

Stereospecific Polymerization of Isobutyl Vinyl Ether with $(\text{EtClAl})_2\text{NPh}$ and its Nuclear-Substituted Derivatives

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ABSTRACT: The stereospecific polymerization of isobutyl vinyl ether (IBVE) initiated with a catalyst system composed of AlEt_2Cl and PhNH_2 , and the crystalline compound, $(\text{EtClAl})_2\text{NPh}$, which was separated from the above catalyst system, was studied. The compound, $(\text{EtClAl})_2\text{NPh}$, is dimeric in benzene and with diethyl ether and tetrahydrofuran forms 1:1 complexes which have no catalytic activity for the polymerization of IBVE. The stereospecificity of polymerization increased on increasing number of times the catalyst was recrystallized. In a highly purified polymerization system, this catalyst gave no polymer of IBVE, however the substances coexisting in the system, especially oxygen, were found to be effective cocatalyst for the stereospecific polymerization of IBVE.

KEY WORDS Stereospecific Polymerization / Isobutyl Vinyl Ether / Aluminum Diethyl Chloride / Donor—Acceptor Complex / Cocatalyst / $(\text{EtClAl})_2\text{NPh}$ Catalyst /

Hirata and Tani reported¹ that AlEt_2Cl , which had been allowed to react with a limited amount of oxygen at -78°C , initiated a stereospecific polymerization of isobutyl vinyl ether (IBVE) to give crystalline polymer in a good yield. Pure AlEt_2Cl was inactive as an initiator.

In parallel with this work, we studied the catalytic behavior of a class of the homogeneous stereospecific catalyst derived from the reaction between organoaluminums and primary amines. This line of research led to three typical crystalline organometallic catalysts for the highly stereospecific polymerization reaction. The first was $(\text{Et}_2\text{Al})_2\text{NPh}$ for the polymerization of acetaldehyde,² the second was $(\text{EtZn})_2\text{Nt—Bu}$ for the polymerization of propylene oxide,³ and the third was $(\text{EtClAl})_2\text{NPh}$ for the polymerization of IBVE. This paper describes the stereospecific polymerization of IBVE by $(\text{EtClAl})_2\text{NPh}$, the effects, on the polymerization, of various substituents in the catalyst's phenyl group, and the purity of catalyst, monomer, and solvent.

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EXPERIMENTAL

Materials

Isobutyl vinyl ether (Mitsubishi Chemical Co.) was repeatedly washed with an equal volume of 2*N*-aq potassium hydroxide until the aq solution remained colorless, washed three times with distilled water, and then dried overnight over potassium hydroxide. IBVE thus treated was refluxed over metallic sodium for 20 hr and distilled. The middle fraction of the distillate, after refluxing over calcium hydride, was stored in sealed glass ampoules under a dry argon atmosphere, bp $82.3\text{—}82.5^\circ\text{C}$, n_D^{25} 1.3946 (lit. 1.3938⁴).

Toluene was repeatedly washed with concd sulfuric acid, washed three times with distilled water, dried overnight over calcium chloride, refluxed over metallic sodium for 12 hr, and then distilled under an argon atmosphere. The middle fraction of the distillate was refluxed over calcium hydride for 12 hr and distilled just before use, bp 109.8°C .

n-Hexane, *m*-xylene, and diethyl ether were purified by conventional methods, refluxed over metallic sodium for 12 hr and distilled. The

middle fraction of the distillate was further distilled over calcium hydride just before use.

Diethylaluminum chloride (Ethyl Co.) was heated at 100°C for 1 hr over sodium chloride, which had been dried *in vacuo* at 100°C for several hours, and distilled, bp 92–93°C (11.0–11.5 mm).

Aniline was refluxed over metallic sodium for 12 hr, and distilled under a dry argon atmosphere, bp 183.5°C.

Other oily amines were distilled over zinc dust under a dry argon atmosphere, and solid amines were recrystallized three times from *n*-hexane to give *p*-bromoaniline, mp 62.0°C; *p*-chloroaniline, mp 70.5°C; *p*-toluidine, mp 65.3°C; *m*-toluidine, bp 196.0°C; *o*-toluidine, bp 193.5°C; α -naphthylamine, mp 49.5°C; β -naphthylamine, mp 109.8°C.

Preparation of the $AlEt_2Cl-PhNH_2$ Catalyst System

Under a dry nitrogen atmosphere a specified amount of $AlEt_2Cl$ was added to a solution prepared by dissolving a known amount of aniline in 10 ml of *m*-xylene. The solution was heated at 110–120°C for 24 hr. An aliquot of this solution was used as a catalyst.

Preparation of $(EtClAl)_2NAr$ (*Ar*, aryl group)

To a solution of an aromatic amine (0.1 mol) in 24 ml of *m*-xylene, 0.2 mol of $AlEt_2Cl$ was added dropwise under a dry argon atmosphere at –78°C. The mixture was heated at 110–120°C for 24 hr. One mole of ethane per mol of $AlEt_2Cl$ was evolved in the reaction. On cooling the reaction mixture to –78°C $(EtClAl)_2NAr$ separated out as colorless needles which were recrystallized from *n*-hexane and toluene. Toluene solutions of these crystalline compounds were used as catalysts. The analytical data are

summarized in Table I.

Preparation of the 1 : 1 Complex of $(EtClAl)_2NPh$ with Etheral Compounds

An excess of diethyl ether or tetrahydrofuran was added to a suspension of $(EtClAl)_2NPh$ in *n*-hexane, and the mixture was heated at *ca.* 40°C with stirring. An oily material which separated out from the mixture after cooling to –78°C was washed three times with *n*-hexane, and *n*-hexane and excess diethyl ether or tetrahydrofuran were evaporated off *in vacuo*. Diethyl ether complex: Al, calcd for 1 : 1 complex, 15.5%; obsd 14.8%. Tetrahydrofuran complex: Al, calcd for 1 : 1 complex, 15.6%; obsd 15.1%.

Polymerization Procedure

Polymerizations were carried out by the following general procedure except where stated otherwise.

A polymerization vessel was heated with a gas burner for 4 hr under reduced pressure (1 mm), and flushed three times with dry argon. The solvent and catalyst solution were introduced into the polymerization vessel by the use of syringes under a dry argon stream, the vessel was cooled in dry ice–methanol bath, and then under a dry argon stream and with vigorous stirring, a known amount of IBVE was added slowly from a syringe at the rate of 30–50 min per 0.0135 mol of IBVE. The polymerization vessel was then sealed-off and kept at –78°C for 24 hr. Polymerization was terminated by adding 25 ml of methanol. The precipitate was suspended in methanol overnight. The methanol-insoluble raw polymer(Total) was dried *in vacuo* for 48 hr.

Fractionation of Raw Polymer

One half gram of the raw polymer was extracted with 100 ml of methyl ethyl ketone(MEK)

Table I. Characteristic constants of $(EtClAl)_2NAr$

Ar	Al, %		Molecular weight		mp, °C
	Calcd for $(C_2H_5ClAl)_2NAr$	Obsd	Calcd for $[(C_2H_5ClAl)_2NAr]_2$	Obsd	
C_6H_5	19.0	18.5	548	560	146
<i>p</i> - $CH_3C_6H_4$	18.7	18.0	576	572	123
<i>p</i> - ClC_6H_4	17.6	17.1	614	620	131
<i>p</i> - BrC_6H_4	15.3	14.8	706	695	142
α -Naphthyl	16.6	15.2	648	643	138

at 30°C for 48 hr. The MEK-insoluble fraction was found to be a crystalline isotactic polymer (Cr) from its X-ray fiber diagram and from the crystalline bands at 988 and 1340 cm^{-1} in its IR spectrum. The MEK-soluble fraction was an amorphous polymer (Am).

Stereospecificity of Polymerization

The degree of stereospecificity of the polymerization was expressed as the index of stereospecificity (*IS*) and defined as the weightpercent of the crystalline polymer relative to the raw polymer. This *IS* value has a reproducibility of $\pm 3\%$ in experiments done repeatedly with the same sample.

$$IS = (\text{weight of Cr} / \text{weight of total}) \times 100$$

Determination of Solution Viscosity

Solution viscosity of the polymer was measured in the concentration range of 0.01–0.005 g/dl in benzene solution at $25.0 \pm 0.1^\circ\text{C}$ by using a Ubbelohde-type viscometer.

RESULTS AND DISCUSSION

Polymerization of IBVE with the *in situ* AlEt_2Cl — PhNH_2 (2:1) Catalyst

Results of the polymerization of IBVE initiated with a reaction mixture of AlEt_2Cl and PhNH_2 in various molar ratios (see Table II) show that the polymer prepared in a good yield with the *in situ* catalyst AlEt_2Cl — PhNH_2 (2:1 or 3:1) has a molecular weight higher than that prepared with AlEt_2Cl alone. Therefore, the *in situ* AlEt_2Cl — PhNH_2 (2:1) catalyst system was chosen for further studies.

Table II. Polymerization of IBVE with the *in situ* AlEt_2Cl — PhNH_2 catalyst system^a

$\text{PhNH}_2/\text{AlEt}_2\text{Cl}$, mol/mol	Polymer yield, %	<i>IS</i> ^b , %	η_{sp}/c
0	71	7.5	2.72
1/3	94	14.5	4.00
1/2	93	8.0	3.72
1.0	trace	—	—
2.0	0	—	—

^a Polymerization conditions: AlEt_2Cl , 3.06×10^{-4} mol; IBVE, 1.53×10^{-2} mol; toluene, 10.0 ml; temp, -78°C ; time, 24 hr.

^b See Experimental section.

The effect of the nature of the solvent on the polymerization was studied. Among the solvents examined, the crystalline polymer was obtained only in aromatic hydrocarbons. No polymerization was observed in diethyl ether or chloroform solution (see Table III).

The effects of the amount of toluene solvent on the polymerization were also examined. When a small amount of solvent was used, the system became heterogeneous and was visually similar to a bulk polymerization. In this case, the stereospecificity of polymerization decreased, while the molecular weight of the polymer remained almost constant. The amount of the amorphous polymer decreased linearly with increasing amounts of solvent, while the amount

Table III. The effect of the nature of the solvent on the polymerization with the *in situ* AlEt_2Cl — PhNH_2 catalyst^a

Solvent	Polymer yield, %	<i>IS</i> , %	η_{sp}/c
<i>n</i> -Heptane	37	0	2.32
Toluene	80	61.5	2.07
<i>m</i> -Xylene	53	11.0	0.60
Dichloromethane	trace	—	—
Chloroform	0	—	—
Diethyl ether	0	—	—

^a Polymerization conditions are the same as that in Table I except for the nature and amount (25 ml) of solvent.

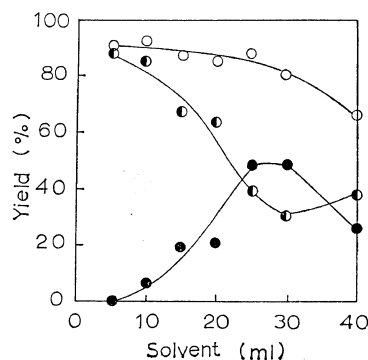


Figure 1. Effect of the amount of solvent on the polymerization: solvent, toluene; IBVE, 0.015 mol; catalyst, 2 mol% of AlEt_2Cl per mol of IBVE; temp, -78°C ; time, 24 hr; ○, total polymer yield; ●, crystalline polymer; ●, amorphous polymer.

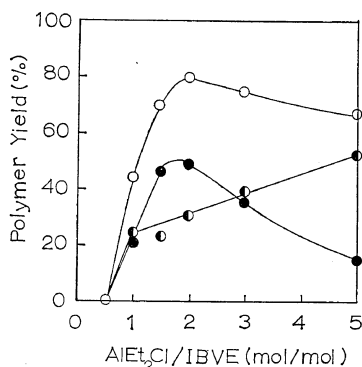


Figure 2. Effect of the amount of catalyst on the polymerization: IBVE, 0.015 mol; toluene, 30 ml; temp, -78°C ; time, 24 hr; ○, total polymer yield; ●, crystalline polymer; ◐, amorphous polymer.

of crystalline polymer followed a bell-shaped curve having a maximum value at a solvent/monomer ratio (v/v) of *ca.* 15 (see Figure 1). Thus, the relative amount of catalyst for giving the amorphous polymer to that for the crystalline one depends on the ratio of the polar monomer to the nonpolar solvent.

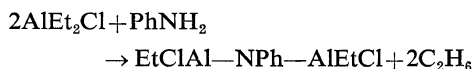
The effect of various amounts of catalyst were also examined. Too low a concentration of catalyst (less than 0.5 mol% relative to monomer) gave no polymer. With increasing in amounts of the catalyst the yield of the amorphous polymer increased linearly, while the yield of the crystalline polymer increased up to a maximum value and then decreased (see Figure 2). This response to catalyst concentration coincides, in principle, to response to various amounts of solvent.

These results suggest that various active species might be present in the *in situ* $\text{AlEt}_2\text{Cl}-\text{PhNH}_2$ catalyst system. In order to obtain more precise knowledge about the true active species of the stereospecific polymerization of IBVE, isolation of the main component of the *in situ* $\text{AlEt}_2\text{Cl}-\text{PhNH}_2$ catalyst system was tried.

Preparation, Structure, and Catalytic Behavior of $(\text{EtClAl})_2\text{NPh}$

The reaction of diethylaluminum chloride with aniline in a molar ratio of 2 : 1 in *m*-xylene at 110°C proceeded smoothly accompanied by the evolution of one mole of ethane per mole of diethylaluminum chloride. A crystalline com-

pound was obtained by cooling the reaction mixture to -78°C . The analytical data of the recrystallized sample correspond to the composition, $(\text{EtClAl})_2\text{NPh}$. This compound was found to be an effective catalyst



for the stereospecific polymerization of IBVE giving a crystalline polymer, with a molecular weight higher than that for the *in situ* $\text{AlEt}_2\text{Cl}-\text{PhNH}_2$ (2 : 1) catalyst system.

The compound, $(\text{EtClAl})_2\text{NPh}$, has a dimeric structure in benzene solution as shown by the molecular weight determined cryoscopically (see Table I). The NMR spectrum of this compound taken at 100 MHz in benzene has two kinds of equal intensity of absorptions originating from ethyl groups linked to aluminum. The two kinds of ethyl group differing in their chemical shifts are assumed to be due to those linked to tri- and tetraordinated aluminum atoms, not to the bridged and nonbridged methyl or methylene groups as observed for low temperature NMR spectra of trimethylaluminum and triethylaluminum.⁶ Thus, the following structure can be assigned to this compound.

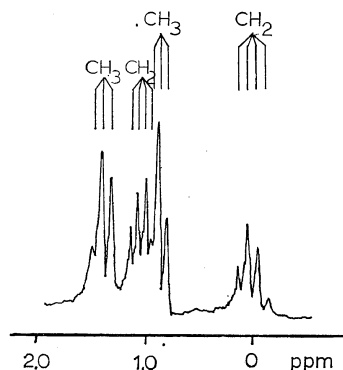
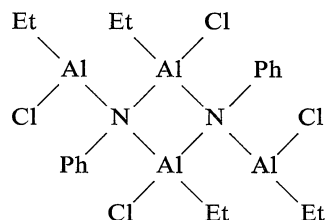


Figure 3. NMR spectrum of $(\text{EtClAl})_2\text{NPh}$ in benzene at 100 MHz.

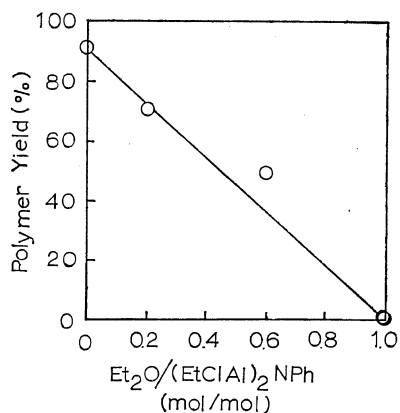
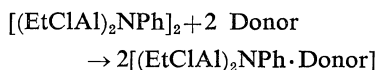
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Figure 4. Effect of added diethyl ether on polymerization: IBVE, 0.0153 mol; $(\text{EtClAl})_2\text{NPh}$, 0.5 mol% to IBVE; toluene, 25 ml; temp, -78°C ; time, 48 hr.

No polymerization was observed in diethyl ether or in tetrahydrofuran solution. In addition, an equimolar amount of diethyl ether was sufficient to inactivate the catalyst (see Figure 4).

The NMR spectrum of this organoaluminum substance in dioxane solution changed on heating the solution at 70°C for 1 hr; the kinds of ethyl groups degenerated to one. This result is interpreted in terms of the simultaneous dissociation of the dimeric form into the monomeric one and the coordination of electron donor to aluminum atoms in the organoaluminum compound.



The 1:1-complexes of $(\text{EtClAl})_2\text{NPh}$ with

diethyl ether and tetrahydrofuran could be obtained in an oily form by refluxing the mixtures of both components at boiling points of the solvents. Peak area ratios in NMR spectra, elemental analyses and molecular weights determined cryoscopically, substantiate the 1:1 complexes for the oily substances. Since IBVE is an ethereal compound, the monomeric form of $(\text{EtClAl})_2\text{NPh}$ is considered to be favored in the presence of IBVE.

The experimental results mentioned above show that the coordination of the monomer to the catalyst is an indispensable step in the polymerization of IBVE with $(\text{EtClAl})_2\text{NPh}$ catalyst.

Effect of the Purity of the Catalyst, Solvent and Monomer on the Polymerization of IBVE with $(\text{EtClAl})_2\text{NPh}$ Catalyst

A cationic polymerization reaction is generally very sensitive to the presence of minute amounts of contaminants which may act as cocatalysts or inhibitors. For the polymerization of IBVE with AlEt_2Cl catalyst, a minute amount of oxygen, carbon dioxide and/or water plays an important and decisive role.¹ Therefore, for the polymerization of IBVE with the $(\text{EtClAl})_2\text{NPh}$ catalyst, separate examinations were performed to determine the effects of purity of the catalyst, solvent and monomer.

Polymerization experiments were carried out using a repeatedly recrystallized catalyst samples (see Table IV). In lower catalyst concentrations, the relative ratio of the crystalline to amorphous fractions of the polymer increased on increasing the number of times the catalyst was recrystallized. In higher concentrations of catalyst the

Table IV. The effect of the purity of $(\text{EtClAl})_2\text{NPh}$ on the polymerization^a

Recrystallizations ^b	Mp of $(\text{EtClAl})_2\text{NPh}$, $^\circ\text{C}$	Amount of catalyst, mol% to monomer					
		0.5		1.0		1.5	
		P.Y., % ^c	IS, %	P.Y., % ^c	IS, %	P.Y., % ^c	IS, %
H (2) T (0)	142	86	38	100	35	80	48
H (2) T (1)	145	93	45	95	30	100	31
H (2) T (2)	146	96	58	100	29	96	25

^a Polymerization condition: IBVE, 1.53×10^{-2} mol; toluene, 25 ml; temperature, -78°C ; time, 24 hr.

^b The catalyst was recrystallized first from *n*-hexane (H) and then from toluene (T). The numbers in parenthesis represent the number of recrystallizations.

^c P.Y. means the polymer yield.

reverse was found. The contaminant, which was probably removed in the course of the recrystallization process, was suspected to be AlEt_2Cl , which was used in a slightly excessive amount in the preparation of the catalyst. A specified amount of AlEt_2Cl was therefore added to the toluene solution of the purified catalyst, the solution was allowed to stand at room temperature for 10 min, and then the monomer was added to the solution at -78°C . In fact, added AlEt_2Cl significantly suppressed the polymerization of IBVE (see Figure 5), and the polymer obtained in the presence of added AlEt_2Cl was amorphous.

The effect of gaseous substances dissolved in the solvent was also examined. Toluene, purified by fractional distillation, was refluxed over Na—K alloy for 24 hr under a nitrogen atmosphere, distilled and stored in a sealed tube at -20°C . Toluene thus treated was further degassed under 1-mm pressure at -78°C for 5 min prior to adding the monomer. By these treatments, the crystalline polymer was obtained in good yield with good reproducibility, even for catalyst concentration as low as 0.2–0.3 mol% of monomer while these treatments had no effect on the yield of the amorphous polymer (see Figure 7). Water and dried air added into the polymerization system resulted in decreasing both the yield of the crystalline and amorphous polymers (see Figures 8 and 9).

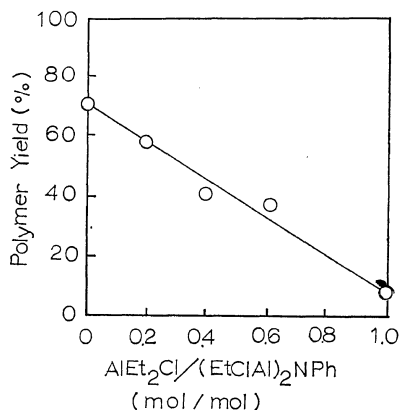


Figure 5. Effect of added AlEt_2Cl on polymerization by $(\text{EtClAl})_2\text{NPh}$ catalyst: IBVE, 0.0153 mol; $(\text{EtClAl})_2\text{NPh}$, 3 mol% to IBVE; toluene, 15 ml; temp, -78°C ; time, 1 hr.

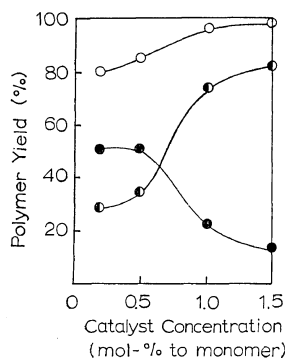


Figure 6. Effect of the amount of catalyst on the polymerization by $(\text{EtClAl})_2\text{NPh}$: IBVE, 0.0153 mol; toluene, 25 ml; temp, -78°C ; time, 24 hr; ○, total polymer yield; ●, crystalline polymer; ◐, amorphous polymer.

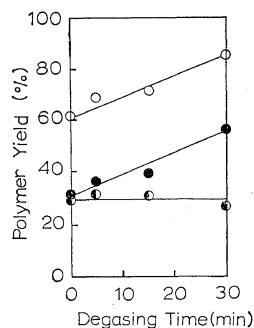


Figure 7. Effect of degassing time on polymerization by $(\text{EtClAl})_2\text{NPh}$: IBVE, 0.0153 mol; $(\text{EtClAl})_2\text{NPh}$, 0.5 mol% to monomer; toluene, 25 ml; temp, -78°C ; time, 24 hr; ○, total polymer yield; ●, crystalline polymer; ◐, amorphous polymer.

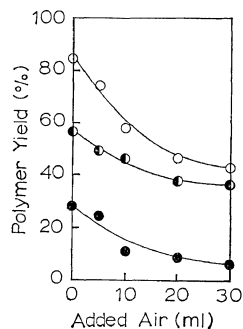


Figure 8. Effect of added air on polymerization by $(\text{EtClAl})_2\text{NPh}$: IBVE, 0.0153 mol; $(\text{EtClAl})_2\text{NPh}$, 0.5 mol% to monomer; toluene, 25 ml; temp, -78°C ; time, 24 hr; ○, total polymer yield; ●, crystalline polymer; ◐, amorphous polymer.

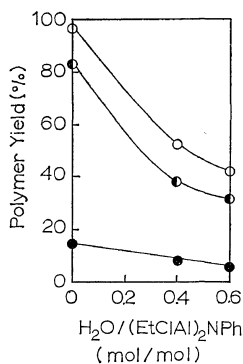
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Figure 9. Effect of added water on polymerization by $(\text{EtClAl})_2\text{NPh}$: IBVE, 0.0153 mol; $(\text{EtClAl})_2\text{NPh}$, 0.5 mol% to monomer; toluene, 25 ml; temp, -78°C ; time, 24 hr; ○, total polymer yield; ●, crystalline polymer; ●, amorphous polymer.

A minute amount of a substance contaminating the purified sample of IBVE was detected by GLPC analysis (tricresyl phosphate column, 70°C). This substance could not be removed by treating the monomer with solid potassium hydroxide for 24 hr, sample (A), but the impurity could be removed by prolonged treatment (three months' contact, Sample (B)). The purity determined by GLPC was 98.9–99.1% for sample (A) and 99.8–99.9% for (B). The amount of this impurity estimated by peak area ratio in GLPC chart, was *ca.* 0.01% of the IBVE, but the impurity could not be identified.

Behavior of these two monomer samples in the polymerization reaction was compared to each other with the use of a catalyst recrystallized three times and under conditions of a

30-min degassing (see Table V). The monomer (A) gave the polymer having a slightly higher (5–10%) stereospecificity than the monomer (B), but the general pattern was similar in both cases.

*Preparation and Catalytic Behavior of $(\text{EtClAl})_2\text{NAr}$ (*Ar*, aryl group)*

Several nuclear substituted derivatives of $(\text{EtClAl})_2\text{NPh}$ were prepared in order to gain an understanding of the relationship between structure and catalytic behavior.

p-Toluidine, *p*-chloroaniline, *p*-bromoaniline and α -naphthylamine gave crystalline compounds, $(\text{EtClAl})_2\text{NAr}$, on their reaction with diethyl aluminum chloride in a molar ratio (2 : 1), while *m*- and *o*-toluidine and β -naphthylamine gave only oily products, perhaps because of steric effects. These crystalline compounds are dimeric in benzene solution as estimated by the molecular weights determined cryoscopically. The chemical shifts of ethyl groups linked to aluminum atoms (NMR spectra taken in dioxane solution) and the $\text{p}K_b$ values of the corresponding aromatic amines are summarized in Table VI. Coupling constants between methyl and methylene protons are 8 Hz for all these compounds, while no correlation was found between the difference in chemical shifts of ethyl groups and $\text{p}K_b$ values of the corresponding aromatic amines.

Except α - and β -naphthyl derivatives, these compounds act as catalysts for the stereospecific polymerization of IBVE. The results of the polymerization with *p*-chloro, *p*-bromo and *p*-methyl derivatives of $(\text{EtClAl})_2\text{NPh}$ were generally similar to these with the unsubstituted

Table V. The polymerization of two different samples of IBVE (A and B) with $(\text{EtClAl})_2\text{NPh}$ as a catalyst^a

Catalyst concentration, mol% to monomer	Monomer A			Monomer B		
	Total yield, %	Crystalline fraction, %	Amorphous fraction, %	Total yield, %	Crystalline fraction, %	Amorphous fraction, %
0.1	0	—	—	0	—	—
0.2	38	14	24	23	6	17
0.4	53	20	33	47	17	30
0.6	64	25	39	61	21	40
0.8	77	27	50	73	19	54
1.0	87	23	64			

^a Polymerization conditions: IBVE, 1.53×10^{-2} mol; toluene, 25 ml; temperature, -78°C ; time, 24 hr. The values in the table show the relative yield of polymer compared to monomer used.

Table VI. Correlations between pK_b values and chemical shifts of ethyl groups of $(EtClAl)_2NAr$ compounds

Ar	pK_b		ppm ^a	
	ArNH ₂ (20°C)	ArNMe ₂ (25°C)	=Al-CH ₂ -CH ₃	=Al-CH ₂ -CH ₃
<i>p</i> -CH ₃ C ₆ H ₄	8.90	8.39	1.10	0.01
C ₆ H ₅	9.40	8.85	1.13	0.03
<i>p</i> -ClC ₆ H ₄	10.02	—	1.12	0.05
<i>p</i> -BrC ₆ H ₄	10.26	9.72	1.15	0.03
α -Naphthyl	10.3	—	1.14	0.10

^a Dioxane was used as an internal standard (3.70 ppm).

Table VII. Polymerization of IBVE with *p*-substituted derivatives of $(EtClAl)_2NPh^a$

Catalyst concentration, mol% to monomer	Yield of polymer, %								
	<i>p</i> -Chloro derivative			<i>p</i> -Bromo derivative			<i>p</i> -Methyl derivative		
	Total	Cryst	Amorph	Total	Cryst	Amorph	Total	Cryst	Amorph
0.1	0	—	—	0	—	—	0	—	—
0.2	69	29	40	88	59	29	87	43	44
0.4	82	38	44	98	53	45	88	46	42
0.6	98	33	65	95	50	45	92	44	48

^a Polymerization conditions: IBVE, 1.53×10^{-2} mol; toluene, 25 ml; temperature, -78°C ; time, 24 hr.

compounds (see Table VII). Thus the electron-withdrawing or -attracting nature of the *p*-substituent has no significant effect on the polymerization in agreement with the NMR results.

Polymerization of IBVE with $(EtClAl)_2NPh$ Catalyst via Three Different Procedures

The effect of impurities probably coexisting in the polymerization system was examined in three different procedures. In procedure I, the toluene solution containing a specified amount of the catalyst was added to the solvent (toluene) which was previously degassed at -78°C for 30 min *in vacuo*, the solution was heated at 110°C for 15 min, and then the monomer was added dropwise to this solution at -78°C with stirring. Procedure II is identical with procedure I except that the toluene solution of the catalyst was stirred for 30 min at room temperature instead of heating at 110°C . In procedure III, the catalyst was added at -78°C to toluene which was previously degassed at -78°C , and the monomer was added to this solution at -78°C .

The activity and stereoregulating ability of

the catalyst were largest in procedure III and smallest in I (see Table VIII). This phenomenon may be explained by assuming that in procedure I, a minute amount of oxygen is consumed by the reaction with the catalyst, but not in procedure III. Also the polymerization results obtained on varying the degassing time in the polymerization by the procedures II and III suggest that removal of oxygen from the polymerization system decreased the yield of polymer, especially that of the crystalline polymer (see Table IX).

Conclusive Remarks

All experimental results mentioned above show that oxygen is an indispensable component for obtaining the crystalline polymer and that water acts as a cocatalyst only for the non-stereospecific polymerization to give amorphous polymer. This phenomenon is quite similar to that observed with $AlEt_2Cl$ catalyst.⁸ Thus, the cocatalyst action of oxygen may be concluded to be a general phenomenon for the stereospecific polymerization of IBVE with organoaluminum catalyst systems.

It is well known that oxygen with organo-

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Table VIII. Polymerization of IBVE with (EtClAl)₂NPh catalyst *via* three different procedures^a

Catalyst concentration, mol% to monomer	Yield of polymer, %								
	Procedure I ^b			Procedure II ^b			Procedure III ^b		
	Total	Cryst	Amorph	Total	Cryst	Amorph	Total	Cryst	Amorph
0.1	0	—	—	20	0	20	90	72	18
0.2	trace	—	—	34	4	30	90	61	29
0.3	18	0	18	51	11	40	85	45	41
0.5	22	0	22	60	15	45	88	20	69
1.0	40	2	38	81	10	71	92	11	81

^a Polymerization conditions: IBVE, 1.53×10^{-2} mol; toluene, 25 ml; temp, -78°C ; time, 24 hr.

^b The procedures I—III are explained in the text.

Table IX. Effect of degassing time on the polymerization of IBVE with (EtClAl)₂NPh^a

Degassing time, min	Procedure II			Procedure III		
	Total yield, %	Crystalline fraction, %	Amorphous fraction, %	Total yield, %	Crystalline fraction, %	Amorphous fraction, %
0	91	63	28	47	11	36
5	97	50	47	46	8	38
10	95	41	54	42	13	29
15	97	44	53	41	10	31
20	93	33	60	47	8	39
30	88	28	60	42	10	32

^a Polymerization conditions: IBVE, 1.53×10^{-2} mol; toluene, 25 ml; catalyst, 0.3 mol% to monomer; temp, -78°C , time, 24 hr. The values in table show the yield of polymer to monomer used.

aluminum compounds react to form alkyl-aluminum alcoholates through peroxides as intermediates.⁷ Nevertheless, ethylchloroaluminum ethylate, Et(EtO)AlCl, and the reaction product of (EtClAl)₂NPh with ethanol in a molar ratio (1:1 and 1:2) at 80°C for 3 hr had no catalytic activity for the polymerization of IBVE, and also IBVE did not polymerize with radical initiators such as benzoyl peroxide and acetyl peroxide, while no information was obtained about the polymerization of IBVE with organometallic peroxides. In the authors' experiments, high-vacuum technique was used in the polymerization, but extremely dried system could not be obtained. From these considerations, the real active species for the polymerization of IBVE is assumed to be the reaction products of organoaluminum peroxide with a minute amount of water in the system.

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