¹³C NMR Study of Poly(propylene oxide)s Prepared with Organotin-Alkyl Phosphate Condensates of Various Degrees of Condensation

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ABSTRACT: Polymerizations of (*S*)- and (*RS*)-propylene oxides were carried out with various organotin-alkyl phosphate condensates derived from dibutyltin oxide (Bu₂SnO) and tributyl phosphate (Bu₃PO₄) as initiators. Regioirregularity of poly((*S*)-(–)-propylene oxide) was studied by ¹³C NMR spectroscopy based on revised peak assignments. The results suggest the presence of alternating irregular units as well as isolated ones, in contrast with poly((*S*)-(–)-propylene oxide)s formed with ZnEt₂–H₂O and AlEt₃–H₂O (acetylacetone), in which only isolated irregular units exist. The benzene–hexane insoluble fraction of poly((*RS*)-propylene oxide) initiated with Bu₂SnO–Bu₃PO₄ (1:2) condensate, which was insoluble in a variety of organic solvents, had isotactic diad of 94% and isotactic triad of 91%. The reactivity of Bu₂SnO–Bu₃PO₄ (1:2) condensate was higher than that of Bu₂SnO–Bu₃PO₄ (1:4) condensate or Bu₂SnO–Bu₃PO₄ (1:1) condensate. Among the Bu₂SnO–Bu₃PO₄ (1:2) condensates, high molecular weight condensate showed higher reactivity than the low molecular weight one.

KEY WORDS Propylene Oxide / Organotin-Alkyl Phosphate Condensate / Irregular Linkage / Tacticity / ¹³C NMR /

Organozinc and organoaluminum compounds are known as highly reactive initiators in ring opening polymerization of oxirane compounds. The structural analyses of the polymers with those initiators have been previously reported.^{1–10} Recently, we reported that organotin-alkyl phosphate condensates also functioned as efficient initiators for the polymerization of oxirane compounds,^{11,12} and these have been used for the industrial production of epichlorohydrin-ethylene oxide rubber.¹³

The organotin-alkyl phosphate condensates exhibit excellent stability and can be stored under air for a long period. A very small amount of the initiators (0.01–0.5% by weight

of the monomer) is effective for rapid polymerization of various oxirane compounds. Polymerization with these initiators in aliphatic hydrocarbons proceeds in slurry. For the polymerization of ethylene oxide by organotin-alkyl phosphate condensates, a bimetallic mechanism shown in Scheme 1 has been suggested by one of the present authors.¹¹ As one of the possible mechanisms, it seems that such structures would be effective for steric control in propagation step in the polymerization of substituted oxiranes.

In this work, the stereochemical structure of poly((*RS*)-propylene oxide) and the regioirregularity of optically active poly((*S*)-(–)-propylene oxide) prepared with dibutyltin oxide

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Scheme 1. Proposed mechanism of initiation and propagation.

(Bu_2SnO)–tributyl phosphate (Bu_3PO_4) condensates were studied by means of ^{13}C NMR spectroscopy. Effects of $\text{Bu}_2\text{SnO}/\text{Bu}_3\text{PO}_4$ ratio on the tacticity of poly(*(RS)*-propylene oxide) are also discussed.

EXPERIMENTAL

Materials

Racemic propylene oxide was refluxed over a mixture of potassium hydroxide and calcium dihydride, and then fractionally distilled under nitrogen atmosphere. (*S*)-(–)-Propylene oxide was obtained from Aldrich Chemical Company, Inc; $[\alpha]_{\text{D}}^{20} = -7.2^\circ$ ($c=1$, CHCl_3), 98.8% *e.e.* The optical purity of (*S*)-(–)-propylene oxide was measured by complexation gas chromatography.¹⁴ Solvents were purified by conventional methods and distilled just before use.

Measurements

^{13}C NMR spectra of the polymers were measured in benzene- d_6 at 50°C on a JEOL JNM-GX 500 spectrometer at 125 MHz. Chemical shifts were referred to the central peak of benzene- d_6 at 128.0 ppm. Gel permeation chromatography (GPC) was performed using a Waters model 150-C instrument equipped with a differential refractometer. Tetrahydrofuran was used as an eluent at a flow rate of 1 ml min^{-1} . The chromatograms were calibrated against standard polystyrene samples. The weight average molecular weight of the polymers were determined by viscometry in benzene at 25°C using the following equation; $[\eta] = 0.81 \times 10^{-4} \bar{M}_w^{0.85}$.¹⁵ The number average molecular weight of the initiator was determined by vapor pressure osmometry (VPO) in benzene at 40°C using a Corona-114 osmometer. Optical rotation of polymers derived from (*S*)-propylene oxide was measured in benzene at a concentration

of 1 g dl^{-1} at 20°C on a JASCO polarimeter model DIP-181. Melting point of polymers were measured on a Perkin-Elmer differential scanning calorimeter model DSC-4 at a heating rate of $10^\circ\text{C min}^{-1}$.

Preparation of $\text{Bu}_2\text{SnO}-\text{Bu}_3\text{PO}_4$ Condensates

Organotin-alkyl phosphate condensates can be prepared from various combinations of organotin compounds such as Bu_2SnO , tributyltin chloride (Bu_3SnCl), and triphenyltin chloride (Ph_3SnCl), with alkyl phosphates such as Bu_3PO_4 , dibutyl phosphate (Bu_2PHO_4), and triethyl phosphate (Et_3PO_4).^{11,13} In the present work, condensates of Bu_2SnO and Bu_3PO_4 prepared in the following manner were used as initiators.

The mixture of Bu_2SnO and Bu_3PO_4 was stirred and heated at 250°C for 20–30 min under dry nitrogen. In the condensation reaction, butane, butene, 1-butanol, and dibutyl ether were distilled out. The condensates formed in the early stage of the reaction were soluble in a variety of organic solvents, but they became insoluble as the degree of condensation increased because of the formation of network structure. The molecular weights and elemental analyses of various $\text{Bu}_2\text{SnO}-\text{Bu}_3\text{PO}_4$ condensates used in the present work are listed in Table I. These condensates were assumed to have the following structure¹¹:

branched or
crosslinked structure

Polymerizations of Propylene Oxide

Polymerization of propylene oxide in benzene was carried out in the following manner. Insoluble $\text{Bu}_2\text{SnO}-\text{Bu}_3\text{PO}_4$ (1:2) condensate was dried in a glass ampoule at 150°C for 1 h *in vacuo*. After cooling, benzene and racemic or optically active propylene oxide were added subsequently into the ampoule under dry nitrogen atmosphere. Polymerizations were carried out at 5°C for 3 or 8 h, and then terminated by adding methanol. The polymerization mixture was diluted with benzene and the insoluble initiator residue was removed by centrifugation. The polymers were recovered from the benzene solution by evaporating the solvent. Benzene-hexane (1:2) insoluble fraction of the polymer was isolated by centrifugation. Benzene-hexane soluble fraction of the polymer was obtained by evaporating the solvents. Polymerization in bulk was carried out in a similar manner at 30°C for 2.5 or 5 h. After the solvent was evaporated, the residual polymer was dried under

Table I. The molecular weights and elemental analyses of various $\text{Bu}_2\text{SnO}-\text{Bu}_3\text{PO}_4$ condensates

$\text{Bu}_2\text{SnO}-\text{Bu}_3\text{PO}_4$ condensates	$\bar{M}_n^a$	Sn	P	C	H
		%	%	%	%
$\text{Bu}_2\text{SnO}-\text{Bu}_3\text{PO}_4$ (1:2) ^b	—	24.5	12.7	29.9	5.7
$\text{Bu}_2\text{SnO}-\text{Bu}_3\text{PO}_4$ (1:2)	11700	24.2	12.4	30.8	6.1
$\text{Bu}_2\text{SnO}-\text{Bu}_3\text{PO}_4$ (1:2)	8300	24.1	12.1	32.7	6.4
$\text{Bu}_2\text{SnO}-\text{Bu}_3\text{PO}_4$ (1:2)	3000	20.1	10.2	33.1	6.4
$\text{Bu}_2\text{SnO}-\text{Bu}_3\text{PO}_4$ (1:4)	4500	12.9	13.9	31.5	6.3
$\text{Bu}_2\text{SnO}-\text{Bu}_3\text{PO}_4$ (1:1)	5600	28.2	8.0	34.9	6.9

^a Determined by VPO.

^b The condensate was insoluble in a variety of organic solvents such as benzene, chloroform, and tetrahydrofuran.

high vacuum.

Polymerizations with diethylzinc (ZnEt_2)- H_2O (1:1) and triethylaluminum(AlEt_3)- H_2O -acetylacetone(AcAc) (1:0.5:0.5) were carried out according to the methods of Oguni^{6,9} and Vandenberg,¹ respectively.

RESULTS AND DISCUSSION

Polymerization of racemic or optically active propylene oxide was carried out with an insoluble $\text{Bu}_2\text{SnO}-\text{Bu}_3\text{PO}_4$ (1:2) condensate in benzene. The results are shown in Table II. The polymers obtained were fractionated into benzene-hexane (1:2, v/v) soluble and insoluble fractions. The insoluble fractions showed melting points but not the soluble ones. The specific optical rotation of the soluble fraction of poly((*S*)-(-)-propylene oxide) was much lower than that of the insoluble one. Although the $\bar{M}_w$ values of the soluble fractions are lower than the insoluble ones, the difference is not so remarkable to explain the differences in these physical properties.

Poly(propylene oxide) may have irregular enchainments (head-to-head and tail-to-tail) as well as regular head-to-tail sequence due to ring-opening reactions in both α - and β -positions:

The absence of melting point and lower optical rotation of the soluble fraction of poly((*S*)-(-)-propylene oxide) are due to the regioirregularity in the polymer chains as described in the followings.

Regioirregularity

For poly((*S*)-(-)-propylene oxide), eight isomeric triads are possible; AAA, AAB, ABA, BAA, ABB, BAB, BBA, and BBB, where A is $-\text{CH}_2\text{CH}(\text{CH}_3)\text{O}-$ (β -cleavage) and B $-\text{CH}(\text{CH}_3)\text{CH}_2\text{O}-$ (α -cleavage) according to Oguni's definition.⁹ However, the fol-

lowing four types of triad are distinguishable by NMR spectroscopy:

AAA(BBB)

AAB(BBA)

ABA(BAB)

BAA(ABB)

It should be noted that the spectrum of the optically active polymer does not involve stereoisomerism and can be analyzed in terms of the above four types of triads.

Figure 1 shows the ^{13}C NMR spectra of benzene-hexane soluble and insoluble fraction of the poly((*S*)-(-)-propylene oxide) prepared with $\text{Bu}_2\text{SnO}-\text{Bu}_3\text{PO}_4$ (1:2) condensate. Signals of each carbon consisted mainly four groups of resonance. The assignments of the ^{13}C NMR spectra of poly((*R*)-(+)-propylene oxide) and poly((*RS*)-propylene oxide) have been reported by Oguni *et al.*⁹ and Schilling *et al.*,¹⁶ respectively.

The assignment of AAA triad can be made easily from Figure 1A. The assignments of other peaks due to irregular units at triad level shown in Figure 1 were made by $^{13}\text{C}-^1\text{H}$ COSY experiment.¹⁷ Some of the peaks, methyl resonances in particular, showed further splittings, which were ascribed to longer sequence distribution of regioirregular enchainment but not to stereosequence distribution in the irregular triads, since the spectrum of poly((*RS*)-propylene oxide) that should contain various stereosequences showed much

Table II. Polymerization of racemic or (*S*)-(-)-propylene oxide in benzene with different initiators

Initiator	Propylene oxide	Time h	Temp. °C	Fraction ^e	Yield %	mp °C	$[\alpha]_D^{20}$	$\bar{M}_w^f$	$\bar{M}_w/\bar{M}_n^g$
Bu ₂ SnO–Bu ₃ PO ₄ (1 : 2) ^a	(<i>RS</i>)-	3	5	Insoluble Soluble	4 4	68 —	— —	1.5×10^5 8.8×10^4	3.8 5.6
Bu ₂ SnO–Bu ₃ PO ₄ (1 : 2) ^b	(<i>S</i>)-(-)-	8	5	Insoluble Soluble	11.3 5.2	69 —	+ 31.5° + 19.2°	1.4×10^5 5.8×10^4	3.0 5.1
ZnEt ₂ –H ₂ O (1 : 1) (<i>in situ</i>) ^c	(<i>RS</i>)-	36	40	Whole	61	57	—	2.3×10^5	55.2
ZnEt ₂ –H ₂ O (1 : 1) (<i>in situ</i>) ^c	(<i>S</i>)-(-)-	24	40	Whole	52	60	+ 29.4°	2.6×10^5	44.2
AlEt ₃ –H ₂ O–AcAc (1 : 0.5 : 0.5) ^d	(<i>RS</i>)-	36	40	Whole	76	63	—	3.2×10^5	2.5
AlEt ₃ –H ₂ O–AcAc (1 : 0.5 : 0.5) ^d	(<i>S</i>)-(-)-	18	40	Whole	62	64	+ 17.2°	1.8×10^5	3.2

^a Monomer 68 mmol, initiator 200 mg, benzene 26 ml.^b Monomer 34 mmol, initiator 100 mg, benzene 13 ml.^c Monomer 34 mmol, initiator 100 mg, benzene 3 ml.^d Monomer 34 mmol, initiator 50 mg, benzene 3 ml. AcAc; acetylacetone.^e Benzene–hexane insoluble or soluble fraction.^f Determined by viscometry (25°C in benzene).^g Determined by GPC.

Figure 1. 125 MHz ^{13}C NMR spectra of poly(*S*)-(-)-(propylene oxide) prepared with insoluble $\text{Bu}_2\text{SnO-Bu}_3\text{PO}_4$ (1:2) condensate measured in benzene- d_6 at 50°C. (A) Benzene-hexane (1:2) insoluble fraction. (B) Benzene-hexane (1:2) soluble fraction.

complicated signals (Figure 2). The present assignments differ from those reported by Oguni⁹ and by Schilling.¹⁶ The assignments by Oguni are based on magnetic shielding effects from the neighboring units, while those by Schilling were made from calculation of the chemical shifts based on γ -gauche effect and rotational isomeric (RIS) model. However, if the assignments by these authors were adopted to the present spectra, the intensity of AAB triad signal would be twice as large as that of BAA signal. AAB and BAA triads should have statistically equal proportion regardless of propagation mechanism. The present assignments shown in Table III satisfy this requirement. The results indicate that chemical shift prediction from simple shielding effect or more elaborated combination of γ -effect and

RIS model is not applicable to the present case.

^{13}C NMR spectra of poly(*S*)-(-)-propylene oxide) prepared with $\text{ZnEt}_2\text{-H}_2\text{O}$ (1:1) and $\text{AlEt}_3\text{-H}_2\text{O-AcAc}$ (1:0.5:0.5) were also analyzed similarly and the results are included in Table III. If an irregular enchainment B ($-\text{CH}(\text{CH}_3)\text{-CH}_2\text{-O}-$) occurs infrequently to give isolated B unit in A sequence ($-\text{AABAA}-$), the fractions of ABA, AAB, and BAA triads are equal to each other. This is the case for the polymers obtained with $\text{ZnEt}_2\text{-H}_2\text{O}$ (1:1) and $\text{AlEt}_3\text{-H}_2\text{O-AcAc}$ (1:0.5:0.5) (Table III). However, the fraction of ABA triad in the polymer formed with $\text{Bu}_2\text{SnO-Bu}_3\text{PO}_4$ condensate is almost twice as large as those of AAB and BAA triads (Table III). The distribution of triad sequences in regard of regio-

Figure 2. 125 MHz ^{13}C NMR spectra of poly(*(RS)*-propylene oxide) prepared with insoluble $\text{Bu}_2\text{SnO}-\text{Bu}_3\text{PO}_4$ (1 : 2) condensate measured in benzene- d_6 at 50°C. (A) Benzene-hexane (1 : 2) insoluble fraction. (B) Benzene-hexane (1 : 2) soluble fraction.

irregularity in this polymer is quite characteristic, even though the total of irregular triad fractions (AAB + ABA + BAA) is close to those for the polymers prepared with $\text{ZnEt}_2-\text{H}_2\text{O}$ and $\text{AlEt}_3-\text{H}_2\text{O}-\text{AcAc}$. Therefore, other types of irregular enchainment than isolated B unit (-AABAA-) should be taken into consideration.

If there exist contiguous irregular units in the chain (-ABBA-), the fractions of AAB and BAA triads are equal but the fraction of ABA triad should be smaller than the former. When the irregular units B exist alternately in regular A sequence (-AABABAA-), the fraction of ABA triad is three times as large as that of AAB or BAA triad. Thus the presence of alternate sequence -ABAB- may contribute to

larger ABA triad fraction. Assuming that irregular units exist either in an isolated manner (-AABAA-) or an alternate manner (-AABA-BAA-), the fractions of the most probable three tetrads were calculated as shown in Table IV.

On the other hand, similar calculations for the polymers formed with $\text{ZnEt}_2-\text{H}_2\text{O}$ and $\text{AlEt}_3-\text{H}_2\text{O}-\text{AcAc}$ confirmed that the polymers scarcely contain alternating irregular units (-AABABAA-) but isolated ones (-AABAA-) (Table IV). The results mean that propagating anion with irregular chain end [B] formed through α -cleavage of propylene oxide attacks the next coming propylene oxide in β -cleavage fashion to reproduce a regular polymer chain end [A];

Table III. Relative abundances (%) of regular and irregular triads in poly((*S*)-(–)-propylene oxide) prepared with several initiators^a

Initiator	CH				CH ₂				CH ₃			
	AAA (75.92)	ABA (76.21)	AAB (75.85)	BAA (75.51)	AAA (73.92)	ABA (73.16)	AAB (74.33)	BAA (73.62)	AAA (17.80)	ABA (18.71)	AAB (18.85)	BAA (17.67)
Bu ₂ SnO–Bu ₃ PO ₄ (1 : 2)												
Whole sample ^b	79	10	6	5	81	9	5	5	79	11	5	5
Insoluble part ^c	90	4	3	3	93	3	2	2	90	4	3	3
Soluble part ^c	54	23	12	11	56	22	11	11	54	25	11	10
ZnEt ₂ –H ₂ O (1 : 1)	85	5	5	5	86	5	4	5	85	5	5	5
AlEt ₃ –H ₂ O–AcAc (1 : 0.5 : 0.5) ^d	76	8	8	8	75	9	8	8	76	8	8	8

^a Chemical shift value for each triad signal is shown in parentheses.^b Determined from the ratio of soluble and insoluble parts.^c Benzene–hexane (1 : 2, v/v).^d AcAc, acetylacetone.K. MURA *et al.*

(1)

(3)

which propagates further in a regular manner.

(2)

Contrastingly, in the polymerization with Bu₂SnO–Bu₃PO₄ (1 : 2) condensate, a part of the reproduced regular chain ends (1) attack propylene oxide in a a-cleavage manner to produce the irregular chain end again;

The ratio of frequencies for the propagation (2) and the propagation (3) is 50 : 50 for the soluble fraction and 86 : 14 for the insoluble fraction, while the propagation (3) did not occur in the polymerization with ZnEt₂–H₂O (1 : 1) and AlEt₃–H₂O–AcAc (1 : 0.5 : 0.5). The reason for this peculiar control of regioregularity in the polymerization with Bu₂SnO–Bu₃PO₄ is not clear at present. However, if the bimetallic catalyst site model (Scheme 1) is adopted for the polymerization, the active site “Sn” is switched in each propagation step and thus irregular enchainment may occur alternately.

Table IV. Fraction of tetrad in regard of regioregularity in poly((S)-(–)-propylene oxide) prepared with several initiators

Initiators	Tetrad			Enchainment ^a	
	–ABAA–	–ABAB–	–AAAA–	ABA→ABAA	ABA→ABAB
	%	%	%	%	%
Bu ₂ SnO–Bu ₃ PO ₄ (1 : 2)					
Whole sample	3.3	2.3	94.4	59	41
Insoluble part	2.5	0.4	97.1	86	14
Soluble part	5.5	5.5	89.0	50	50
Et ₂ Zn–H ₂ O (1 : 1)	5.0	0	95.0	100	0
AlEt ₃ –H ₂ O–AcAc (1 : 0.5 : 0.5)	8.0	0	92.0	100	0

^a Relative frequency of occurrence of ABAA and ABAB tetrad after ABA triad.

Table V. Polymerization of racemic propylene oxide with various Bu₂SnO–Bu₃PO₄ condensates in bulk at 30°C^a

Bu ₂ SnO–Bu ₃ PO ₄	$\bar{M}_n^b$	Time h	Yield %	$\bar{M}_w^c$ × 10 ⁵	Tacticity/%				
					Dyad (–CH ₂ –)		Triad (–CH–)		
					<i>m</i>	<i>r</i>	<i>mm</i>	<i>mr</i>	<i>rr</i>
(1:2) ^d	—	2.5	98	5.3	71	29	63	18	19
(1:2)	11700	2.5	72	3.9	68	32	61	15	17
(1:2)	8300	2.5	46	3.0	66	34	57	21	22
(1:2)	3000	5	26	2.8	59	41	46	27	27
(1:4)	4500	5	12	1.9	72	28	59	26	15
(1:1)	5600	5	no polymer		—	—	—	—	—

^a Monomer 200 mmol, initiator 0.12 mg atom of Sn.^b Determined by VPO in benzene at 40°C.^c Determined by viscometry using following equations: $[\eta] = 0.81 \times 10^{-4} \bar{M}_w^{0.85}$ in benzene at 25°C.^d The condensate was insoluble in a variety of organic solvents such as benzene, chloroform and tetrahydrofuran.

(*RS*)-Propylene oxide was polymerized with the insoluble Bu₂SnO–Bu₃PO₄ (1:2) condensate and the polymer formed was fractionated into benzene–hexane soluble and insoluble fractions. Figure 2 shows ¹³C NMR spectra of the both fractions, which are informative concerning the stereoregularity of the polymer.⁵ The distributions of diad and triad sequences were estimated from the signals in methylene and methine carbon regions. Signals due to irregular linkages were assigned from the comparison with the ¹³C NMR spectra of poly((*S*)-(–)-propylene oxide) (Figure 1).

Stereoregularity

Polymerization of (*RS*)-propylene oxide was also carried out with various Bu₂SnO–Bu₃PO₄ condensates in bulk at 30°C for 2.5 or 5 h. The molar ratio of tin atom in Bu₂SnO–Bu₃PO₄ condensates against the monomer was set to be constant in every polymerization. The results of the polymerization are shown in Table V. The activity of the initiator, the molecular weight and the stereoregularity of the polymers are affected by the molecular weight of the initiator. Bu₂SnO–Bu₃PO₄ (1:2) condensate exhibited higher reactivity than Bu₂SnO–Bu₃PO₄ (1:4) and Bu₂SnO–Bu₃PO₄

(1:1) condensates. The reactivity of Bu₂SnO–Bu₃PO₄ (1:2) condensate as well as the isotacticity of the polymer formed increased as molecular weight of the condensate increased. Bu₂SnO–Bu₃PO₄ (1:2) condensate of $\bar{M}_n$ 3000 exhibited higher reactivity than Bu₂SnO–Bu₃PO₄ (1:4) condensate of $\bar{M}_n$ 4500. However, Bu₂SnO–Bu₃PO₄ (1:4) condensate of $\bar{M}_n$ 4500 gave the polymer with higher isotacticity than the Bu₂SnO–Bu₃PO₄ (1:2) condensate. Bu₂SnO–Bu₃PO₄ (1:1) condensate of $\bar{M}_n$ 5600 gave no polymer. From these results, higher molecular weight and higher proportion of Bu₃PO₄ of Bu₂SnO–Bu₃PO₄ condensates are the important factors for the higher reactivity as well as higher stereospecificity.

Stereoregularity of poly((*RS*)-propylene oxide) prepared with several initiators is shown in Table VI. Benzene–hexane insoluble fraction of poly((*RS*)-propylene oxide) formed with Bu₂SnO–Bu₃PO₄ (1:2) condensate was found to be highly isotactic. (*RS*)-Propylene oxide can be polymerized by a wide variety of initiators (anionic, cationic, and ionic coordination initiators). Generally, the ionic coordination initiators such as ZnEt₂–H₂O, ZnEt₂–ROH, and AlEt₃–H₂O–AcAc afford

Table VI. Stereoregularity of poly((*RS*)-propylene oxide)s prepared with different initiators

Initiators	Tacticity/%					References
	Dyad (–CH ₂ –)		Triad (–CH–)			
	<i>m</i>	<i>r</i>	<i>mm</i>	<i>mr</i>	<i>rr</i>	
Bu ₂ SnO–Bu ₃ PO ₄ (1 : 2) ^a						
Whole sample	76	24	67	16	17	This work
Insoluble part ^b	94	6	91	6	3	This work
Soluble part ^b	63	37	52	24	24	This work
Et ₂ Zn–MeOH (1 : 1.65)	71	29	54	31	15	ref 7
Et ₂ Zn–MeOH (1 : 2)	66	34	47	33	20	ref 8
Et ₂ Zn–H ₂ O (1:1) (<i>in situ</i>)	66	34	51	33	16	This work
AlEt ₃ –H ₂ O–AcAc (1 : 0.5 : 0.5) ^c	72	28	58	30	12	This work
KOH	50	50	27	47	26	ref 7
^t BuOK	50	50	25	50	25	ref 5

^a The condensate was insoluble in common organic solvents.^b Benzene–hexane (1:2, v/v).^c AcAc, acetylacetone.

the polymers with high molecular weight as well as with high stereoregularity.^{6–10} On the contrary, the anionic initiators such as potassium hydroxide and potassium butoxide give regular head-to-tail polymers with low molecular weight and random distribution of configuration in the chain.^{5,7} Cationic initiators such as AlEt₃–H₂O and (PhCHOCH₃)⁺–(SbCl₆)[–] lead to polymers having irregular enchainments due to ring-opening reactions at both α - and β -positions of propylene oxide.^{5,18} Ionic coordination mechanism has been well established for the ZnEt₂–H₂O,^{8,19} ZnEt₂–MeOH,^{20,21} and AlEt₃–H₂O–AcAc¹ initiated polymerizations. Bu₂SnO–Bu₃PO₄ condensates exhibit very similar catalytic activity to those of the zinc and aluminum initiators, that is, high regioselectivity and stereospecificity, although the sequence distribution of irregular enchainment existed in small amounts was quite different. The fact suggests that ionic coordination mechanism is also predominant for the polymerization of propylene oxide with Bu₂SnO–Bu₃PO₄ condensates. The present studies indicate the higher isotactic specificity of Bu₂SnO–Bu₃PO₄

than the zinc or aluminum initiator as well as the peculiar regioirregular enchainment.

REFERENCES

1. E. J. Vandenberg, *J. Polym. Sci., A-1*, **7**, 525 (1969).
2. K. E. Steller, *Am. Chem. Soc. Symp. Ser.*, **6**, 136 (1975).
3. A. Dworak, *Makromol. Chem., Rapid Commun.*, **6**, 665 (1985).
4. H. N. Cheng and D. A. Smith, *J. Appl. Polym. Sci.*, **34**, 909 (1987).
5. N. Oguni, K. Lee, and H. Tani, *Macromolecules*, **5**, 819 (1972).
6. N. Oguni, S. Watanabe, M. Maki, and H. Tani, *Macromolecules*, **6**, 195 (1973).
7. T. Uryu, H. Shimazu, and K. Matsuzaki, *J. Polym. Sci.*, **11**, 275 (1973).
8. M. Ishimori, K. Tsukigawa, T. Nakada, and T. Tsuruta, *J. Macromol. Sci., Chem.*, **11**, 379 (1977).
9. N. Oguni, S. Shinohara, and K. Lee, *Polym. J.*, **11**, 755 (1979).
10. H. C. W. M. Buys, H. G. J. Overmas, and J. G. Naltes, "Coordination Polymerization," C. C. Price and E. J. Vandenberg, Ed., Plenum Publishing Corporation, New York, N.Y., 1983, pp 75–93.
11. T. Nakata, "Coordination Polymerization," C. C. Price and E. J. Vandenberg, Ed., Plenum Publishing Corporation, New York, N.Y., 1983, pp 55–74.
12. K. Miura, T. Kitayama, K. Hatada, and T. Nakata, *Polym. J.*, **22**, 671 (1990).

13. T. Nakata and K. Kawamata, Osaka Soda Co., Ltd., U.S. Patent 3,773,694 (Nov. 20, 1973).
14. V. Schurig, *J. Chromatogr.*, **441**, 135 (1988).
15. E. J. Vandenberg, "Kirk-Othmer: Encyclopedia of Chemical Technology," Vol. 8, 3rd ed, 1979, pp 568—582.
16. F. C. Schilling and A. E. Tonelli, *Macromolecules*, **19**, 1337 (1986).
17. K. Miura, T. Kitayama, K. Hatada, and T. Nakata, *Polym. J.*, **25**, 697 (1993).
18. T. Iijima, Y. Sakamoto, and H. Kakiuchi, *J. Polym. Sci., Polym. Chem.*, **26**, 3189 (1988).
19. M. Ishimori, O. Nakasugi, N. Takeda, and T. Tsuruta, *Makromol. Chem.*, **115**, 103 (1968).
20. S. Inoue, T. Tsuruta, and J. Furukawa, *Makromol. Chem.*, **79**, 34 (1964).
21. S. Inoue, I. Tsukuma, M. Kawaguchi, and J. Furukawa, *Makromol. Chem.*, **103**, 151 (1967).