in the thermogram of the reaction product. However, the product's thermogram is identical with the 2-phenylbenzimidazole thermogram, showing melting at about 275° and boiling at about 410°.

Since benzimidazoles absorb strongly in the ultraviolet region, the electronic spectra of 2-methylbenzimidazole, 2-phenylbenzimidazole, and the reaction product were obtained in methanol. The spectra are shown in Figures 11 and 12. The spectrum of the residue is that of 2-phenylbenzimidazole. However, since the extinction coefficients for 2-methylbenzimidazole are lower than those for 2-phenylbenzimidazole the detection of 2-methylbenzimidazole in 2-phenylbenzimidazole cannot be put on a straightforward mole-to-mole basis. Table III gives the extinctions and absorption maxima for the two benzimidazoles in methanol.

In order to improve the sensitivity of the method, a differential ultraviolet analysis was developed. In this method, synthetic mixtures of 2-methylbenzimidazole in 2-phenylbenzimidazole were made up in methanol. A solution containing 2-phenylbenzimidazole alone at the same molar concentration was used in the reference cell so the absorptions due to 2-phenylbenzimidazole would be subtracted out in the recording of the spectra. It was found that about 0.8% by weight 2-methylbenzimidazole in 2-phenylbenzimidazole could be detected in this fashion. No 2-methylbenzimidazole was detected in the reaction mixture indicating that elimination is predominately, if not entirely, of the methyl group to yield methane and 2-phenylbenzimidazole.

By analogy with the reaction mechanism of this model compound system, it can be concluded that 1,4-diacetylbenzene and 3,3′,4,4′-tetraaminobiphenyl will react preferentially to form the fully aromatic polybenzimidazole with the elimination of methane. This accounts for the high molecular weight, film-forming polymer obtained by this reaction.

Acknowledgment. The authors wish to thank Mr. Wilson Lochte for the thermogravimetric analysis, Dr. G. P. Shulman for the mass spectrometric thermal analysis, and Professor Robert T. Conley for many helpful discussions.

Behavior of the >Al–C_2H_5 Group in the Polymerization by Triethylaluminum–Water Catalyst

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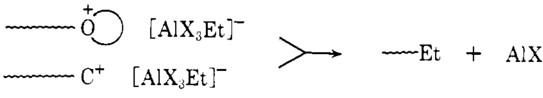
Received June 7, 1968.

ABSTRACT: In the polymerization of cyclic ethers and vinyl ether by the $AlEt_3$–H_2O system, the change of the amount of the >AlEt group of the catalyst was examined. The amount of the >AlEt group was determined by the volume of ethane gas evolved in the hydrolytic decomposition of the polymerization system with 6 *N* H_2SO_4 at room temperature or with 1 *N* NaOH at reflux temperature. In the polymerization of tetrahydrofuran (THF) by the ternary catalyst system of $AlEt_3$–H_2O–epichlorohydrin (ECH) (2:1:0.2), the >AlEt group remained intact during the polymerization. These results agreed with a postulated mechanism of stepwise addition without chain termination. In the THF–ECH (1:1) copolymerization and the ECH homopolymerization, however, noticeable amounts of the >AlEt group were consumed. These results are in accord with our previous assumption that the reaction of the >AlEt group with ECH gives rise to the formation of an aluminum alkoxide species which in turn induces the coordinate anionic polymerization of ECH. In the cationic polymerization of vinyl ether with the $AlEt_3$–H_2O (1:1) system, the >AlEt group for the most part remained intact.

During the past few years, the catalytic activity of alkylaluminum compounds has attracted much attention in the fields of polymerizations of aldehyde, cyclic ethers and vinyl compounds. $AlEt_3$ itself is a Lewis acid and is able to induce cationic polymerization.[1,2] The acid strength of $AlEt_3$ is increased by treatment with a controlled amount of water. The $AlEt_3$–H_2O system exhibits a superior catalyst activity in some cases. In polymerizations of alkylene oxide initiated by $AlEt_3$ and the $AlEt_3$–H_2O system, the catalyst species is more complicated; *i.e.*, a part of the >AlEt group is converted into aluminum alkoxide group by the reaction with the alkylene oxide monomer. Introduction of an alkoxyl group to alkylaluminum species decreases the acid strength. Thus $AlEt_3$ and $AlEt_3$–H_2O are transformed into species of decreased acid strengths, which in turn induce the coordinate anionic polymerization of alkylene oxide.

The ethyl group attached to aluminum is nucleophilic. Therefore, the reaction of the propagating species of cationic polymerization with the >AlEt group is possible, which thus constitutes the termination reaction.



The present study was undertaken to examine the behavior of the >AlEt group of the $AlEt_3$–H_2O catalyst during the homopolymerizations of tetrahydrofuran

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[1] T. Saegusa, H. Imai, S. Hirai, and J. Furukawa, *Makromol. Chem.*, **53**, 203 (1962).

[2] T. Saegusa, H. Imai, and J. Furukawa, *ibid.*, **64**, 224 (1963).

TABLE I
ANALYSIS OF >AlEt GROUP OF $AlEt_3$–H_2O (ABOUT 2:1) SYSTEM[a]

	Solvent, 20 ml			
	THF		CH_2Cl_2	
$AlEt_3$, mmol	17.26	17.79	16.10	16.68
H_2O–$AlEt_3$ ratio	0.47	0.48	0.52	0.50
C_2H_6 evolved (%) in $AlEt_3$–H_2O reaction[b]	98.6	99.0	100.8	99.4
C_2H_6 evolved (%) in acid decompn[c]	100.0	98.7	98.5	99.1

[a] Two runs of analysis were carried out in each solvent. [b] Calculated on the basis of the equation $2{>}AlEt + H_2O \rightarrow {>}Al\text{–}O\text{–}Al{<} + 2C_2H_6$. [c] The amount of remaining >AlEt group in the $AlEt_3$–H_2O system was calculated from the volume of ethane gas evolved in the $AlEt_3$–H_2O reaction as well as the amout of $AlEt_3$.

(THF), epichlorohydrin (ECH) and isobutyl vinyl ether (IBVE), and the THF–ECH copolymerization. The amount of ethyl groups attached to aluminum was determined by the volume of ethane gas evolved in the hydrolytic decomposition of the polymerization system.

Results and Discussion

A method for the determination of the >AlEt group has been established. Table I indicates the details of the reaction of $AlEt_3$ with water. It is shown that 1 mol of water produces 2 mol of ethane at a $AlEt_3$–H_2O ratio of 2. The remaining >AlEt group in the $AlEt_3$–H_2O system was then quantitatively converted into ethane by acid hydrolysis. At an $AlEt_3$–H_2O ratio of 1, the reaction of water with the >AlEt group was not quantitative. A small but definite amount of hydroxyl group remained unreacted. These results are in accord with those of our previous experiment[3] using tritiated water as a tracer.

The concentration of the >AlEt group during the course of polymerization, and the polymer yield as well as polymer characterization, are given in Table II. In the THF polymerization, the >AlEt group remained intact. This observation is in accord with our previous study showing that the THF polymerization by the $AlEt_3$–H_2O system with ECH as promoter[4] proceeds

TABLE II
POLYMERIZATION BY $AlEt_3$–H_2O

Catalyst system[a]							
$AlEt_3$, mmol	H_2O, mmol	Polymerizn time, min	*A*,[b] >AlEt before polymerizn (C_2H_6 gas, ml)	*B*,[c] >AlEt after polymerizn (C_2H_6 gas, ml)	$B/A \times 100$	Polymer yield, %	Remarks
			THF Polymerization (at 0°)[d]				
18.30	8.54	20	847.3	847.9	100.0		
15.00	8.10	20	644.8	638.0	98.9	8.0	Mol wt 7,540
17.23	8.73	40	765.1	763.5	99.8		
17.03	9.01	40	740.8	736.9	99.5	14.2	Mol wt 10,500
17.99	9.01	60	805.5	808.0	100.3		
17.43	8.75	60	779.0	764.2	98.1	26.7	Mol wt 21,800
			THF–ECH (1:1) Copolymerization (at 0°)[e]				
16.33	8.46	20	718.7	694.3	96.6		
16.76	8.60	20	741.2	718.2	96.9	3.0[f]	Soluble[g] 92.7% Insoluble 7.3%
16.16	8.51	60	704.6	666.6	94.6		
16.54	8.09	60	748.9	711.5	95.0	4.5[f]	Soluble[g] 87.8% Insoluble 12.2%
18.37	8.41	300	857.5	813.0	94.9		
16.45	8.56	300	721.6	682.0	94.5	18.7[f]	Soluble[g] 83.7% Insoluble 16.3%
			ECH Polymerization (at 0°)[g]				
16.10	7.79	60	732.9	555.5	75.8		
12.89	6.64	60	569.1	435.4	76.5	71.5	Soluble[g] 91.6% Insoluble 8.4%
16.32	8.35	60	723.0	559.6	77.4		
			IBVE Polymerization (at −78°)				
14.98	15.84	60	335.9	332.1[h]	98.9	45.0	
12.74	13.43	60	279.8	275.0[h]	98.3		

[a] The $AlEt_3$–H_2O system was prepared by the method described in the Experimental Section. [b] The amount of >AlEt linkage is expressed by the amount of ethane gas which is to be evolved in acid hydrolysis. The amount of >AlEt linkage was calculated from the volume of ethane gas evolved in the preparation of the $AlEt_3$–H_2O system. [c] The amount of the >AlEt linkage which survived the reaction was expressed by the volume of ethane gas which was evolved in hydrolytic decomposition. Here, a correction was made for the change of the solubility of ethane gas in the reaction system caused by the progress of polymerization. [d] THF, 20 ml (0.24 mol), bulk polymerization at 0°. [d] THF and ECH each was 0.15 mol. [f] Calculated on the basis of the combined amounts of THF and ECH monomers. [g] The total polymer was fractionated into acetone-soluble and the acetone-insoluble portions at room temperature. [h] Decomposition of >AlEt linkage into ethane after IBVE polymerization was performed with boiling aqueous alkaline solution.

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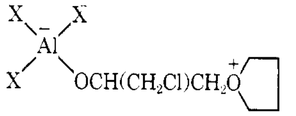
(3) T. Ueshima, T. Fujii, T. Saegusa, and J. Furukawa, *Macromol. Chem.*, **98**, 58 (1966).

(4) H. Imai, T. Saegusa, S. Matsumoto, T. Tadasa, and J. Furukawa, *ibid.*, **102**, 222 (1967).

without being interrupted by chain termination or chain transfer. The ethyl group of the >AlEt group has a nucleophilic reactivity, which might terminate the polymerization through its reaction with the cationic propagating species. The absence of such termination by the >AlEt group, however, has been confirmed in the present study. The data of the THF polymerization in Table II also show the linear relationship between per cent conversion and the molecular weight of product polymer. These results are compatible with a mechanism of stepwise addition without chain transfer.

In our previous study the THF polymerization catalyzed by the $AlEt_3$–H_2O–ECH system was stopped short at an early stage by sodium methoxide, and the half-ether of glycol, $HOCH(CH_2Cl)CH_2O(CH_2)_4OCH_3$ (I), was detected and assigned to the cyclic trialkyloxonium ion of the initiating species.[5] Beside the

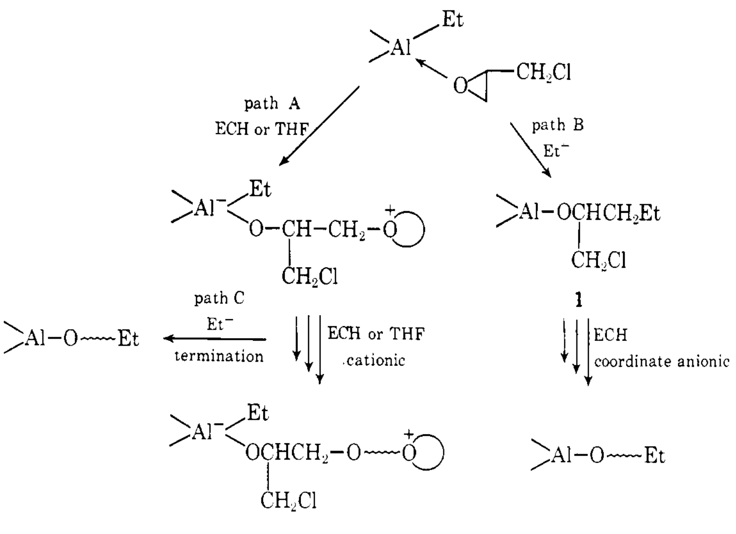


X = Et or –O–

alcohol I, no species which would be derived by the nucleophilic transfer of an ethyl group from aluminum was detected in the short stopping mixture.

In the THF–ECH copolymerization (monomer ratio 1:1), about 5% of the >AlEt group had reacted after 5 hr copolymerization. In the THF–ECH copolymerization, two modes of polymerizations have been assumed.[6] One is the cationic mechanism (Scheme I, path A) to give the THF–ECH copolymer. The other is the coordinate anionic mechanism (path B), giving crystalline ECH homopolymer, which is caused by aluminum alkoxide species **1** produced by the reaction of the >AlEt group and ECH. In the present study, both the THF–ECH copolymer and crystalline ECH homopolymer were actually isolated. In our previous study, it was shown that the aluminum alkoxide species was produced even at an early stage of polymerization.[6] The observed decrease in the >AlEt group (about 5%) may be ascribed to the formation of such aluminum alkoxide species as well as to the termination of the cationic copolymerization by the Et transfer to the propagating chain end (path C). The absence of reaction of the >AlEt group in the THF homopolymerization is ascribed to a very small amount of ECH added as "promoter."[5]

SCHEME I
THF–ECH Copolymerization



In the ECH homopolymerization with the $AlEt_3$–H_2O (2:1) system, there is a pronounced decrease of the >AlEt group. In this polymerization, cationic and coordinate anionic are also considered. The acetone-insoluble, crystalline polymer of ECH was probably produced by a coordinate anionic catalyst of aluminum alkoxide which was formed *in situ* by the reaction of the >AlEt group and ECH. The products of the reactions of the >AlEt group with ECH had been isolated in our previous study.[6] In the cationic polymerization of IBVE with the $AlEt_3$–H_2O (1:1) system, the >AlEt group of the catalyst remained intact. It is of interest to note that the propagating species of the carbonium ion does not react with a nucleophile of the >AlEt group.

Experimental Section

Reagents. $AlEt_3$. The commercial reagent was purified by vacuum distillation under nitrogen, bp 59.5° (1 mm).

THF. The commercial reagent was treated successively with potassium hydroxide pellets, with sodium metal and with disodium benzophenone and finally distilled under nitrogen over sodium–potassium alloy, bp 65.8°.

ECH. The commercial reagent was refluxed over calcium hydride and distilled under nitrogen, bp 117°.

IBVE. The commercial reagent was thoroughly washed with 20% aqueous sodium hydroxide solution, distilled over sodium hydroxide pellets, and finally distilled over sodium metal, bp 83.5°.

CH_2Cl_2. The commercial reagent was treated with concentrated sulfuric acid, washed with an aqueous solution of sodium hydroxide and then with water, dried over calcium hydride and distilled, bp 40°.

Apparatus. The apparatus for the measurement of ethane gas volume consisted of a 100-ml flask equipped with a reflux condenser, a 5-ml dropping funnel, and a septum inlet. The top of the condenser was connected to a 1 l. gas

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(5) T. Saegusa, S. Matsumoto, and T. Ueshima, *Macromol. Chem.*, **105**, 132 (1967).

(6) T. Saegusa, T. Ueshima, and S. Tomita, *ibid.*, **107**, 131 (1967).

buret *via* a 20-ml trap immersed in a Dry Ice–methanol bath. The gas buret was filled with a salt solution which had been saturated with ethane gas. The accuracy of reading of gas buret was within 0.1 ml.

General Procedure. Quantitative Analysis of the >AlEt Group. The >AlEt group was quantitatively determined from the volume of ethane gas which evolved in the hydrolytic decomposition of the system with sulfuric acid or with alkali. The reaction system containing 10–20 mmol of the $AlEt_3$–H_2O system in 20 ml of solvent, which had been saturated with ethane gas prior to the polymerization, was treated with 5 ml of 6 N H_2SO_4 at room temperature or with 5 ml of 1 N NaOH solution at reflux temperature. This analytical procedure has been verified by a reference experiment using pure $AlEt_3$ as the sample. The amounts of ethane gas evolved in two runs of the acid decomposition in THF were, respectively, 100.3 and 99.0% of the calculated one, and those in two runs of CH_2Cl_2 were 99.3 and 99.7%.

In the polymerization of IBVE, the hydrolytic decomposition was carried out with 5 ml of a 1 N NaOH solution at reflux temperature for 1 hr, because the addition of acid to the polymerization system caused difficulties due to the polymerization of the remaining vinyl ether monomer. Two reference runs of alkaline decomposition employing $AlEt_3$ as the standard sample evolved 99.2 and 98.0%, respectively, of the calculated amount of ethane gas.

Preparation of the $AlEt_3$–H_2O System. A small ampoule of $AlEt_3$ was placed in a THF, CH_2Cl_2, or THF–CH_2Cl_2 mixture containing the desired amount of water. The solvent had been saturated with ethane gas. The system was cooled to −78° and the ampoule of $AlEt_3$ was broken by means of a magnetic stirrer. The $AlEt_3$–H_2O system was allowed to warm gradually to the refluxing temperature and was refluxed for 1 hr. Then the system was cooled to room temperature. The ethane gas evolved by the $AlEt_3$–H_2O reaction was measured. The amount of ethane gas evolved in the $AlEt_3$–H_2O (about 2:1) reaction and of the remaining >AlEt group is shown in Table I. It is noted that 1 mol of water produces almost quantitatively 2 mol of ethane.

Polymerization of THF. The $AlEt_3$–H_2O (2:1) system was prepared in 20 ml of THF. At 0°, a small amount of ECH (10 mol % of $AlEt_3$ used in the preparation of the catalyst system) was added through the septum inlet. Polymerization started immediately. After a desired period of polymerization, the >AlEt group was determined by gasometry of ethane evolved in the acid hydrolysis. It was found that the solubility of ethane gas in the polymerization system was decreased by the formation of polymer. The decrease of solubility of ethane was approximately estimated in a separate gasometry determination, in which a definite amount of the THF polymer as well as 5 ml of 6 N H_2SO_4 were dissolved in ethane-saturated THF and the increase of the ethane gas volume was measured. The correction of the volume of the ethane gas was 4.0 ml at a conversion of 8.0% (polymerization time 20 min), 5.5 ml at 14.2% (40 min), and 8.0 ml at 26.6% (60 min). These corrections have been made to the data in Table II.

The THF polymer was isolated by evaporation of the polymerization system and dissolved in benzene. The benzene solution was centrifuged and finally evaporated *in vacuo*. The solution viscosity of the polymer was measured in ethyl acetate at 30°, and the molecular weight was calculated from the intrinsic viscosity (100 ml/g) according to the equation[7]

$$\log [\eta] = -3.375 \times 0.654 \log \overline{M}_v$$

THF–ECH Copolymerization. The $AlEt_3$–H_2O (2:1) system was prepared in a mixture of CH_2Cl_2 (20 ml) and THF (12.3 ml). At 0°, 11.7 ml of ECH was added to the mixture through the septum inlet to initiate the copolymerization. The >AlEt group in the polymerization system was analyzed by the same procedure as that in the THF polymerization. The decrease of ethane solubility during the progress of copolymerization was estimated, using the ECH–THF copolymer prepared separately under the same conditions. The decrease of the ethane solubility was estimated to be 0.0 ml at 3.0% of conversion (reaction time 20 min), 0.5 ml at 4.5% (60 min) and 6.0 ml (300 min).

In order to avoid extraneous polymerization of ECH caused by H_2SO_4, the polymeric product was prepared in a separate run under the same reaction conditions. The polymeric product freed from solvent and monomers by evaporation was dissolved in hot dioxane. The dioxane solution was centrifuged, and finally evaporated *in vacuo*. The polymeric product was extracted in a large quantity of acetone. In accord with our previous study,[6] the acetone-soluble portion was shown to be the ECH–THF copolymer and the acetone-insoluble portion was the crystalline homopolymer of ECH.

Polymerization of ECH. The $AlEt_3$–H_2O (2:1) system was prepared in 20 ml of CH_2Cl_2, to which 24 ml of ECH was added at 0°. After 1 hr, the polymerization was terminated by the addition of 5 ml of 6 N H_2SO_4. The >AlEt group was analyzed as before. The correction for the decrease of the ethane solubility was 12.5 ml at a conversion of 71.5%. The polymer was fractionated into an acetone-soluble (amorphous) and acetone-insoluble (crystalline) portion at room temperature.

Polymerization of IBVE. For the IBVE polymerization, the catalyst activity of $AlEt_3$–H_2O appeared at the H_2O–$AlEt_3$ ratio above 1.0. The $AlEt_3$–H_2O ($\backsim$1:1) system was prepared in 20 ml of CH_2Cl_2 and cooled at −78°, to which 20 ml of IBVE was added. The >AlEt group was analyzed by the hydrolytic decomposition by 1 N NaOH aqueous solution before and after polymerization for 1 hr. The correction for the decrease of the ethane solubility was 9.0 ml.

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(7) M. Kurata, H. Uchiyama, and K. Kamada, *Makromol. Chem.*, **88**, 281 (1965).