

## Alkylaluminum-Lewis Base Complexes as Initiators of Vinyl Polymerization

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### Synopsis

Complexes of aluminum alkyls with Lewis bases catalyze the polymerization of vinyl chloride. Triethylaluminum is most effective, but other compounds of type  $R_3Al$ ,  $R_2AlCl$ ,  $R_2AlH$ , and  $LiAlR_4$  are operable. Dialkylmagnesiums are active, but Grignard reagents, as well as a number of other metal alkyls are inactive. Among Lewis bases, tetrahydrofuran (THF) and tetrahydropyran give the best yields of poly(vinyl chloride). Oxygen bases, such as ethers and esters, are more effective than nitrogen bases, e.g., tertiary amines. Cyclic compounds are better than acyclic ones. The polymerization occurs in a variety of hydrocarbon, chlorinated hydrocarbon, or ether solvents, but especially well in  $CCl_4$ . Radical polymerization is probably initiated through the reaction  $R_3Al:Base + CCl_4 \rightarrow R_2AlCl:Base + R\cdot + Cl_3C\cdot$ , to form trichloromethyl radical.

### INTRODUCTION

In an investigation of the polymerization of vinyl chloride by trialkylaluminum compounds, findings showed that a complex of triethylaluminum ( $Et_3Al$ ) with tetrahydrofuran (THF) is an active polymerization catalyst and that the polymerization rate is accelerated by carbon tetrachloride. This phenomenon was studied in considerable detail to elucidate the nature of the initiation reaction and to study the effect of several variables on the polymerization.

More recently, several publications have described the use of alkylboron<sup>1-6</sup> and alkylaluminum<sup>1,7-12</sup> compounds as radical initiators of vinyl polymerization. Generally a coagent is required; thus, trialkylboron compounds are catalysts only in the presence of oxygen<sup>1,13</sup> or of other materials<sup>2,14</sup> capable of generating a peroxyboron compound. Trialkylaluminum compounds have been claimed to initiate polymerization of polar monomers alone<sup>12</sup> and in the presence of benzoquinone,<sup>2</sup> transition metal compounds,<sup>7-10</sup> or boron trifluoride etherate.<sup>11</sup> Our work with the alkylaluminum-Lewis base complexes is described here, inasmuch as evidence indicates that the initiation reaction is different from those already described in the literature.

## EXPERIMENTAL

### Materials

Vinyl chloride (Matheson C.P.) was distilled from a cylinder and used without further purification.

Aluminum alkyls were Hercules Powder Company samples; they are now available commercially from the Texas Alkyls Company. Triethylboron was obtained from the Rocky Mountain Chemical Company.

Tetrahydrofuran (THF) and tetrahydropyran were dried over potassium hydroxide and distilled from lithium aluminum hydride or from triisobutylaluminum (TIBAL). Chloroform was washed with concentrated sulfuric acid, then with water, dried over calcium chloride and distilled. Dioxane, ether, and *n*-heptane were dried over sodium. Troeger's base was prepared according to the procedure of Goecke.<sup>15</sup> Other solvents and complexing agents were reagent-grade chemicals used without further purification.

### Polymerization Procedure

Polymerizations were run in 250-ml. pressure bottles capped by crown caps with self-sealing Buna rubber liners. Except where noted, about 20–25 ml. of solvent, usually so chosen that the total diluent would be 25 ml. after catalyst solutions and slurries were added, was placed in the bottle. After capping, the bottle was evacuated for 30–60 sec., then repressured to 10–20 psig with N<sub>2</sub> and evacuated for two cycles. The evacuated bottle was charged with 10 g. of vinyl chloride, unless otherwise noted, and placed in a rotating tumbler in a constant temperature bath at 30 or 60°C. for at least 30 min. The catalyst, generally prepared by adding complexing agent to metal alkyl in a separate capsule under nitrogen, was then injected hypodermically. Solid complexing agents were added to the bottle, with the diluent, before sealing. This procedure was also used when a liquid complexing agent coagulated a suspension of aluminum compound, such as AlH<sub>3</sub> or LiAlH<sub>4</sub>. Metal alkyls were added as solutions or as ball-milled suspensions in heptane.

The polymerizations were quenched with 2–5 ml. of methanol or ethanol, the contents of the bottle were mixed with 150 ml. of methanol or ethanol, filtered, dried in a vacuum oven or vacuum desiccator overnight and weighed (crude product). The crude product was purified by dissolving in 15–20 ml. of THF per gram of polymer, filtering the solution to remove inorganic and crosslinked material, and precipitating with 4–5 volumes of methanol or heptane.

Viscosities were determined on 0.1% solutions in cyclohexanone at 25 or 135°C., and are reported as reduced specific viscosities,  $\eta_{red} = \eta_{sp}/c$ .

## RESULTS

Table I lists the effect of varying the structure of the organometallic compound complexed with THF on the polymerization of vinyl chloride

in  $\text{CCl}_4$ . Good activity was observed generally with compounds of the type  $\text{AlR}_3$  and  $\text{LiAlR}_4$ , where R is alkyl, aryl or H; catalyst solubility was not a necessary criterion for activity. Diethylaluminum chloride ( $\text{Et}_2\text{AlCl}$ ) was a fairly good catalyst, but ethylaluminum dichloride ( $\text{EtAlCl}_2$ ) and aluminum trichloride were essentially inert. Alkylaluminum alkoxides, either complexed or uncomplexed, showed little activity. Dialkylmagnesium compounds, including the methylenemagnesium polymer,<sup>16</sup> were active, but diphenylmagnesium and Grignard reagents were not. Weak alkylating agents, such as tetraethyltin and diethylmercury were inert.

In Table II are shown the results of polymerizing vinyl chloride in  $\text{CCl}_4$  with  $\text{Et}_3\text{Al}$  and different complexing agents. The complexing agent appears to serve several functions: it greatly accelerates the rate of

TABLE I  
Vinyl Chloride Polymerization by Organometallic-THF Complexes in Carbon Tetrachloride<sup>a</sup>

Organometallic component	Complex, mmole	Monomer, g.	Conversion, %	$\eta_{\text{red}}$
$(\text{CH}_3)_3\text{Al}$	4	10	6	0.14 <sup>b</sup>
$(\text{C}_2\text{H}_5)_3\text{Al}$	4	10	100	0.20 <sup>b</sup>
$(i\text{-C}_4\text{H}_9)_3\text{Al}$	4	10	60	0.27 <sup>b</sup>
$(n\text{-C}_8\text{H}_{17})_3\text{Al}$	4	10	55	
$(\text{C}_6\text{H}_5)_3\text{Al}^c$	3	7.5	30	
$(i\text{-C}_4\text{H}_9)_2\text{AlH}$	4	10	33	
$\text{AlH}_3^c$	1.6	7.5	18	0.31 <sup>d</sup>
$(\text{C}_2\text{H}_5)_2\text{AlCl}$	2.4	7.5	35	0.46 <sup>d</sup>
$\text{C}_2\text{H}_5\text{AlCl}_2$	2.4	7.5	1	0.31 <sup>d</sup>
$\text{AlCl}_3$	3.5	7.5	0	
$(\text{C}_2\text{H}_5)_2\text{AlOC}_2\text{H}_5$	2	7.5	3	0.38 <sup>d</sup>
$(\text{C}_2\text{H}_5)_2\text{AlOC}_2\text{H}_5^e$	2	7.5	2	
$(\text{C}_2\text{H}_5)_2\text{AlO-tert-C}_4\text{H}_9$	2	7.5	2.5	0.44 <sup>d</sup>
$\text{C}_2\text{H}_5\text{Al}(\text{OC}_2\text{H}_5)_2$	2	7.5	1.2	
$\text{C}_2\text{H}_5\text{Al}(\text{OC}_2\text{H}_5)_2^e$	2	7.5	2	0.38 <sup>d</sup>
$\text{LiAl}(n\text{-C}_4\text{H}_9)_4$	4	10	21	0.17
$\text{LiAlH}_4^c$	3	7.5	83	
$n\text{-C}_4\text{H}_9\text{Li}$	1	10	0.7	
$n\text{-C}_4\text{H}_9\text{Li}^e$	0.4	10	1.7	0.33
$(\text{CH}_3)_2\text{Mg}$	4	10	41	0.20
$(\text{CH}_2\text{Mg})_n$	4	10	52	0.11
$(n\text{-C}_{10}\text{H}_{21})_2\text{Mg}$	4	10	11	0.20
$(\text{C}_6\text{H}_5)_2\text{Mg}$	4	10	0	
$\text{C}_2\text{H}_5\text{MgCl}$	4	10	0	
$(\text{C}_2\text{H}_5)_4\text{Sn}$	4	10	0	
$(\text{C}_2\text{H}_5)_2\text{Hg}$	4	10	0	
$(\text{C}_6\text{H}_5)_3\text{As}$	4	10	0	
$(\text{C}_6\text{H}_5)_3\text{Sb}$	4	10	0	

<sup>a</sup> Solution of 10 g. of vinyl chloride in 25 ml. of  $\text{CCl}_4$  at 30°C. for 20 hr.

<sup>b</sup> In cyclohexanone at 135°C. 0.1%.

<sup>c</sup> Catalyst insoluble in reaction medium.

<sup>d</sup> In cyclohexanone at 25°C. 0.1%.

<sup>e</sup> Uncomplexed.

TABLE II  
Effect of Lewis Bases on Polymerization of Vinyl Chloride with Triethylaluminum<sup>a</sup>

Base	Complex, mmole	Conversion, %	$\eta_{red}^b$
None	3	6.4 <sup>c</sup>	
Diethyl ether	3	26	0.22
Diisopropyl ether	3	21	
Trimethylene oxide	4	24	
Tetrahydrofuran	3	90	0.13
Tetrahydropyran	3	84	0.18
Anisole <sup>d</sup>	3	9	
<i>p</i> -Methylanisole <sup>d</sup>	3	12	
Diphenyl ether <sup>e</sup>	4	20 <sup>e</sup>	
Ethyl acetate	3	58	0.16
Methyl benzoate <sup>d</sup>	3	17	
Methyl <i>m</i> -chlorobenzoate <sup>d</sup>	3	12	
$\gamma$ -Butyrolactone	3	85	0.13
Triethylamine	3	26	0.42
Pyridine <sup>d</sup>	3	37	0.15
2,4-Dimethylpyridine <sup>d</sup>	3	42	0.24
2,6-Dimethylpyridine <sup>d</sup>	3	36	
2-Chloropyridine <sup>d</sup>	3	70	0.18
Troeger's base <sup>d</sup>	3	23	0.22
Triphenylphosphine <sup>d</sup>	3	49	
Succinic anhydride	3	5	
Dimethyl sulfoxide	4	11	
Thiophene <sup>e</sup>	5	14 <sup>e</sup>	

<sup>a</sup> Solution of 10 g. of vinyl chloride in 25 ml. of CCl<sub>4</sub> at 30°C. for 20 hr.

<sup>b</sup> In cyclohexanone at 25°C., 0.1%.

<sup>c</sup> Product black and insoluble.

<sup>d</sup> Complex prepared *in situ*, with complexing agent added before alkyl.

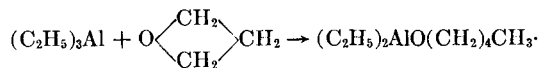
<sup>e</sup> Polymerization at 60°C.

polymerization, it prevents the polymer degradation which occurs with uncomplexed Et<sub>3</sub>Al, and it moderates the reaction of Et<sub>3</sub>Al with CCl<sub>4</sub>. Judging by initial pressure drop, the Et<sub>3</sub>Al-THF complex initiates polymerization at about five times the rate of the uncomplexed alkyl. This polymerization continues for a long time, whereas in the absence of complexing agent, the polymerization dies rapidly.

The small amount of polymer initially formed with uncomplexed Et<sub>3</sub>Al appears normal if isolated within a few hours of catalyst addition. If isolated only after the usual 16-20 hr., the polymer is dark and insoluble. Similar results were obtained with Et<sub>2</sub>AlCl.

A number of Lewis bases were found to be operable, consisting mostly of ethers, esters, and tertiary amines. In any one class, the activity appeared to be a function of the complexing ability expected from both electrical and steric effects. Thus, with ethers, the order of activity was cyclic ethers > dialkyl ethers > aryl ethers. However, in the cyclic ethers, the expected order was not observed. Although the order of basicity is trimethylene oxide > tetrahydrofuran > tetrahydropyran,<sup>17</sup> trimethylene

oxide gave a poor catalyst. This anomaly is probably a result of ring opening by the  $\text{Et}_3\text{Al}$  [eq. (1)].



Dialkylaluminum alkoxides are known to be poor catalysts (Table I), i.e.,  $\text{R}_2\text{AlOR}'$  cannot be substituted for  $\text{R}_3\text{Al:OR}_2'$ . Some polymerization of trimethylene oxide could also have occurred.<sup>18</sup>

With esters, the order of activity followed fairly well the expected order of basicity:  $\gamma$ -butyrolactone > ethyl acetate > methyl benzoate > methyl *m*-chlorobenzoate. With tertiary amines, it did not. Thus, 2,6-dimethylpyridine was more active than triethylamine in spite of its being both a weaker and a more highly hindered base. Similarly, 2-chloropyridine was more active than pyridine, yet its base strength would be expected to be lower. Oxygen-containing compounds in general were better activators than tertiary amines, in spite of the greater basicity of the latter.

Polymerization was not limited to  $\text{CCl}_4$ , as shown in Table III. It gave the fastest rate and the lowest viscosity polymer with a  $\text{Et}_3\text{Al}$ -THF catalyst, but reasonable yields of polymer of much higher molecular weight were obtained in *n*-heptane and in ethylene dichloride. Chloroform gave a moderate amount of polymer of low molecular weight, while benzene, methylene chloride, THF, and dioxane were poor diluents for polymerization. Bulk polymerization gave very little polymer of very high molecular

TABLE III  
Polymerization of Vinyl Chloride with a Triethylaluminum-THF Catalyst in Various Diluents<sup>a</sup>

Diluent	Initiator, mmole	Conversion, % <sup>b</sup>	$\eta_{\text{red}}$
Carbon tetrachloride	5.3	81	0.18 <sup>c</sup>
	2.7	82	0.14 <sup>d</sup>
<i>n</i> -Heptane	5.3	24	0.29 <sup>c</sup>
Ethylene dichloride	4	38	0.66 <sup>c</sup>
Methylene chloride	5.3	6	0.30 <sup>c</sup>
Chloroform <sup>e</sup>	5.3	27	0.16 <sup>c</sup>
Benzene	2.7	1.3	0.57 <sup>d</sup>
Tetrahydrofuran	2.7	6	0.22 <sup>d</sup>
Dioxane	4	12	0.46 <sup>c</sup>
None <sup>f</sup>	2.7	3.9	1.52 <sup>d</sup>

<sup>a</sup> Solution of 10 g. of monomer in 25 ml. of total diluent, including *n*-heptane added with the catalyst (1-1.35*M* solution of  $\text{Et}_3\text{Al}$ -THF complex in *n*-heptane).

<sup>b</sup> In 20 hr. at 30°C.

<sup>c</sup> In cyclohexanone at 135°C., 0.1%.

<sup>d</sup> In cyclohexanone at 25°C., 0.1%.

<sup>e</sup> Polymerization at 25°C.

<sup>f</sup> Bulk polymerization of 31 g. of vinyl chloride, except for 2.0 ml. of *n*-heptane added with the initiator.

weight. Bromotrichloromethane gave very rapid reaction to 1:1 and 2:1 vinyl chloride- $\text{BrCCl}_3$  telomers.

The addition of catalytic quantities of  $\text{CCl}_4$  to other solvents often resulted in a considerable increase in rate with only a moderate drop in viscosity (Table IV). The effect was most pronounced in initially poor polymerizations. Thus, where bulk polymerization gave a 4% yield of polymer with  $\eta_{\text{red}}$  of 1.52, the addition of 5 mmole of  $\text{CCl}_4$  resulted in an 85% yield of polymer with  $\eta_{\text{red}}$  of 1.37.

TABLE IV  
Effect of Carbon Tetrachloride on the Polymerization of Vinyl Chloride with Triethylaluminum-THF Catalyst in Various Diluents<sup>a</sup>

Diluent	$\text{CCl}_4$ , mmole	Conversion, %	$\eta_{\text{red}}^b$
<i>n</i> -Heptane	0	5.4	0.59
	1	64	0.40
	3	60	0.44
	10	68	0.42
Methylene chloride	0	2.7	0.53
	1	58	0.48
	10	92	0.33
	30	91	0.31
Benzene	0	3	0.57
	10	52	0.37
THF	0	6	0.22
	20	40	0.16
None <sup>c</sup>	0	3.9	1.52
	5	85	1.37

<sup>a</sup> Solution of 10 g. of vinyl chloride in 25 ml. of total diluent at 30°C. for 20 hr., with 2.7 mmole of  $\text{Et}_3\text{Al}$ -THF complex added as a 1.3*M* solution in *n*-heptane.

<sup>b</sup> In cyclohexanone at 25°C., 0.1%.

<sup>c</sup> No solvent, except for 2 ml. of *n*-heptane introduced with the initiator; 34 g. monomer.

Solutions of the  $\text{Et}_3\text{Al}$ -THF complex in *n*-heptane did not change in activity on standing at room temperature, although, on occasion, a precipitate formed. In  $\text{CCl}_4$ , however, activity was lost quite rapidly, the catalyst being essentially inactive after seven days. Thus, there can be little doubt that  $\text{CCl}_4$ , when present, is involved in the polymerization.

Temperature and initiator concentration had the expected effects on polymerization. An increase in temperature increased the conversion to polymer and lowered molecular weight (Table V). However, at 60°C. the catalyst was apparently destroyed, since conversion was lower than at 30°C. Similarly, an increase in initiator concentration increased polymerization rate and lowered molecular weight (Table VI). Since molecular weight was found to be constant throughout a polymerization, chain transfer to initiator appears to take place.

Nitric oxide, even at very low levels, inhibited the polymerization of vinyl chloride in  $\text{CCl}_4$  by  $\text{Et}_3\text{Al}$  complexed with THF or with pyridine

(Table VII). That the inhibition was not the result of destroying the complex, was shown by treating the complex with nitric oxide and then degassing the solution before adding it to monomer; polymerization was normal. *p*-Benzoquinone, on the other hand, inhibited polymerization only when present in a molar concentration greater than that of the initiator complex. Apparently, the quinone can displace the Lewis base, and the

TABLE V  
Effect of Temperature on Polymerization of Vinyl Chloride with Triethylaluminum-THF<sup>a</sup>

Diluent	Temp., °C.	Time, hr.	Conversion, %	$\eta_{red}^b$
Carbon tetrachloride	-15	46	14	0.34
	30	20	100	0.20
	60	19	79	0.12
<i>n</i> -Heptane	-15	46	15	0.39
	30	20	93	0.27
	60	19	73	0.27

<sup>a</sup> Conditions: 10 g. of vinyl chloride with 4 mmole Et<sub>3</sub>Al-THF in 25 ml. of solvent for 20 hr.

<sup>b</sup> In cyclohexanone at 135°C., 0.1%.

TABLE VI  
Effect of Initiator Concentration on Vinyl Chloride Polymerization<sup>a</sup>

Diluent	Initiator, mmoles	Initial rate, psi/min.	Conversion, %	$\eta_{red}^b$
Carbon tetrachloride	0.5	0.005	3.5	0.28
	1	0.013	45	
	2	0.037	70	0.20
	4	0.09	86	0.16
	8	0.24	78	0.11
Ethylene dichloride	0.5		1.3	1.04
	1		7	0.92
	2		13	0.82
	3		18	0.79
	4		38	0.66

<sup>a</sup> Solution of 10 g. of vinyl chloride in 25 ml. of diluent with triethylaluminum-THF initiator for 20 hr. at 30°C.

<sup>b</sup> In cyclohexanone at 25°C., 0.1%.

resulting complex is not an inhibitor. Traces of styrene did not affect the ultimate polymerization of vinyl chloride, but caused a considerable induction period before polymerization started.

Because of the similarity between trialkylaluminum and trialkylboron compounds, the polymerization of vinyl chloride, using the latter as catalyst, was investigated. As is evident from Table VIII, the two initiators are quite different in their action; triethylboron initiation is not improved

TABLE VII  
Effect of Inhibitors on the Polymerization of Vinyl Chloride in Carbon Tetrachloride<sup>a</sup>

Initiator		Inhibitor		Conversion, %
Compound	Amt., mmole	Compound	Amt., mmole	
Et <sub>3</sub> Al-THF	4	—	—	85
	4	NO	0.8	14
	4	NO <sup>b</sup>	1.0	85
	4	Quinone	2	71
	1.5	Quinone	2	1
	1.5	—	—	89
	2.7	Styrene	1	65 <sup>c</sup>
Et <sub>3</sub> Al-C <sub>6</sub> H <sub>5</sub> N	4	—	—	41
	4	NO	0.8	3
Et <sub>3</sub> Al-NEt <sub>3</sub>	3	—	—	26
	3	Quinone	1	18
	1.5	Quinone	2	2.9

<sup>a</sup> Solution of 10 g. vinyl chloride in 25 ml. of CCl<sub>4</sub> for 20 hr. at 25–30°C.

<sup>b</sup> Initiator reacted with NO for 1 hr. at 60°C., then degassed.

<sup>c</sup> Induction period >1 hr. before polymerization started.

TABLE VIII  
Vinyl Chloride Polymerization with Triethylboron Initiators<sup>a</sup>

Initiator	CCl <sub>4</sub> , mmole	O <sub>2</sub> , mmole	Reaction time, hr.	Conversion %	
Et <sub>3</sub> B	—	—	1.1	4	
	5	—	1.1	10	
	—	0.25	1.1	15	
	5	0.25	1.1	24	
	—	—	19	1.3	
	5	—	19	2.4	
	—	0.25	19	32	
	5	0.25	19	25	
	Et <sub>3</sub> B-THF	—	—	19	3.5
		5	—	19	0.4
—		0.25	19	9	
5		0.25	19	7	

<sup>a</sup> Solution of 4–5 g. of vinyl chloride in 15 ml. of heptane at 22°C., with 0.5 mmole of Et<sub>3</sub>B initiator.

by CCl<sub>4</sub>, either in the presence or absence of oxygen, nor does THF improve the polymerization.

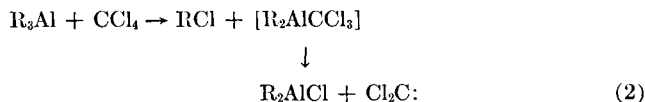
## DISCUSSION

All the evidence points to a free-radical process for the polymerization of vinyl chloride by alkylaluminum compounds complexed with Lewis bases. Thus, the inhibition by nitric oxide and by benzoquinone is typical of radical polymerization. Styrene is known to inhibit the radical poly-

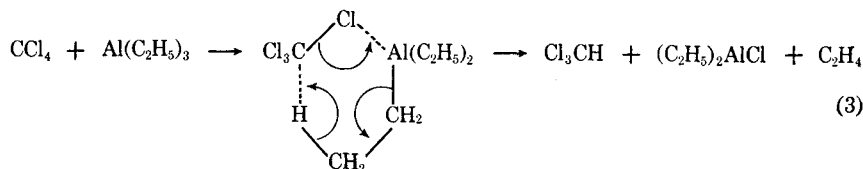


merization of vinyl chloride, and the same phenomenon is encountered here. Similarly, the action of  $\text{CCl}_4$  as a chain-transfer agent to lower molecular weight is typical of radical polymerization.

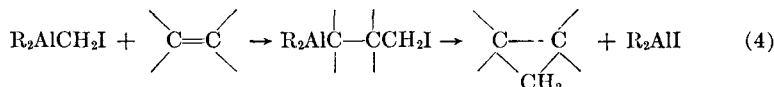
The nature of the reaction between aluminum alkyls and halogenated compounds is uncertain. According to Collette,<sup>19</sup> TIBAL reacts with carbon tetrachloride to give isobutyl chloride and diisobutylaluminum chloride, the mechanism postulated being as shown in eq. (2), where R is isobutyl.



Since the yield of diisobutylaluminum chloride was quantitative, we assumed that it does not react with  $\text{CCl}_4$ . According to Reinheckel,<sup>20</sup> however, both ethylaluminum sesquichloride and  $\text{Et}_3\text{Al}$  explode when a chilled mixture with  $\text{CCl}_4$  is allowed to warm to room temperature. The products with  $\text{CCl}_4$  are chloroform, methylene chloride, and methyl chloride, formed, according to the author, by the route shown in eq. (3).



Miller<sup>21</sup> reacted several halogenated compounds with aluminum alkyls in the presence of unsaturated compounds and showed that cyclopropanes are formed. Hoberg<sup>22</sup> had shown that the addition of  $\text{R}_2\text{AlCH}_2\text{I}$  to olefins to give cyclopropane derivatives does not involve a carbene intermediate, being instead an addition-elimination reaction [eq. (4)].



However, Miller's finding that his alkylaluminum-halogenated compound intermediates react with aromatics to give cycloheptatriene derivatives seems to raise the possibility of carbene intermediates in these reactions.

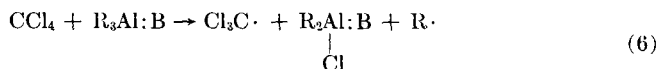
There are several alternatives available to explain the origin of free radicals required to initiate the polymerization. One is to assume the formation of dichlorocarbene from the organometallic and  $\text{CCl}_4$ . This might then react with additional  $\text{CCl}_4$  to form two trichloromethyl radicals in an energetically favored reaction [eq. (5)].



Urry and Eiszner<sup>23</sup> have postulated a similar reaction between carbene and  $\text{CCl}_4$  to explain the formation of pentaerythrityl tetrachloride from

diazomethane and  $\text{CCl}_4$ . This, however, would not explain initiation in the absence of chlorinated solvents, since it appears quite unlikely that carbene would be formed from vinyl chloride or from the polymer.

A more reasonable assumption would be that the reaction between the organometallic and a halogenated compound takes a different course in the presence of a Lewis base, perhaps leading directly to free radicals by the reactions (6) and (7).



The fact that  $\text{R}_2\text{AlCl}$  is also an initiator indicates that it can undergo the same reaction to give  $\text{RAlCl}_2$ , but that the latter does not react with  $\text{CCl}_4$  to form radicals. The order of activation corresponds with that expected for radical formation, i.e.,  $\text{BrCCl}_3 > \text{CCl}_4 > \text{CHCl}_3 > \text{CH}_2\text{Cl}_2$ . Presumably, in the absence of a halogenated solvent, vinyl chloride itself would have to form the initiator by a reaction similar to that shown above.

A third possibility is that polymerization is initiated by traces of oxygen, as it is with trialkylborons. However, as shown in Table VIII, the two systems act quite differently. Thus,  $\text{CCl}_4$  has little, if any, effect on a triethylboron system, and tetrahydrofuran decreases, if anything, the yield of polymer in the presence of oxygen. The fact that only very low yields of polymer are obtained with  $\text{Et}_3\text{B}$  is a good indication that only minimal amounts of oxygen are introduced into the system with the technique used in the polymerizations. The stability of the catalyst prepared from  $\text{Et}_3\text{Al}$  and THF argues against catalysis by peroxide in the ether.

**Note:** Since the submission of this manuscript, Razuvaev et al. have described the polymerization of vinyl chloride by alkylaluminum and alkyl halides, including  $\text{CCl}_4$ .<sup>24</sup> They mentioned that complexing agents promoted polymerization but reduced yields, in contrast to our findings that complexing bases increased rates, yields, and polymer purity.

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### Résumé

Les complexes des alcoylaluminium avec les bases de Lewis catalysent la polymérisation du chlorure de vinyle. Le triéthylaluminium est le plus efficace mais d'autres composés du type  $R_3Al$ ,  $R_2AlCl$ ,  $R_2AlH$  et  $LiAlR_4$  sont efficaces. Le dialcoylmagnésium est actif mais les réactifs de Grignard, de même qu'un grand nombre d'autres organométalliques sont inactifs. Parmi les bases de Lewis, le tétrahydrofurane (THF) et le tétrahydropyrane fournissent le meilleur rendement en chlorure de polyvinyle. Les bases oxygénées telles que les éthers et esters étaient plus efficaces que les bases azotées telles que les amines tertiaires. Les composés cycliques sont meilleurs que les acycliques. La polymérisation se passe dans une grande variété d'hydrocarbure, de carbures halogénés, de solvants étherés, mais particulièrement bien dans le tétrachlorure de carbone. La polymérisation radicalaire est probablement initiée au moyen de la réaction  $R_EAl: \text{base} + CCl_4 \rightarrow R_2AlCl: \text{base} + R \cdot + Cl_3C \cdot$ , avec production de radicaux trichlorométhyles.

### Zusammenfassung

Komplexe aus Aluminiumalkylen und Lewis-Basen katalysieren die Vinylchlorid-polymerisation. Triäthylaluminium ist am wirksamsten, doch auch andere Verbindungen vom Typ  $R_3Al$ ,  $R_2AlCl$ ,  $R_2AlH$  und  $LiAlR_4$  sind brauchbar. Magnesiumdialkyle sind aktiv, Grignardverbindungen sowie eine Anzahl anderer Metallalkyle jedoch inaktiv. Unter den Lewis-Basen geben Tetrahydrofuran (THF) und Tetrahydropyran die besten Ausbeuten an Polyvinylchlorid. Sauerstoffbasen, wie Äther und Ester, sind wirksamer als Stickstoffbasen, z.B. tertiäre Amine. Cyclische Verbindungen sind besser geeignet als acyclische. Die Polymerisation findet in einer Vielzahl von Kohlen-

wasserstoff-, Chlorkohlenwasserstoff- oder Atherlösungsmitteln statt, besonders gut aber in  $\text{CCl}_4$ . Die radikalische Polymerisation wird wahrscheinlich durch die Reaktion  $\text{R}_3\text{Al}:\text{Base} + \text{CCl}_4 \rightarrow \text{R}_2\text{AlCl}:\text{Base} + \text{R}\cdot + \text{Cl}_3\text{C}\cdot$ , welche ein Trichlormethylradikal liefert, gestartet.

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