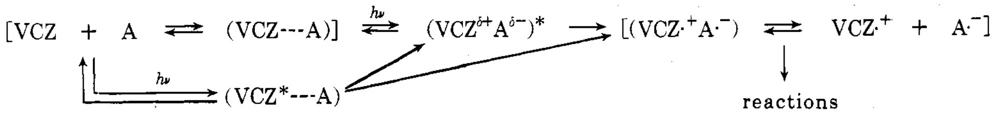
Scheme I
Primary Process in the Photosensitized Reaction of *N*-Vinylcarbazole in the Presence of the Organic Electron Acceptor (A)



charge-transfer complex and mainly through the charge-transfer interaction in the excited state of VCZ. Solvent effects on the dual nature of VCZ cation radical observed in the systems using rather high concentrations of the electron-accepting monomer are in good agreement with those observed in the systems with catalytic amounts of various organic electron acceptors as shown in Scheme I and Table VIII where the generalized reaction courses are summarized.

Summary

The photosensitized reaction of VCZ in the presence of the organic electron acceptor has been found to take entirely different reaction courses depending upon the reaction conditions. They are classified into four major groups: (1) cationic homopolymerization of VCZ, (2) cyclodimerization of VCZ, (3) radical homopolymerization of VCZ, and (4) radical copolymerization between VCZ and an electron-accepting monomer. Cationic homopolymerization of VCZ occurred in less basic solvents such as benzene, dichloromethane or nitrobenzene, while cyclodimerization of VCZ generally took place exclusively in such polar, basic solvents as acetone, acetonitrile or methanol. On the other hand, radical homopolymerization of VCZ proceeded in dimethylformamide or in Me_2SO. When the electron acceptor is a monomer capable of undergoing radical polymerization or copolymerization and is present in relatively large amounts instead of in catalytic amounts, radical copolymerization between VCZ and the electron-accepting monomer took place in addition to cationic homopolymerization and cyclodimerization of VCZ, the reaction course also being dependent upon the solvent and the concentration of the electron-accepting monomer.

The multireaction courses are systematically explained in terms of the intermediacy of VCZ cation radical formed by the photochemical electron transfer from VCZ to the electron acceptor. The VCZ cation radical exhibits the dual cationic and free radical activity. The cationic reactivity of VCZ cation radical is shown as cationic homopolymerization of VCZ, while its radical reactivity leads to either cyclodimerization of VCZ or radical homopolymerization of VCZ. Radical homopolymerization of VCZ is naturally replaced by radical copolymerization when the electron acceptor is a monomer which can copolymerize with VCZ. The choice of the multireaction courses may be determined by the following factors: (a) polarity of solvent, (b) basicity, that is, cation-solvating ability of solvent, (c) stability of the anion radical of the electron acceptor formed as a counterpart for VCZ cation radical, (d) radical trapping ability of the electron acceptor or of the solvent, and (e) polymerizability of the electron acceptor. It must be stressed that among these factors, basicity, that is, cation-solvating ability, of the solvent is almost decisively important in determining the reaction course in the photosensitized reaction of VCZ in the presence of the organic electron acceptor.

Stereospecific Polymerization of Aliphatic Monoaldehydes

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ABSTRACT: Stereospecific polymerization of acetaldehyde to give the isotactic polymer was investigated by using a series of effective catalysts: $R_2AlOCR'NPh$ and its acetaldehyde complexes $R_2AlOCR'NPh{\cdot}MeCHO$. The most characteristic feature of this type of catalyst is the formation of the monomer-catalyst complex in a quantitative yield by the reaction with acetaldehyde above the ceiling temperature (−40°) of the polymerization and that of the isotactic polyacetaldehyde below that temperature in a high yield. The catalyst behavior of this type of catalyst and its derivatives under various conditions are discussed in relation to their structures. Water and peracetic acid proved to be indispensable cocatalysts. A novel molecular mechanism of the stereospecific polymerization of acetaldehyde is proposed based on these experimental results.

Rather extensive work has been reported on the stereospecific polymerization of acetaldehyde by several research groups.[1-5] The importance of the coordination of the monomer to the catalyst in the initiation step of the polymerization was shown using organoaluminum catalysts and a coordinate anionic mechanism was proposed for in-

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(1) J. Furukawa, T. Saegusa, and H. Fujii, *Makromol. Chem.*, **37**, 149 (1960).

(2) G. Natta, G. Mazzanti, P. Corradini, and I. W. Bassi, *Makromol. Chem.*, **37**, 156 (1960).

(3) O. Vogl, *J. Polym. Sci., Part A*, **46**, 261 (1960).

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terpreting stereoregulation in the propagation step. The experimental evidence referred to in these papers, however, is not conclusive because the reaction of common organoaluminum catalysts with acetaldehyde monomer is rather complex due to the cooccurrence of side reactions leading to esters or ketones derived from Thishchenko[6,7] or Meerwein-Ponndorf[8-10] reactions. One approach to the elucidation of the molecular mechanism underlying these stereospecific polymerization reactions is to find a catalyst system which causes the stereospecific polymerization to proceed quantitatively without being accompanied by any side reaction. A novel type of crystalline organoaluminum, $[R_2AlOCR'NPh]_2$,[11,12] was found to be an excellent stereospecific catalyst ideally suitable for such an approach. This type of catalyst is unique among organoaluminum catalysts known until now with respect to its behavior toward aldehydes: it gives the crystalline monomer-catalyst complex without accompanying side reactions at temperatures above the ceiling temperature of polymerization (−40°). Therefore, the structure and chemical reaction of this type of catalyst and its derivatives which relate intimately to the understanding of the polymerization process have been studied extensively. In this paper, the behavior of this type of catalyst under various polymerization conditions and the indispensable role of the cocatalyst are reported. A novel molecular mechanism of the stereospecific polymerization is proposed, based on three-dimensional structures, stoichiometric reactions and the catalytic behavior of these organoaluminums and their derivatives, as well as on the role played by cocatalysts.

Experimental Section

Materials. Acetaldehyde was prepared by decomposing paraldehyde at 35° in an argon atmosphere using *p*-toluenesulfonic acid (1 mol % of paraldehyde) as a catalyst. Paraldehyde was dried over calcium hydride and distilled before use. Acetaldehyde thus obtained was dried over calcium hydride at 0° for 3 days and distilled twice under an argon atmosphere (acetaldehyde Ca). It was dried over synthetic zeolite (F9, Wako Chemical Co.) for 2 days to obtain a purer sample at 0° and then distilled (Acetaldehyde Ze). Synthetic zeolite was activated by heating at 150° (1 mm) for 12 hr and was mixed with acetaldehyde after cooling to −78°. Commercial deuterated acetaldehyde (Merck Co.) was purified in the same manner as described above. Commercial samples (Nakarai Chemical Co.) of propionaldehyde, butyraldehyde, benzaldehyde, and tolualdehyde were purified by distillation in an argon atmosphere after being dried over calcium hydride. Toluene and benzene were dried over potassium-sodium alloy and purified by distillation in an argon atmosphere. Trimethylamine oxide was synthesized according to the method described by Meisenheimer.[13]

Catalyst. All the organoaluminum compounds were prepared according to the methods described in previous papers.[11,12]

Procedure for Polymerization. Procedure A was applied to the calcium hydride dried monomer. The monomer was charged using a hypodermic syringe which had been previously dried in a glass container by heating *in vacuo* (10^{-2} mm). A Schlenk tube (inner volume, 15 ml) used for polymerization was filled with dry argon after being thoroughly dried by flaming *in vacuo*. After the purified catalyst was dissolved in the solvent (4 ml) in this Schlenk tube, the monomer (4 ml) was charged with vigorous stirring at a specified temperature, and then the tube was sealed off. Polymerization reaction was carried out at −78° for a specified time, and was terminated by adding 1 ml of methanol at −78°.

Procedure B was applied to the zeolite-dried monomer. A Schlenk tube (A), which contains the monomer charged by distillation, was connected through a breakable seal with a Schlenk tube (B) containing toluene and a specified amount of water and equipped with two breakable seals. The monomer was transferred by distillation from Schlenk tube (A) into Schlenk tube (B) through a breakable seal. The toluene solution of the catalyst in the Schlenk tube (C) was poured into the tube (B) through a breakable seal, and then the contents of the tube (B) was allowed to stand at −78° to allow the polymerization to proceed after sealing off the tube.

Fractionation of the Polymer. The terminated polymerization mixture (8 ml) was mixed with 100 ml of *n*-hexane, and the precipitate was dried under reduced pressure at 30° for 10 hr. The total yield was calculated by the weight of the crude polymer. The crude polymer thus obtained was extracted with chloroform at room temperature (100 ml/1 g of the polymer). The index of the stereospecificity (IS) was defined as the ratio of the chloroform-insoluble fraction to the *n*-hexane-insoluble one. The chloroform-soluble fraction was an amorphous polymer as evidenced by its ir spectrum.

Measurement. Nmr spectra of the catalyst system and of the chloroform-soluble polymer were taken with Varian A-60 Model spectrometer. Polarized ir spectra of the polymer were recorded with Japan Spectroscopic Co. Model GC-202 spectrometer. A thin-strip cut from the polymer swelled in chloroform was stretched by rolling. The oriented film thus obtained, which was used for X-ray measurements, was further rolled by binding it between two silver chloride plates to obtain an extremely thin film, which was used for recording polarized ir spectrum. X-Ray measurement of the polymer was undertaken with a Rigaku Denki D3F Model for the powdered sample of the polymer and the values 2 sin θ calculated from the fiber diagrams of the oriented samples were found to be identical with those reported by Natta *et al.*[14]

Results and Discussion

Structure and Chemical Properties of the Catalyst. The trialkylaluminum-acid amide (1:1) catalyst system proved to be an excellent catalyst for the stereospecific polymerization of acetaldehyde. A typical example of the effects of the molar ratios of secondary acid amides to alkylaluminums on the polymerization results is illustrated in Figure 1. A maximum yield of the isotactic polymer and a minimum yield of the atactic were observed at a molar ratio of about 1:1. This result indicates that an equimolar reaction product between AlR_3 and R′CONHPh is a catalyst species for the stereospecific polymerization of acetaldehyde. In practice, a series of crystalline organoaluminums $[R_2AlOCR'NPh]_2$, equimolar reaction products between AlR_3 and R′CONHPh, proved to be excellent catalysts for the stereospecific polymerization of acetaldehyde to give isotactic polymers in nearly quantitative yield with good reproducibility (Table I). The addition of 0.1 mol of AlR_3 or 0.2 mol of an acid amide per mol of $[R_2AlOCR'NPh]_2$ remarkably decreased the catalytic activity of the latter and the yield of isotactic polymer, as expected from the result illustrated in Figure 1. This fact suggests that the isolation of the catalyst is a prerequisite for obtaining good reproducibility of the polymerization and that an *in situ* catalyst system is inadequate for this purpose.

Various kinds of reaction of crystalline organoaluminums $[R_2AlOCR'NPh]_2$ and their derivatives with acetaldehyde could be studied at temperatures higher than the ceiling temperature[4] of the acetaldehyde polymerization (−40°), because no side reaction such as ester or ketone formation reaction occurred between them at these tem-

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(8) H. Meerwein, B. V. Bock, B. Kirschnick, W. Lenz, and A. Mizze, *J. Prakt. Chem.*, **147**, 211 (1937).

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(12) H. Yasuda, T. Araki, and H. Tani, *J. Organometal. Chem.*, in press.

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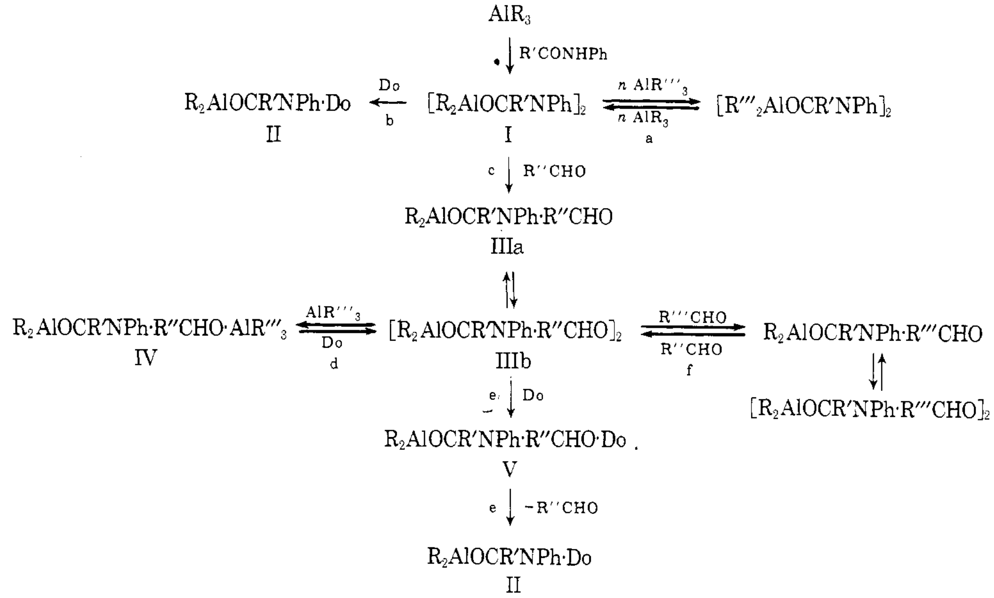
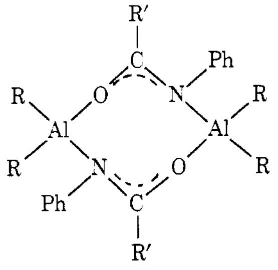
Scheme I^a



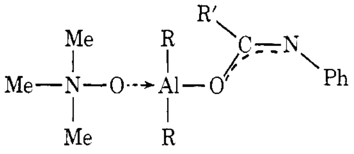
^{a}R = Me, Et or *i*-Bu; R' = Me or Ph;
R'' = Me, Et or *n*-Pr; R''' = Me or Et;
Do = Me_3NO or HMPA

peratures, in sharp contrast to the usual organoaluminums such as $AlMe_3$ and R_2AlOR. Only stereospecific polymerization occurred below the ceiling temperature.

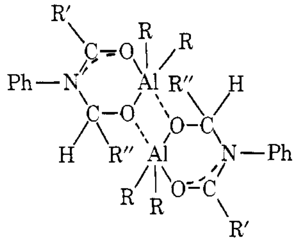
A series of reactions of the organoaluminums $[R_2AlOCR'NPh]_2$, which are important in understanding the polymerization mechanism, are summarized in Scheme I. Four types of organoaluminums, I,[15] II,[16] IIIb,[17,18] and IV,[19] were isolated in crystalline states and three-dimensional structures of four representative organoaluminums (I, R = Me, R' = Rh; II, R = Me, R' = Ph, Do = $ONMe_3$; IIIb, R = R'' = Me, R' = Ph; IV, R'' = Me) were determined by X-ray analyses.



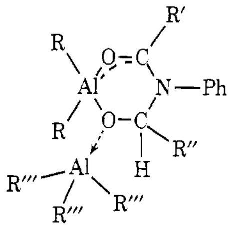
I



II



IIIb



IV

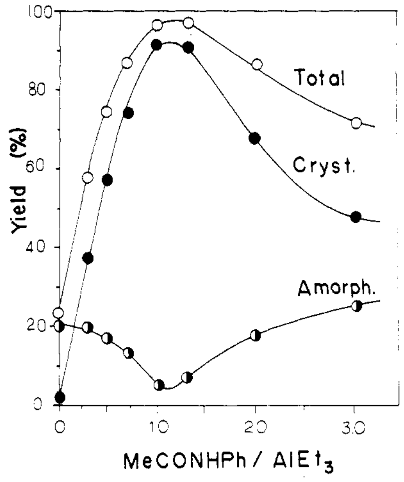


Figure 1. Effect of the molar ratio of $AlEt_3$ to acetanilide on the polymerization of acetaldehyde. Cryst, chloroform-insoluble crystalline polymer. Amorph, chloroform-soluble amorphous polymer. Polymerization, −78° for 50 hr in toluene. Catalyst concentration, 1 mol % of monomer.

Reaction a is a reversible alkyl-exchange reaction in which alkyl groups linked to an aluminum atom of $R_2AlOCR'NPh$ are exchanged for a trialkylaluminum AlR'''_3. No stable complex formation was observed in this reaction. Reaction b is the formation of a monomeric electron donor complex of the organoaluminum II which has an open-chain structure formed by breaking Al-N bonds of the eight-membered ring of I. This reaction indicates that Al-N bonds in I are broken in preference to Al-O bonds by the attack of a strong donor to give the monomeric donor complex II. Reaction c is a type of donor complexation reaction similar to reaction b; in this reaction, a monomeric aldehyde complex (IIIa) having an unusual six-membered structure is formed. The aldehyde complex-

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Table I
Polymerization of Acetaldehyde by $R_2AlOCR'NPh$ Catalyst[a]

Catalyst			
R	R′	Yield (%)	IS[b] (%)
Me	Me	99	98
Me	Ph	97	99
Et	Me	99	99
Et	Ph	99	100
i-Bu	Me	100	100

[a]Acetaldehyde (Ca) was mixed with a catalyst at 0°, aged for 1 min, and polymerized at −78° for 40 hr. Catalyst concentration, 0.5 mol % of monomer. [b]Index of stereospecificity, see Experimental Section.

Table II
Polymerization by Trimethylamine Oxide Complexes[a]

Catalyst	Yield (%)	IS (%)
$Me_2AlOCMeNPh{\cdot}ONMe_3$	3	80
$Me_2AlOPhNPh{\cdot}ONMe_3$	2	85
$Me_3Al{\cdot}ONMe_3$	5	75

[a]Acetaldehyde (Ca) was charged at 0° and polymerized at −78° for 70 hr. Catalyst concentration, 1 mol % of monomer.

es can be visualized as monomer–catalyst complexes. This type of complex exists as an equilibrium mixture of the monomer and the dimer in benzene solution. Reaction d is the reaction to form the trialkylaluminum complex of the monomeric aldehyde complex. The structures of IIIb and IV clearly show that an aluminum atom is the electron-accepting site and that an oxygen atom of the aldehyde moiety is the electron-donating site in the monomeric aldehyde complex IIIa. Reaction e is a ligand-exchange reaction to form the electron donor complex II. This reaction occurs only when the donor property of an electron donor is stronger than that of an aldehyde. Reaction f is the aldehyde-exchange reaction in which the complexed aldehyde is readily replaced by another kind of aldehyde. This reaction is a type of ligand-exchange reaction and should occur actively in the solution of IIIb in the presence of a large amount of aldehyde, that is in the polymerization system.

Polymerization of Aldehydes by $[R_2AlOCR'NPh]_2$ and Their Derivatives. It is important to point out that the isolated aldehyde complex IIIb, *i.e.*, the monomer–catalyst complex, has an excellent catalytic activity for the stereospecific polymerization of acetaldehyde, and can be obtained in a quantitative yield by contacting I with an aliphatic or aromatic aldehyde in solution for only 30 sec at 0°. These results indicate that the complexation of an aldehyde with the catalyst I is an essential process in the first step of the stereospecific polymerization of the aldehyde in agreement with the generally known coordination of a carbonyl compound to a organoaluminum.[7,20-22]

The polymerization was inhibited by the presence of a Lewis base whose basicity is stronger than that of an aldehyde monomer, although isotactic polymers were obtained in high yields by the catalyst I in relatively weak donor solvents such as triethylamine, tetrahydrofuran, diethyl ether, and ethyl acetate. In fact, the complex of trimethylamine oxide (Me_3NO) with $AlMe_3$ or $Me_2AlOCPhNPh$ was completely inactive, in sharp contrast to the noncomplexed organoaluminums (Table II). This phenomenon strongly supports the above deduction that the coordination of the monomer to the catalyst is an essential factor for the stereospecific polymerization to occur.

In order to know whether any correlation exists between the polymerization and the aldehyde-exchange reaction, the polymerizations of three kinds of aliphatic monoaldehyde catalyzed by four kinds of aliphatic monoaldehyde complexes derived from these monoaldehydes were studied. The relative stability of the aldehyde complexes III in aldehyde-exchange reactions follows the order:[12] $CH_3CHO > C_2H_5CHO > C_3H_7CHO \gg C_6H_5CHO$. Results in polymerization experiments (Table III) can be explained satisfactorily in terms of this relative stability. The polymer yield in the polymerization of an aldehyde decreased as the alkyl group of the aldehyde moiety in the complex III became less bulky. This general tendency was exaggerated remarkably in experiments in which a monomer was charged at a low temperature (−78°). When the benzaldehyde complex was used as a catalyst, all aliphatic aldehydes tested were polymerized in high yields to give isotactic polymers. Thus, the yield of the isotactic polymer is closely related to the stability of the aldehyde complex, and the polymer is obtained in a high yield only under such conditions that the aldehyde-exchange reaction is likely to occur readily. Polarities of the carbonyl groups of acetaldehyde, propionaldehyde, and butyraldehyde are estimated to be nearly equal, since the frequencies of the carbonyl absorptions observed in ir spectra recorded for benzene solution are equal (1725 cm^{-1}) for the three aldehydes. As a result, the difference observed between polymer yields mentioned above is assumed to be due to the difference in the polymerization rate, which may be attributable mainly to the difference in the bulkiness of the alkyl group of the aldehyde.

The initial rate of polymerization was determined by measuring the amount of polymer obtained at various times and by using a modified dilatometer, in order to test the validity of this assumption. An aldehyde monomer was mixed with a toluene solution of $[Me_2AlOCMeNPh]_2$ and aged at 0° for 1 min to ensure the formation of the aldehyde complex, and then the mixture was cooled rapidly to −78° to allow the polymerization to proceed. The relative rate of polymerization (Figure 2), $CH_3CHO > C_2H_5CHO > n\text{-}C_3H_7CHO > i\text{-}C_3H_7CHO$, paralleled the relative stability of the aldehyde complex. Therefore, it is possible to conclude that both the stability of the aldehyde complex and the rate of polymerization are related closely to the bulkiness of the alkyl group of the aldehyde.

The monomer charging temperature, *i.e.*, the temperature at which a monomer and a catalyst is mixed together, has been reported by Ishida for an $AlEt_3$–H_2O catalyst systems[4] and by Furukawa *et al.*[23] for an $AlEt_3$–alcohol system to have a significant effect on the polymerization of acetaldehyde. Typical experimental results on the effect of the monomer charging temperature on the polymerization of acetaldehyde by four polymerization catalysts (Table IV) can be explained satisfactorily by assuming that a monomeric monometallic organoaluminum is an active catalyst and that the first step in the polymerization reaction is the formation of the aldehyde complex of the catalyst. This assumption is supported by the following experimental results.

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Table III
Polymerization of Aliphatic Aldehydes by a Series of Aldehyde Complexes, $Me_2AlOCMeNPh{\cdot}RCHO^a$

		Monomer Charging Temperature^b			
		0°		−78°	
RCHO	Monomer	Yield (%)	IS (%)	Yield (%)	IS (%)
CH_3CHO	CH_3CHO	95	98	32	95
	C_2H_5CHO	36	91	8	90
	n-C_3H_7CHO	10	92	1	91
	C_6H_5CHO	0	0	0	0
C_2H_5CHO	CH_3CHO	97	93	72	93
	C_2H_5CHO	79	86	10	90
	n-C_3H_7CHO	65	98	2	85
n-C_3H_7CHO	CH_3CHO	93	97	88	92
	C_2H_5CHO	60	98	12	78
	n-C_3H_7CHO	70	97	1	85
C_6H_5CHO	CH_3CHO	96	96	90	95

[a] Polymerization condition, −78°, 48 hr in toluene. Catalyst concentration, 1 mol % of monomer. [b] Monomer was added at this temperature to catalyst solution.

Table IV
Effect of the Monomer Charging Temperature on the Polymerization Results^a

	−78° ^{b}		0° ^{b}	
Catalyst	Yield (%)	IS (%)	Yield (%)	IS (%)
$Me_2AlOCPhNPh{\cdot}MeCHO$	18	96	95	99
$Me_2AlOCMeNPh{\cdot}MeCHO$	32	95	95	98
$Et_2AlOCPhNPh{\cdot}MeCHO$	60	92	99	100
$Et_2AlOCMeNPh{\cdot}MeCHO$	78	93	100	99
i-$Bu_2AlOCMeNPh{\cdot}MeCHO$	96	95	100	99
$Me_2AlOCPhNPh{\cdot}MeCHO{\cdot}HMPA$	95	95	100	95
$Me_2AlOCMeNPh{\cdot}MeCHO{\cdot}HMPA$	99	98	99	99
$Me_2AlOCPhNPh{\cdot}HMPA$	93	95	98	98

[a] Catalyst concentration, 1 mol % of monomer. Polymerization, −78°, 40 hr. [b] Monomer was added at this temperature to catalyst solution.

First, the relative ease of the dissociation of dimeric acetaldehyde complexes to monomeric ones, $R_2AlOCR'NPh{\cdot}MeCHO$ (i-Bu, Et, Me for R and Me, Ph for R′), agrees well with the activity of the catalyst, especially at low temperatures.

Second, the monomeric donor complexes, $Me_2AlOCMeNPh{\cdot}OP(NMe_2)_3$ and $Me_2AlOCMeNPh{\cdot}MeCHO{\cdot}OP(NMe_2)_3$, gave isotactic polyacetaldehydes in nearly quantitative yields, practically independent on the monomer charging temperature. Since the coordinating power of hexamethylphosphoramide (HMPA) is the same or only slightly stronger than that of acetaldehyde, the complexed HMPA should be replaced by a large excess amount of acetaldehyde to give the monomeric acetaldehyde complex.

Third, the difference in the catalytic behavior was observed between $[Me_2AlOCPhNPh]_2$ and its acetaldehyde complex $Me_2AlOCPhNPh{\cdot}MeCHO$ (Figure 3). Both compounds have similar activities in the polymerization of acetaldehyde when the monomer was charged at 0°, the mixture was aged for 1 min at 0° and then rapidly cooled to −78° to allow the polymerization to proceed. In contrast to this, when the monomer was charged at −78°, the yield of the polymer was higher in the polymerization by $[Me_2AlOCPhNPh]_2$ than that by $Me_2AlOCPhNPh{\cdot}MeCHO$. This result suggests that the monomeric acetaldehyde complex formed *in situ* by the reaction of acetaldehyde with $[Me_2AlOCPhNPh]_2$ initiates the polymerization prior to being stabilized as its dimer and that the preformed dimeric complex is hardly dissociated into the monomeric form at a low temperature even in the presence of a large amount of acetaldehyde.

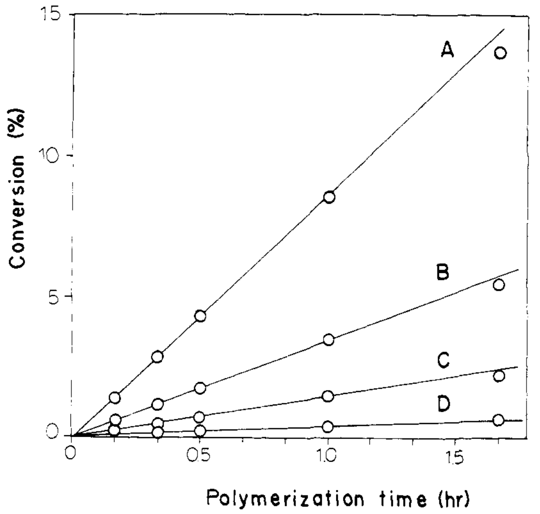

Figure 2. Initial rate of polymerization of some aliphatic aldehydes. Catalyst, 0.1 mol % of monomer, $Me_2AlOCMeNPh$. (A) Acetaldehyde, (B) propionaldehyde, (C) n-butyraldehyde, (D) isobutyraldehyde.

In contrast to $Me_2AlOCR'NPh{\cdot}R''CHO$, the complex $Me_2AlOCR'NPh{\cdot}MeCHO{\cdot}AlMe_3$ which was obtained by reacting $AlMe_3$ with IIIb polymerized acetaldehyde to give the chloroform-soluble atactic polymer (Table V). The complex $Me_3Al{\cdot}R'CONPh_2$ obtained from $AlMe_3$ and a

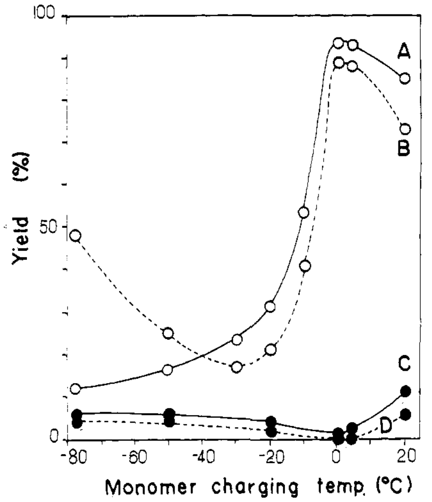

Figure 3. Effect of monomer charging temperature on the polymerization results. (A) Crystalline polymer and (C) amorphous one were obtained by $Me_2AlOCPhNPh{\cdot}MeCHO$ complex. (B) Crystalline and (D) amorphous polymer were obtained by $Me_2AlOCPhNPh$. Polymerization, −78° for 50 hr. Catalyst concentration, 1 mol % of monomer

Table V
Polymerization by a Series of $AlMe_3$ Complexes

Catalyst[a]	Yield (%)	IS (%)
$Me_2AlOCPhNPh{\cdot}MeCHO{\cdot}AlMe_3$	20	31
$Me_2AlOCMeNPh{\cdot}MeCHO{\cdot}AlMe_3$	30	22
$Me_3Al{\cdot}Ph_2NCOPh$	28	25
$Me_3Al{\cdot}Ph_2NCOMe$	19	28
Me_3Al	25	35

[a] Catalyst concentration, 1 mol % of monomer. Acetaldehyde (Ca) was charged at 0° and polymerized at −78° for 40 hr.

tertiary acid amide also gave the atactic polyacetaldehyde. The behavior of the polymerization catalyzed by these two types of $AlMe_3$ complexes is quite similar to that by $AlMe_3$; the rates of polymerization are very rapid although the polymer yields are about 30% (see ref 4) and the microstructures of polymers determined by nmr spectra are hetero-rich ones in good agreement with those reported by Vogl[24] and Goodman.[25] These results can be interpreted in terms of the donor-exchange reaction which occurred between acetaldehyde and these $AlMe_3$ complexes. $AlMe_3$ liberated in this reaction polymerizes acetaldehyde with the rate far higher than the acetaldehyde complex IIIb liberated simultaneously. This interpretation is supported by the fact that $AlMe_3$ moiety of the complex IV and of $AlMe_3{\cdot}R'CONPh_2$ is expelled readily by a relatively weak Lewis base such as tetrahydrofuran or triethylamine.

Indispensable Role of a Cocatalyst. In order to prepare the oligomer and to accumulate the information on the propagation reaction, the toluene-d_8 solutions of the mixtures of acetaldehyde monomer and some catalysts (dimeric $[Me_2AlOCPhNPh]_2$, its aldehyde complex and monomeric complex $Me_2AlOCPhNPh{\cdot}HMPA$) in a molar ratio of 1:5 were allowed to stand at the polymerization temperature of −78°. The polymer, not the oligomer, was obtained in these experiments.

Temperature dependences of the nmr and ir spectra of these mixtures were measured by lowering the temperature from 20 to −80°; no change in the structures of these catalysts were observed in nmr spectra,[12] although isotactic polymers which could not contribute to nmr spectra for its low solubility was produced in about 80% yields. Similarly, no change was observed in ir spectra except for the appearance of the absorptions due to the polymer.

These results suggest that only a minute fraction of the added catalyst effectively acts as an active catalyst. Two hypotheses can be offered for this result: first, the propagation rate is far faster than the initiation rate; and second, a real catalyst species is formed by the reaction between the catalyst and a trace amount of some contaminated cocatalyst which cannot be detected by ir, nmr, or glpc analyses. To test the validity of the former hypothesis, the polymerization was allowed to proceed at temperatures of −45 to −50°, which are only slightly lower than the ceiling temperature of polymerization (−40°). Only isotactic polymers, not oligomers, were obtained also in this case. These experimental results are difficult to interpret in terms of the coordinate anionic mechanism in which the initiation and propagation reaction proceed by the insertion of the monomer into the Al–O bond, and suggest that the rate-determining step in the polymerization reaction is the initiation reaction which might be started by the action of some cocatalyst. The cooperative catalytic action of a trace amount of water and peracetic acid in the so-called "crystallization polymerization" of acetaldehyde reported by Letort[26] supports the assumption. Therefore, the purification of acetaldehyde was studied extensively.

In the experiments mentioned above, acetaldehyde was used as a monomer after treating it with calcium hydride. Hereafter, this monomer is referred to as acetaldehyde (Ca). This monomer did polymerize to give an amorphous polymer in 30% yield in the "crystallization polymerization" condition at −135° in the absence of any added catalyst, although the presence of any impurity in this monomer sample could not be detected by glpc and ir method.

The acetaldehyde samples which were obtained by treating acetaldehyde (Ca) with various kinds of drying agents in order to remove off any contaminant were allowed to polymerize after charging them directly into the polymerization vessel by vacuum distillation. A quite important result was obtained from this experiment; the polymerization reaction by $[R_2AlOCR'NPh]_2$ catalyst was almost completely suppressed when the monomer was treated with magnesia or synthetic zeolite F-9 (Table VI). Hereafter, the acetaldehyde sample treated with zeolite is referred to as acetaldehyde (Ze). This monomer sample did not polymerize in the crystallization polymerization condition even in the presence of an added catalyst. The purity of this monomer sample was checked by differential thermal analysis in addition to glpc analysis; only one peak was observed at the freezing point of acetaldehyde even though crystallization and melting were repeated. This result shows that the monomer sample is satisfactorily pure. Thus, it is reasonable to conclude that some cocatalytically active substance is contained in acetaldehyde (Ca), but not in acetaldehyde (Ze).

The most plausible candidate for the cocatalytically active substance is water and/or peracetic acid. Therefore, the cocatalytic activities of these compounds were examined by adding these compounds separately to acetaldehyde (Ze).

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Table VI
Effect of the Nature of Drying Agent on the Polymerization of Acetaldehyde by $Me_2AlOCPhNPh$ Catalyst[a]

Drying Agent	Yield (%)	IS (%)
$MgO-K_2CO_3$[b,c]	2	13
Zeolite-K_2CO_3[b,c]	4	17
Zeolite	5	23
K_2CO_3[c]	18	10
EtZnOCPhNPh	18	15
Al_2O_3[c]	25	40
$MgSO_4$[c]	28	15
$EtZnNPh_2$	25	13
CaH_2	65	85

[a] Acetaldehyde treated with a drying agent was charged by distillation *in vacuo* and was polymerized at −78° for 24 hr after the mixture of monomer and catalyst was aged for 1 min at 0°. Catalyst concentration, 0.5 mol % of monomer. [b] K_2CO_3 (2 mol % of drying agent) was added to remove acetic acid and peracetic acid in the monomer. [c] Activated by heating at 150° *in vacuo*.

The effect of water on the polymerization was studied by adding various amounts of water to acetaldehyde (Ze). A maximum yield of the isotactic polymer was obtained in the presence of an optimum amount of water, while the atactic one remained constant. The optimum amount of added water corresponded to about $\frac{1}{30}$th mol/mol of the catalyst or to about 10^{-4} mol/mol of the monomer (Figure 4).

Dried oxygen which was charged into acetaldehyde (Ze) by bubbling just before allowing the polymerization to proceed had no such cocatalytic effect on the polymerization, and only amorphous-rich polymer was obtained in a low yield (about 10%). Thus, it is concluded that molecular oxygen is inactive as a cocatalyst.

Oxygen has been known to react with acetaldehyde slowly at 0° to give solely peracetic acid.[27] A small amount of dried oxygen ($\frac{1}{10}$th mol/mol of the catalyst) was bubbled through acetaldehyde (Ze) in a closed vessel at 0° and the system was allowed to stand at 0°. After various reaction times, aliquots of the reaction mixture were used as monomers for polymerizations. The interrelationship observed between the reaction time, which parallels the amount of peracetic acid, and the polymer yield suggests that peracetic acid formed *in situ* acts as a cocatalyst (Figure 5). In this case also, the existence of an optimum reaction time at which the yield of the isotactic polymer reaches a maximum value was observed. Acetic acid and benzoic acid were inactive as cocatalysts in any ratio and only amorphous polymer was obtained in a low yield (about 10%).

Thus, an optimum amount of water or peracetic acid does activate the catalyst to cause the polymerization of acetaldehyde (Ze) stereospecifically, not nonstereospecifically, to give almost exclusively the isotactic polymer. In addition, these experimental results afforded the important information that water and peracetic acid have a dual function. They act as activators at lower concentrations and as inhibitors at higher concentrations. This fact is incompatible with the speculation that the stoichiometric reaction product between water and the catalyst is the real active species. In fact, a reaction mixture of the catalyst and water (1:1 and 2:1 mol/mol) gave only an amorphous polymer in a low yield (about 10%).

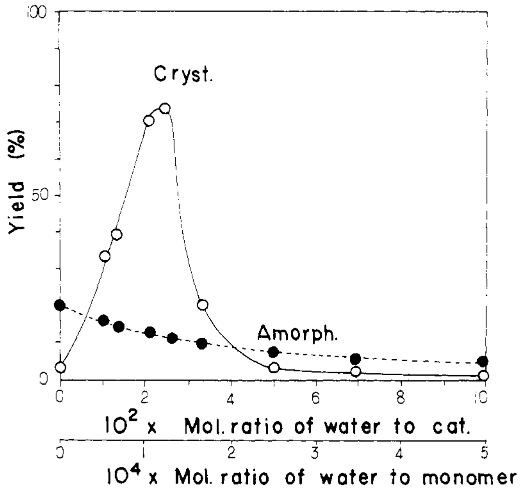

Figure 4. Cocatalytic effect of added water on the polymerization results. Catalyst, $Me_2AlOCPhNPh$, 0.5 mol % of monomer. Polymerization, −78° for 20 hr.

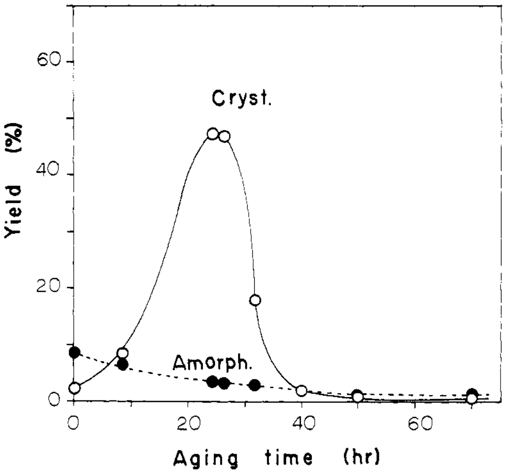

Figure 5. Effect of reaction time between acetaldehyde and a trace amount of molecular oxygen on the polymerization. Oxygen (0.05 mol % of monomer) was added and the mixture was aged at 0°.

The indispensable role of a cocatalyst was proved also in the stereospecific polymerization of acetaldehyde by four kinds of diethylaluminum alkoxides (Et_2AlOR; R = *n*-Bu, *i*-Bu, *sec*-Bu, and *t*-Bu)[28] and EtZnO-*sec*-Bu which are purified by repeating the distillation. The following very remarkable behavior was observed. Acetaldehyde (Ze) could not be polymerized by these alkoxides when water was not present in the monomer and could be polymerized in the presence of a trace amount of water. The optimum amount of added water corresponded to about $\frac{1}{20}$th mol/mol of the catalyst. These results show that the molecular mechanisms for polymerization by diethylaluminum alkoxide and ethylzinc alkoxide are identical with that by $R_2AlOCR'NPh$ catalyst and that the metal alkoxide itself is not the real catalyst species.

In order to determine the step at which the cocatalyst plays a decisive role, the effects of water added to acetaldehyde (Ze) on the aldehyde complex formation and on the aldehyde-exchange reaction were examined.

A large amount of acetaldehyde (Ze) (0.1 mol) was charged by distillation into the solution of 0.01 mol of

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Table VII
Effect of Added Water or Oxygen on Aldehyde-Exchange Reaction

		Concn of Addn to Catalyst (Mol Ratio)					
	Addns	0	0.7×10^{-2}	1.5×10^{-2}	2.5×10^{-2}	5.0×10^{-2}	10×10^{-2}
Content (%) of CH_3CHO	Water	44	50	52	47	45	47
in the complex[a]	Oxygen	50	52	55	49	47	51

[a] Determined by nmr spectra after 5-fold equimolar amount of CH_3CHO was reacted with $Me_2AlOCPhNPh \cdot CD_3CDO$ in benzene at 0° for 10 min.

Table VIII
Polymerization of Aliphatic Monoaldehyde by Various Kinds of Catalysts[a]

	CH_3CHO		C_2H_5CHO		n-C_3H_7CHO		i-C_3H_7CHO	
Catalyst	Yield (%)[c]	IS (%)	Yield (%)[c]	IS (%)	Yield (%)[c]	IS (%)	Yield (%)[c]	IS (%)
H_2SO_4	10 (e)	0	25 (f)	75	75 (f)	92	92 (f)	98
$TiCl_4$	15 (e)	25	25 (f)	50	20 (f)	65	20 (f)	90
Et_2AlCl[b]	80–10 (e–f)	80–10	80 (f)	75	90 (f)	95	90 (f)	90
i-Bu_3Al[b]	90–20 (e–f)	95–15	80 (f)	70	85 (f)	80	70 (f)	75
$Me_2AlOCPhNPh$	95 (f)	95	85 (f)	90	75 (f)	90	10 (f)	80
Et_2AlO-*sec*-Bu	95 (f)	95	80 (f)	95	80 (f)	95	15 (f)	50
Ph_3COK	80 (e)	0	65 (p)	80	75 (p)	85	90 (p)	90
n-BuLi	0		50 (p)	75	75 (p)	90	80 (p)	90

[a] Polymerization, −78°; 40-hr catalyst concentration, 1 mol % of monomer. [b] Catalyst concentration, 0.05–0.1 mol %. Polymerization was terminated by $MeOH$–NEt_3–K_2CO_3 mixture. [c] Appearance of raw polymer is indicated in parentheses: (e) elastomeric, (f) fibrous, (p) powdery.

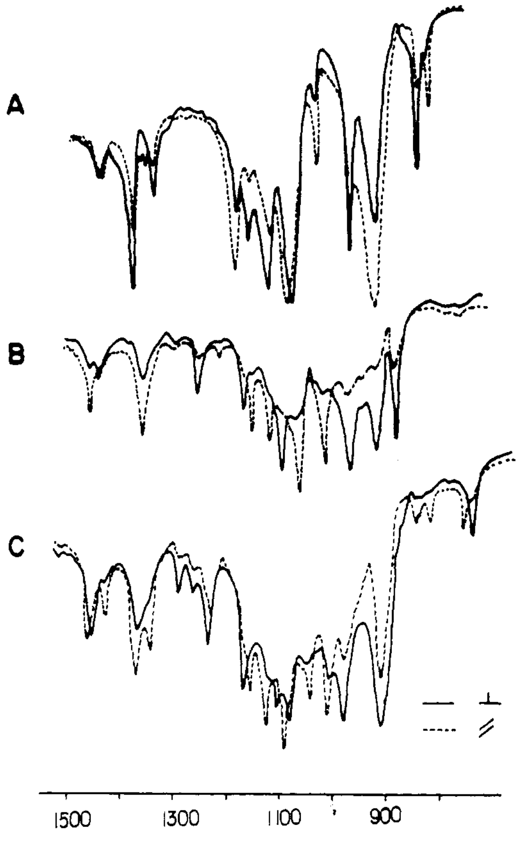


Figure 6. Polarized infrared spectra of crystalline polymer. (A) Polyacetaldehyde, (B) polypropionaldehyde, (C) poly-*n*-butyraldehyde.

$[Me_2AlOCMeNPh]_2$ in 40 ml of toluene at −50°, and *n*-hexane was then added to the solution after cooling to −78°. The aldehyde complex $Me_2AlOCMeNPh \cdot MeCHO$ was obtained in quantitative yield as a precipitate, unaccompanied by any polymer formation. In contrast to this, the polymer was obtained in about 50% yield from acetaldehyde (Ca) under identical conditions.

The effect of water added to acetaldehyde (Ze) on the aldehyde-exchange reaction was examined in benzene solution at 10° using acetaldehyde (Ze) and $Me_2AlOCMeNPh \cdot CD_3CDO$ in a molar ratio of 5:1. The ratio of the amount of free CH_3CHO to that of the complexed CH_3CHO measured by the nmr technique is independent of the presence of water or oxygen (Table VII).

These experimental results indicate that neither complex formation nor the aldehyde exchange reaction require a catalyst. Thus, it is concluded that the cocatalyst is essential solely for initiating the polymerization.

Polymerization of Aliphatic Monoaldehydes by Various Types of Catalysts. Polymerizations of some aliphatic monoaldehydes by typical anionic and cationic catalysts were investigated in order to elucidate the characteristic features of $[R_2AlOCR'NPh]_2$ catalyst (Table VIII).

Only a small amount of amorphous-rich polyacetaldehyde, together with a large amount of aldol and paraldol, were obtained by *n*-BuLi or Ph_3COK catalyst. The former could be separated from the latter by extracting with *n*-hexane because the amorphous polymer is insoluble but the aldol condensation products are easily soluble in it. Crystalline polymer could not be obtained from acetaldehyde by the anionic catalyst at −78°, while it could be obtained easily from higher aldehydes in high yield as white powdery substance in agreement with the results of Vogl.[3]

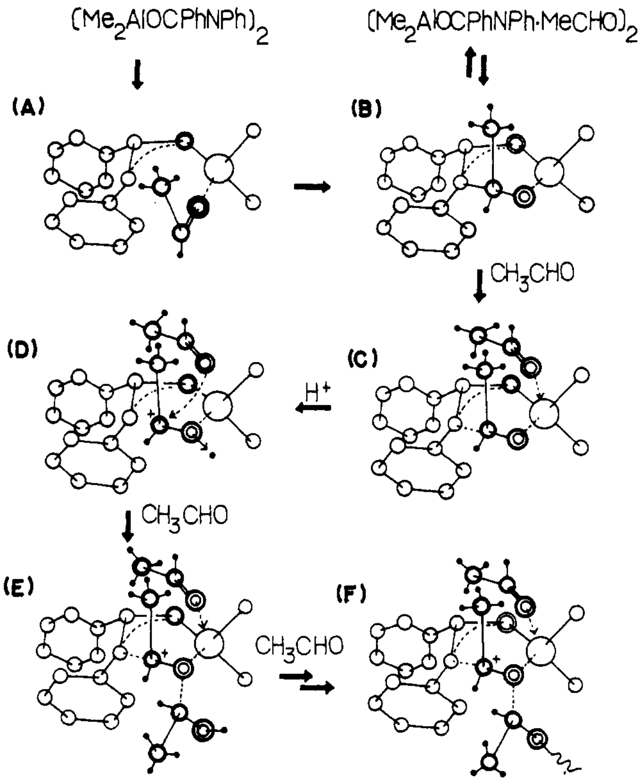
Typical cationic catalysts such as $TiCl_4$ and H_2SO_4 gave only a small amount of amorphous polymers from acetaldehyde, but gave the crystalline isotactic polymer from higher aldehydes in good yields. The clear oriented films of the latter crystalline polymers showed polarized ir spectra (Figure 6). The organoaluminum $R_2AlOCR'NPh$ also gave identical crystalline polymers from the aldehyde monomers. The yield was decreased with increase in the bulkiness of the alkyl group of aldehyde monomers. The catalytic action of diethylaluminum alkoxide was quite similar to that of $R_2AlOCR'NPh$.

Polymerization of acetaldehyde by Et_2AlCl or Al-*i*-Bu_3 depended on the concentration of the catalyst; the crystalline polymer was obtained in good yield at a low catalyst concentration (0.02 mol % to monomer) and its yield was decreased sharply by increasing the catalyst concentration. Polymerization of higher aldehydes gave crystalline polymers.

Molecular Mechanism Proposed for the Isotactic Polymerization of Aliphatic Monoaldehydes. A molecular mechanism is proposed for the stereospecific polymerization of aliphatic monoaldehydes, especially of acetaldehyde, based on the experimental evidence concerning the structure and the chemical and polymerization behavior of $[R_2AlOCR'NPh]_2$ and its derivatives.

The proposed mechanism is illustrated in Scheme II.

Scheme II



The catalyst $[R_2AlOCR'NPh]_2$ that has a centrosymmetric eight-membered ring structure can be visualized as the dimeric form of $R_2AlOCR'NPh$, because it reacts with a strong electron donor Me_3NO to give the complex $Me_3NO{\cdot}AlR_2COR'NPh$. It is reasonable therefore to conclude that acetaldehyde attacks an aluminum atom of the catalyst as an electron donor with simultaneously breaking of the bond between an aluminum and a nitrogen atom to form the monomeric acetaldehyde complex $MeHCO{\cdot}AlR_2OCR'NPh$ (A), which has a structure identical in type with that of Me_3NO complex. The acetaldehyde complex A is, in contrast to the Me_3NO complex, stabilized by forming a bond between the carbonyl carbon and the nitrogen atom of the acid amide moiety to give the six-membered ring structure B. This monomeric aldehyde complex B tends to be stabilized by dimerization when the alkyl groups attached to the aluminum atom and/or to the carbon atom in the aldehyde moiety are not too bulky.

When the second acetaldehyde molecule interacts with the monomeric acetaldehyde complex B, the formation of the unstable complex C in which an aluminum atom assumes the pentacoordinate state is conceivable. The stabilized pentacoordinate aluminum atom is found to exist in the dimeric acetaldehyde complex and in the monomeric complex $ME_2AlOCPhNPh{\cdot}MeCHO{\cdot}OP(NMe_2)_3$. This unstable complex C is the most plausible intermediate in the aldehyde exchange reaction which is observed between the aldehyde complex and an aldehyde monomer. The examination of molecular models indicates that the steric constraint forces the two methyl groups of the two aldehyde molecules coordinated to the catalyst to assume relative position as far apart as possible as illustrated in the structure C. This relative position is fundamentally identical with that assumed by two molecules of acetaldehyde at low temperatures in which two C=O bonds lie nearly perpendicular to each other.[25,29,30]

The polymerization is started only in the presence of a cocatalyst, while aldehyde complex formation and the aldehyde-exchange reaction can proceed even in the absence of such a cocatalyst. It is reasonable to assume that the proton formed from the cocatalyst interacts with the oxygen atom of the acetaldehyde moiety, which is the donor center in the monomeric acetaldehyde complex molecule B, to initiate the polymerization in the manner illustrated in the formula D. A cationic center, then, transfers from the proton to the carbonyl carbon of the acetaldehyde moiety to form a bond between the carbonyl oxygen atom and the proton. The carbonium ion attacks the oxygen atom of the incoming acetaldehyde monomer. Thus, the proton acts as a "trigger" for starting the polymerization reaction, and the succeeding propagation reaction proceeds in a concerted manner while maintaining adequate interaction with the catalyst.

Examination of molecular models indicates that the methine hydrogen atom of acetaldehyde and the initiating proton or the propagating carbonium ion assume the cis relative position in the initiation and the propagation steps, because the trans position is impossible for steric reasons. The same relative position is proposed by Olah *et al.*,[31,32] for protonated aliphatic monoaldehydes in a strongly acidic medium, $HSO_3F–SbF_5–SO_2$, at −60°. It is reported that the methine hydrogen and the proton linked to the oxygen atom assume a cis position quantitatively for propionaldehyde and *n*-butyraldehyde, but assume cis and trans positions in a ratio of 8:2 for acetaldehyde. These results parallel those obtained in the free cationic polymerization of aliphatic monoaldehydes: propionaldehyde and *n*-butyraldehyde give crystalline isotactic polymer and acetaldehyde gives isotactic-rich amorphous polymer (the ratio of isotactic to syndyotactic dyads is 7:3).

It is reasonable to conclude that isotactic polyacetaldehyde is obtained only when the carbonyl cation attacks the oxygen atom from the cis side. The organoaluminum catalysts assist the acetaldehyde monomer to attack the carbonium end of the growing polymer solely from the cis side by aligning these reactants in an appropriate relative

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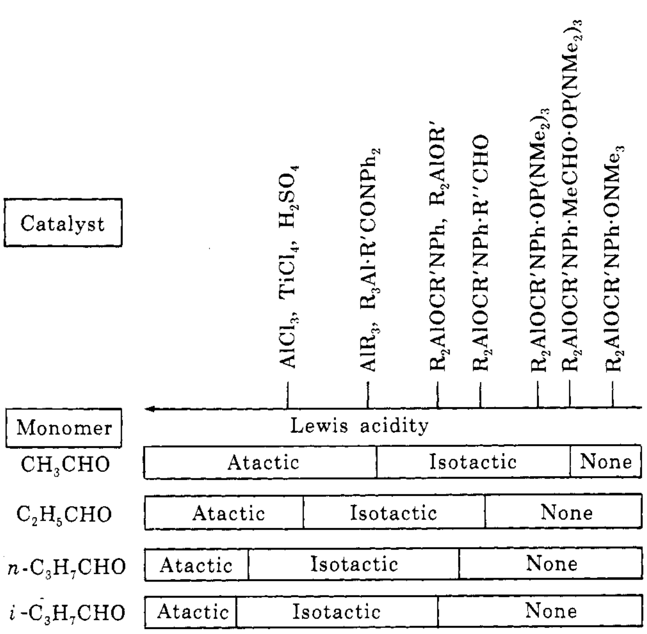
Scheme III



position using the fourth and fifth coordination sites of the aluminum atom, as mentioned above. Propionaldehyde and its higher homologs require no such assistance because of its alkyl groups being relatively large.

Therefore, the stereospecific polymerization of an aldehyde is interpretable more reasonably by a coordinate cationic mechanism than a coordinate anionic one. The presence of an optimum amount of a cocatalyst and the inhibition of the polymerization by a strong base are, in fact, quite similar to the well-known characteristic feature of cationic polymerizations in general.

Conclusion

In the stereospecific polymerization of an aliphatic monoaldehyde catalyzed by some organoaluminums, the bulkiness of the alkyl group of the aldehyde is the most important factor in the stereoregulation of the polymerization reaction; the catalyst enhances the degree of stereoregulation by controlling the mode of approach of the incoming monomer sterically through the coordination. Therefore, the structural requirement for the catalyst in relation to stereoregulation is the most severe for the lowest homolog, *i.e.*, acetaldehyde.

In general, the Lewis acidity of the catalyst suitable for each member the aldehyde series is resticted to a rather narrow range. When the Lewis acidity is too strong, only an amorphous polymer is obtained and when it is too weak no polymer is obtained. The same tendency is also observed for the Lewis basicity of the catalyst. These correlations are shown in Scheme III.

Although isotactic polyacetaldehyde cannot be obtained by strong acid or base, an isotactic polymer of a higher aldehyde can be obtained by strong acid or base.

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Kinetic Studies on Ring-Opening Polymerization of Unsubstituted, 3-Methyl-, and 3,3-Dimethyloxacyclobutanes by Boron Trifluoride Catalyst. Methyl-Substituent Effects on Rate of Propagation

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ABSTRACT: The effect of the methyl substituent at the 3 position on the propagation rate constant, k_p, of the cationic ring-opening polymerization of oxacyclobutanes (oxetanes) was investigated. The rate constants and kinetic parameters of the propagation reaction were determined in the BF_3-catalyzed polymerizations of oxetane (1), 3-methyloxetane (2), and 3,3-dimethyloxetane (3) carried out in methylcyclohexane and methylene dichloride solvents. The kinetic analyses were made on the basis of the time–[P*] relationships, in which [P*], the concentration of propagating species, was determined by the phenoxyl end-capping method. At −20°, the k_p value of 1, 2, and 3 in methycyclohexane followed the relative ratio 1:5.1:19; *e.g.*, the introduction of the methyl group into the oxetane ring increased the rate. This result cannot be explained on the basis of ring strain or basicity. Examination of activation parameters showed that substitution of the methyl group decreased the negative value of the activation entropy (favorable for the k_p increase) whereas it increased the activation enthalpy (unfavorable for the k_p). These findings were interpreted mainly in terms of the solvation–desolvation phenomenon. The effects of the solvents methylcyclohexane and CH_2Cl_2 were found to be important for the polymerization kinetics, which were quite compatible with the S_N2 mechanism of propagation.

We have reported kinetic studies upon the cationic ring-opening polymerizations of cyclic ethers, oxacyclobutane (oxetane),[1] tetrahydrofuran (H_4furan),[2-5] and oxacycloheptane,[6] using the phenoxyl end-capping method. From these results, the correlation between the reactivity and the monomer ring size has been extensively discussed

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