(9) R. Sakata, T. Tsuruta, T. Saegusa, and J. Furukawa, *Makromol. Chem.*, **40**, 64 (1960); R. J. Herold, S. L. Aggarwal, and V. Neff, *Can. J. Chem.*, **41**, 1369 (1963).

Thermodynamic Properties of Poly(*trans*-1,4-butadiene) Crystals. Relationship to Molecular Structure

J. M. Stellman,[1a] **A. E. Woodward,***[1a] **and S. D. Stellman**[1b]

Department of Chemistry, City College of the City University of New York, New York, New York, and the Department of Biochemical Sciences, Princeton University, Princeton, New Jersey.

Received January 19, 1973

ABSTRACT: Heat capacity measurements of melt crystallized poly(*trans*-1,4-butadiene) (PTBD) were carried out in the 50–130° region and the entropy change from 73° to the melting point, 139°, was calculated. A value of the entropy change obtained using the rotational isomeric state approximation is found to underestimate the experimental entropy change. Theoretical energy calculations were carried out using empirical potential energy functions for a single PTBD chain, a unit cell and a lattice of cells. Minimization of the lattice energy with respect to two of the monoclinic cell constants for the low-temperature crystal form gave results in good agreement with X-ray diffraction data. The energy of transition from the low-temperature form was calculated and a theoretical heat capacity curve was obtained.

Recent studies of poly(*trans*-1,4-butadiene) single crystals (PTBD) have led to an assessment of surface and interior amorphousness and to a determination of the average number of monomer units in the fold surface.[2a,b] It seems a logical next step to see whether or not the thermodynamic properties of PTBD crystals can be predicted from the postulated molecular structure.

One of the major problems encountered in performing theoretical calculations is the difficulty of doing theoretical "experiments" which can be compared to a laboratory experiment without the use of drastic approximations. With PTBD, however, many of these approximations can be avoided, since it undergoes a solid-solid phase transition between two forms for which thermodynamic and structural data are available.[2b,3,4] Therefore, theoretical calculations of transitional energies can be made which are not based on assuming any hypothetical conformation for the polymer. PTBD thus provides a system for testing energy functions and single-chain approximations commonly used by workers in the field.

(1) (a) City College of the City University of New York, New York, N. Y. (b) Princeton University, Princeton, N. J.

(2) (a) J. M. Stellman and A. E. Woodward, *J. Polym. Sci., Part A2*, **9**, 59 (1971). (b) S. B. Ng, J. M. Stellman, and A. E. Woodward, *J. Macromol. Sci., Phys.*, **7**, 533 (1973).

(3) S. Iwayanagi, I. Sakurai, T. Sakurai, and T. Seto, *J. Macromol. Sci., Phys.*, **2**, 163 (1968).

(4) K. Suehiro and M. Takayanagi, *J. Macromol. Sci., Phys.*, **4**, 39 (1970).