

Polymerization Catalyst of the Triethylaluminum-Chloral Hydrate System. I. Triethylaluminum-Chloral Hydrate Reaction and Catalyst Activity in Cationic Polymerization

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In reaction of AlEt_3 with chloral hydrate has been investigated. The reaction system was examined by means of infrared and NMR spectra and by the vapor-phase chromatographic analysis of the acidolysis product of this system. The gas evolved during the reaction was also analyzed. The AlEt_3 -chloral hydrate system was proved to contain the linkages of $>\text{AlOCH}_2\text{CCl}_3$, $>\text{AlOCH}(\text{CCl}_3)\text{OAl}<$, $>\text{AlOCH}(\text{Et})\text{CCl}_3$, $>\text{AlOAl}<$, $>\text{Al-Et}$ and $>\text{Al-Cl}$. This system showed a very high catalytic activity for the cationic polymerization of *i*-butyl vinyl ether. Tetrahydrofuran, 3,3-bis(chloromethyl)oxacyclobutane, α -methylstyrene, and styrene were also polymerized by this catalytic system. The acid strength of the AlEt_3 -chloral hydrate system was examined by two methods, the Hammett indicator method and shift of the infrared carbonyl band of xanthone caused by coordination to Lewis acid. It has been shown that the acid strength of this system is as strong as $\text{AlEt}_3\text{-H}_2\text{O}$ (1 : 0.8) and Et_2AlCl . The relation between the strong acid character of the AlEt_3 -chloral hydrate system and its structure was discussed.

We have studied the polymerizations of aldehydes and cyclic oxides by the catalyst systems derived from aluminum alkyls.¹⁻¹⁰ Additives, such as water and alcohol, improve or markedly change the catalyst properties of the parent aluminum alkyl. In cationic polymerization, it is quite interesting that when AlEt_3 is treated with a controlled amount of water (about an equimolar amount), the acid strength is increased and, hence, the catalyst activity is much enhanced.²⁾

In the present study, we have examined the reaction of AlEt_3 with chloral hydrate and the catalyst activity of the reaction product.

Experimental

Reagents. AlEt_3 . A commercial reagent was rectified under a reduced nitrogen atmosphere, bp 83—84°C/4 mmHg.

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1) J. Furukawa, T. Saegusa and H. Fujii, *Makromol. Chem.*, **44/46**, 398 (1960).

2) T. Saegusa, H. Imai, S. Hirai and J. Furukawa, *ibid.*, **53**, 203 (1962).

3) T. Saegusa, Y. Fujii, H. Fujii and J. Furukawa, *ibid.*, **55**, 232 (1962).

4) T. Saegusa, H. Imai and J. Furukawa, *ibid.*, **56**, 55 (1962).

5) T. Saegusa, H. Imai and J. Furukawa, *ibid.*, **65**, 60 (1963).

6) T. Saegusa, H. Imai and J. Furukawa, *ibid.*, **79**, 207 (1964).

7) T. Saegusa, H. Imai and J. Furukawa, *ibid.*, **81**, 92 (1965).

8) H. Imai, T. Saegusa and J. Furukawa, *ibid.*, **81**, 92 (1965).

Chloral Hydrate. A commercial reagent was dried over phosphoric anhydride.

The monomers and solvents were dried and purified by the usual methods.

Reaction of AlEt_3 with Chloral Hydrate. A typical example was as follows. A solution of 5 mmol of chloral hydrate in 100 ml of toluene was added, drop by drop, into 100 ml of a toluene solution containing 10 mmol of AlEt_3 with stirring at -50 — -60°C . The mixture was gradually warmed to room temperature over a 2-hr period, and then kept at 40°C for additional 2 hr. The reaction systems were homogeneous unless the molar ratios of chloral hydrate to AlEt_3 exceeded 1.5.

Analyses of Reaction Products. *Acidolysis.* The volatile matters were distilled off under reduced pressure (2—3 mmHg) at temperatures from room temperature to 40°C , and the residue was decomposed with an excess of glacial acetic acid. The acid decomposition product was analyzed by vapor-phase chromatography.

Vapor-phase Chromatography (VPC) Analysis. An apparatus, Model 2C, of the Shimadzu Co. (Japan) was used. In the analysis of the acid-decomposition mixture, a silicon column (3 m) was used (column temperature: 125°C ; carrier gas: hydrogen; gas speed: 40 ml/min). Ethane and ethylene gases were analyzed by using a column of silica gel (3 m) at 40°C , with hydrogen as the carrier gas (flow rate: 60 ml/min).

Analysis of Inorganic Chlorine. The aluminum-chlorine linkage was formed in the chloral hydrate- AlEt_3 reaction. This inorganic chlorine was determined by the silver

9) H. Fujii, I. Tsukuma, T. Saegusa and J. Furukawa, *ibid.*, **82**, 32 (1965).

10) T. Iwata, T. Saegusa, H. Fujii and J. Furukawa, *ibid.*, **97**, 49 (1966).

nitrate method after the reaction product had been decomposed by nitric acid.

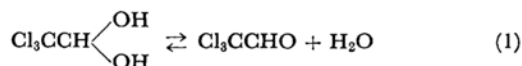
Nuclear Magnetic Resonance (NMR) Measurements. The NMR spectra were taken with a Varian 60 MC spectrometer; the peak positions were determined by using tetramethylsilane as the internal reference.

Measurement of Acid Strength. Indicator Method. The acid strength of the catalytic system was measured by a method similar to that described in a previous paper.⁹⁾

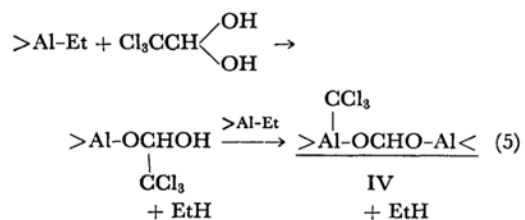
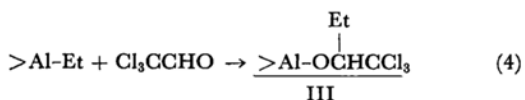
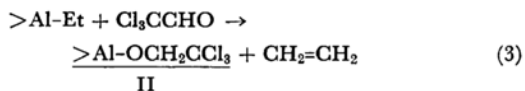
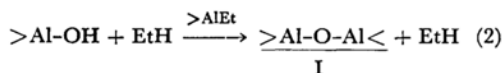
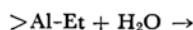
Xanthone Method. The shift of the carbonyl band in the infrared spectrum of xanthone coordinating onto the catalytic systems was examined by the method of Cook.¹¹⁾ Solutions of the catalyst system and xanthone, both in a concentration of 0.5 mol/l, were mixed at room temperature, and the difference between the free and the shifted carbonyl bands was determined.

Results and Discussion

Reaction of AlEt_3 with Chloral Hydrate. Chloral hydrate exists in the following equilibrium:



Therefore, five possible ways of reaction may be postulated:



The linkage (IV) has not yet been known; it is a special aluminum alkoxide.

The reaction mixture of AlEt_3 with chloral hydrate was decomposed by glacial acetic acid and analyzed by VPC. The results are shown in Table 1.

In the reaction in both ether and toluene, the linkage (II) derived from the reduction of chloral with the Al-Et linkage by Eq. (3) was mainly produced. The linkage (III) was formed very little in ether, but it was formed to a considerable extent in toluene. The regeneration of chloral by the acidolysis suggests the presence of the linkage (IV), be-

TABLE 1. ANALYSIS OF ACID DECOMPOSITION MIXTURE OF AlEt_3 -CHLORAL HYDRATE (2 : 1) REACTION SYSTEM

Product	Mol%	
	in ether	in toluene
Cl_3CCHO	22	32
$\text{Cl}_3\text{CCH}_2\text{OH}$	72 (70) ^{a)}	44
$\text{Cl}_3\text{CCH}(\text{Et})\text{OH}$	trace	4
Cl^\ominus	2	20

a) The value in the parenthesis was calculated from volume of ethylene gas evolved in the course of the reaction.

cause, before the acidolysis, the reaction mixture did not exhibit the absorption bands characteristic of OH and $>\text{C}=\text{O}$ groups. The amount of linkage (I) was taken to be equal to be the sum of the linkages (II) and (III), because the reaction mixture did not show any indication of the presence of OH (water) or $>\text{C}=\text{O}$ (free chloral).

The formation of a considerable amount of inorganic chloride, especially in the reaction in a toluene solvent, is due to the reaction between the trichloromethyl group and the Al-Et group. This reaction seems very complicated. No dichloroacetaldehyde, monochloroacetaldehyde, or acetaldehyde, or any of their derivatives were detected by the VPC analyses of the acidolysis mixture.

The volume of the gas evolved in the course of the reaction was then measured using a gas burette. By VPC analysis, the gas was shown to be a mixture of ethane and ethylene. From the volume of ethylene, the amount of linkage (II) was calculated (see Table 1). The two values, the one from the ethylene and the other from the $\text{Cl}_3\text{CCH}_2\text{OH}$ in the acidolysis mixture, agreed with each other.

Further support was given by the NMR spectra of this system. Chemical shifts of 5.6–5.7 τ and 4.4–4.6 τ were observed in the spectra of this system; these shifts were assigned to the protons of $>\text{Al}-\text{OCH}_2\text{CCl}_3$ and $>\text{Al}-\text{OCH}(\text{CCl}_3)\text{O}-\text{Al}<$ respectively. The area ratios of the two peaks ($>\text{Al}-\text{OCH}_2\text{CCl}_3 / >\text{Al}-\text{OCH}(\text{CCl}_3)\text{O}-\text{Al}<$) were 6.5 (in ether) and 2.8 (in toluene); these values are in fairly good agreement with the values calculated from $\text{Cl}_3\text{CCH}_2\text{OH}$ and Cl_3CCHO in the acidolysis mixture (cf. Table 1).

Catalyst Behavior in Cationic Polymerization. The reaction mixture of AlEt_3 and chloral hydrate showed a high catalytic activity in the cationic polymerizations of isobutyl vinyl ether and tetrahydrofuran (Tables 2 and 3). Isobutyl vinyl ether was polymerized especially rapidly by this catalytic system.

The results shown in Table 2 indicate that the AlEt_3 -chloral hydrate system is fairly active in initiating cationic polymerizations. The activating effect of the treatment with chloral hydrate has been well

11) D. Cook, *Can. J. Chem.*, **41**, 526 (1963).

demonstrated. No additional cocatalyst is required. It may be assumed that a part of the hydroxy group of chloral hydrate remains unreacted, thus affording the initiator proton. Even at low catalyst concentrations (0.2 mol% to monomer), the AlEt_3 -chloral hydrate system induced the vinyl ether polymerization at a fairly high rate. The product polymers contained no methyl ethyl ketone-insoluble (crystal-

line) part. The lack of stereospecificity in the polymer produced by the AlEt_3 -chloral hydrate system is unlike the case with the AlEt_3 -water system, which gives the crystalline polymer of isobutyl vinyl ether.^{6,7)}

The polymerization of tetrahydrofuran by the AlEt_3 -chloral hydrate-epichlorohydrin system is illustrated in Table 3.

The AlEt_3 -chloral hydrate system also induced the

TABLE 2. POLYMERIZATION OF ISOBUTYL VINYL ETHER

Catalyst	mol ratio	mmol	Polymer yield (%)	$[\eta]_{30^\circ\text{C}}^{\text{benzene}}$	$\text{CH}_3\text{COC}_2\text{H}_5$ -insoluble part (%)
$\text{Cl}_3\text{CCHO} \cdot \text{H}_2\text{O} / \text{AlEt}_3$	0	1	0	—	—
	0.5	1	21.3	0.51	0
	1.0	1 ^{b)}	25.4	—	0
	1.0	1	71.2	—	0
	1.0	0.1	97.5	0.62	0
	1.5	1	100	0.22	0
$\text{H}_2\text{O} / \text{AlEt}_3$	2.0	1	27.2	0.16	0
	0.8	1 ^{c)}	28.0	1.35	5.3
Et_2AlCl	0.8	1	0	—	—
Et_2AlCl		1 ^{c)}	62.0	0.87	0
AlEt_3 - H_2O - EtOH (1 : 0.8 : 0.4)		3 ^{d)}	0	—	—

a) Insoluble part deposited from a hot solution of 1 g of polymer in 100 ml of methyl ethyl ketone was kept standing at room temperature.

b) Polymerization was carried out in ether solvent (20 ml).

c) Equimolar amount of *t*-butyl chloride (to Et_2AlCl) was added as cocatalyst.

d) Equimolar amount of acetyl chloride (to AlEt_3) was added as cocatalyst.

TABLE 3. POLYMERIZATION OF TETRAHYDROFURAN
(Monomer: 0.1 mol; Catalyst: 2 mmol; Epichlorohydrin: 2.5 mmol; Polymn.: 0°C, 3.5 hr)

Catalyst	mol ratio	Polymer yield (%)	$[\eta]_{30^\circ\text{C}}^{\text{CH}_3\text{COOEt}}$
$\text{Cl}_3\text{CCHO} \cdot \text{H}_2\text{O} / \text{AlEt}_3$	1/3	43.7	0.20
	1/2	44.4	0.26
	1/1	36.5	0.19
	1/5	4.5	0.33
	1/2 ^{a)}	100	—
$\text{H}_2\text{O} / \text{AlEt}_3$	0.8/1	29.0	0.48
Et_2AlCl		8.1	0.08

a) Polymerization in ether solvent for 1 day.

TABLE 4. POLYMERIZATION OF SOME MONOMERS
 AlEt_3 - $\text{Cl}_3\text{CCHO} \cdot \text{H}_2\text{O}$ (2 : 1): 1.5 mmol; Cocatalyst: 1 mmol

Monomer (mol)	Cocatalyst	Solvent (ml)	Temp. (°C)	Time (hr)	Yield (%)
BCMO (0.05)	CH_3COCl	Toluene (20)	0	24	93.4
	—	Toluene (20)	0	24	82.0
	$\text{ECH}^{\text{a)}$	Ether (10)	0	24	82.8
St (0.05)	$t\text{-C}_4\text{H}_9\text{Cl}$	Toluene (20)	-78	24	47.5
	—	Toluene (20)	-78	24	0
$\alpha\text{-MeSt}$ (0.025)	$t\text{-C}_4\text{H}_9\text{Cl}$	Toluene (20)	-78	15 min	trace
	— ^{b)}	Toluene (20)	-78	15 min	91.2

a) ECH: epichlorohydrin.

b) AlEt_3 - $\text{Cl}_3\text{CCHO} \cdot \text{H}_2\text{O}$ (1 : 1): 1 mmol.

TABLE 5. ACID STRENGTH OF ORGANOALUMINUM COMPOUNDS

Catalyst	mol ratio	Indicator ^{a)}						$\Delta\nu_{C=O}$ by xanthone method (cm ⁻¹)
		I	II	III	IV	V	VI	
Cl ₃ CCHO · H ₂ O/AlEt ₃	1/3	A	A	A	A	A	B	88
	1/2	A	A	A	A	A	B	104
	1/1			— ^{b)}				100
Et ₂ AlCl		A	A	A	A	A	A	104
H ₂ O/AlEt ₃	0.8/1	A	A	A	A	A	?	100
AlEt ₃		A	A	A	A	B	B	83
AlEt ₃ -H ₂ O-EtOH (1 : 0.8 : 0.4)		B	B	B	B	B	B	0
Al(OCH ₂ CCl ₃) ₃		—	A	A	A	A	B	90

a) Indicators

I : Phenylazonaphthylamine;

III: Benzeneazodiphenylamine;

V : Benzalacetophenone;

A : Acidic

II : Butter yellow;

IV: Dicinnamalacetone;

VI: Anthraquinone

B : Basic

b) It was impossible to notice the color change because of the coloration of the system.

polymerizations of 3,3-bis(chloromethyl)oxacyclobutane (BCMO), α -methylstyrene (α -MeST), and styrene (St) (Table 4).

It has been established that, in many cases, a Lewis acid alone does not cause the cationic polymerization of vinyl monomers or four- and five-membered cyclic ethers. Therefore, a cocatalyst or a promoter^{5,12)} was used in the present study.

From one observations in the polymerizations of several monomers (Tables 2, 3, and 4), it is certain that the AlEt₃-chloral hydrate system is a cationic polymerization catalyst. Therefore, the acid strength of this system was examined by the Hammett indicator method and by the extent of the shift of the infrared carbonyl band ($\Delta\nu_{C=O}$) by the xanthone method¹¹⁾ (Table 5).

Table 5 shows that the AlEt₃-chloral hydrate systems are strong acids, much stronger than AlEt₃ itself. The systems of AlEt₃/chloral hydrate=1.0 and 2.0 are as strong as AlEt₃/H₂O (1/0.8) and

Et₂AlCl.

It is interesting to compare the strong acid character of the AlEt₃-chloral hydrate system with the acid nature of the AlEt₃-H₂O-EtOH (1 : 0.8 : 0.4) system. It has previously been reported by us⁷⁾ that the systems containing aluminum alkoxide linkages are generally weaker acids. AlEt₃-H₂O-EtOH is a weaker acid (Table 5) and does not induce the cationic polymerization of vinyl ether. Although the AlEt₃-chloral hydrate system contains considerable amount of aluminum alkoxide linkages (Eqs. (2) to (5)), it is a strong acid.

Such a characteristic behavior of this system may be attributed to the electron-withdrawing effect of the trichloromethyl group of the alkoxyl groups in the AlEt₃-chloral hydrate system. In fact, aluminum trichloroethoxide prepared by the reaction of AlEt₃ with trichloroethanol shows great acid strength¹³⁾ and high catalytic activities in cationic polymerizations.¹³⁾

12) T. Saegusa, S. Matsumoto and T. Ueshima, *Makromol. Chem.*, **105**, 132 (1967).

13) T. Saegusa and T. Ueshima, *Inorg. Chem.*, **6**, 1679 (1967).