

# Low-Pressure Polymerization of Ethylene. II

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## SYNOPSIS

This paper presents the kinetic study of polymerization of ethylene with  $\text{VOCl}_3$  and aluminum alkyls such as  $\text{Et}_3\text{Al}$  and  $\text{Et}_2\text{AlCl}$ . The effect of various parameters like the  $[\text{Al}]/[\text{V}]$  ratio, catalyst concentration, reaction time, temperature, solvents, and additives on rate of the reaction, yield, and molecular weight is reported. Each of these parameters has a remarkable effect on the yield and the rate of polymerization for both catalyst systems. Triethylamine is found to increase the catalyst efficiency and the rate. It is also observed that aliphatic hydrocarbons acted as a better polymerization medium than did the aromatic ones.

## INTRODUCTION

Ethylene polymerization using  $\text{TiCl}_4$  or  $\text{TiCl}_3$  with aluminum alkyls has been studied in great detail.<sup>1-3</sup> Though reports are available for ethylene polymerization using  $\text{VOCl}_3$ ,<sup>4-6</sup> no extensive or systematic study has been reported. This was actually the main motivation for studying the polymerization of olefins with  $\text{VOCl}_3$  and aluminum alkyls. Low-pressure polymerization of propylene using  $\text{VOCl}_3$  and aluminum alkyls has been reported from this laboratory.<sup>7</sup> In the present paper, we report an extensive study carried out at low pressure for the polymerization

of ethylene using  $\text{VOCl}_3$  in combination with triethylaluminum (TEAL) and diethylaluminum chloride (DEAC). The study carried out includes variation of the cocatalyst-to-catalyst ratio, catalyst concentration, aging time of the catalyst, reaction time, and temperature of polymerization and the effect of solvents and additives.

## EXPERIMENTAL

Details of the experimental techniques and polymerization procedure were described in Part I.<sup>7</sup> The

**Table I** Variation of Cocatalyst-to-Catalyst Ratio (System: TEAL +  $\text{VOCl}_3$ )

Sample No.	$[\text{Al}]/[\text{V}]$	[Alkyl] (mol L <sup>-1</sup> )	Yield (g)	Rate $\times 10^2$ (g PE/g $\text{VOCl}_3$ h)
1	0.38	0.971	—	—
2	0.74	1.941	3.425	12.6
3	0.86	2.232	5.420	19.9
4	1.12	2.912	3.339	12.2
5	1.86	4.853	3.234	11.9
6	2.22	5.824	2.656	9.8
7	2.41	6.301	0.983	3.6

*n*-Hexane = 30 mL;  $[\text{VOCl}_3] = 0.0759$  mol L<sup>-1</sup>; reaction time = 90 min; reaction temperature = 303 K; flow rate of ethylene = 35 mL min<sup>-1</sup>.

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**Table II** Variation of Cocatalyst-to-Catalyst Ratio (System: DEAC + VOCl<sub>3</sub>)

Sample No.	[Al]/[V]	[Alkyl] (mol L <sup>-1</sup> )	Yield (g)	Rate × 10 <sup>2</sup> (g PE/g VOCl <sub>3</sub> h)
1	0.53	1.393	0.915	3.37
2	1.06	2.786	4.876	17.95
3	1.33	3.483	2.991	11.01
4	1.86	4.876	1.788	6.58
5	2.66	6.966	1.761	6.48
6	3.20	8.359	0.766	2.82

*n*-Hexane = 30 mL; [VOCl<sub>3</sub>] = 0.0759 mol L<sup>-1</sup>; aging time = 10 min; reaction time = 90 min; reaction temperature = 303 K; flow rate of ethylene gas = 35 mL min<sup>-1</sup>.

flow rate of ethylene gas was maintained at 35 mL min<sup>-1</sup>.

## RESULTS AND DISCUSSION

### Cocatalyst-to-Catalyst Ratio

Cocatalyst-to-catalyst ratio was varied by keeping the amount of VOCl<sub>3</sub> constant and varying the amount of alkyl. The data are presented in Tables I and II.

The optimum conditions can be seen from the above tables. If these results are looked at from another angle, i.e., on the basis of alkyl concentration, a direct correlation between the [Al]/[V] ratio and the alkyl concentration on the yield and, subsequently, on the rate of polymerization can be seen. Only at a specific ratio is maximum yield obtained. This may be because at this ratio the maximum number of active sites are formed that are capable of propagating the polymer chain. At higher alkyl

concentration, there may be a competitive equilibrium between the monomer molecules and the excess alkyl in the solution and this may reduce the yield. Moreover, these alkyls by reversible adsorption on active centers can form temporarily inactive centers. This behavior has been reported by Tait and co-workers.<sup>11</sup> The important point to be noted is that the optimum results are obtained only if a particular sequence of addition of the components is maintained, i.e., solvent, alkyl, VOCl<sub>3</sub>, and additive (if added).

### Catalyst Concentration

Tables III and IV and Figure 1 illustrate the details of the effect of catalyst concentration on the yield and rate of polymerization.

Variation of catalyst concentration was carried out by diluting the reaction mixture with the solvent. From Tables III and IV it can be seen that, even at a narrow range of catalyst concentration, there is an enormous effect on the yield obtained and, hence, on the rate of polymerization. There is a possibility

**Table III** Variation of Catalyst Concentration

Sample No.	[Catalyst] (mol L <sup>-1</sup> )	Yield (g)	Rate × 10 <sup>2</sup> (g PE/g VOCl <sub>3</sub> h)
1	0.115	2.236	8.23
2	0.079	5.482	20.18
3	0.049	6.235	22.95
4	0.041	7.489	27.57
5	0.032	7.624	28.07
6	0.028	5.188	19.10
7	0.025	2.677	9.85
8	0.013	2.132	7.85

[TEAL] = 2.232 mol L<sup>-1</sup>; other conditions are the same as in Table I.

**Table IV** Variation of Catalyst Concentration

Sample No.	[Catalyst] (mol L <sup>-1</sup> )	Yield (g)	Rate × 10 <sup>2</sup> (g PE/g VOCl <sub>3</sub> h)
1	0.081	4.875	17.95
2	0.049	6.527	24.03
3	0.0316	6.896	25.39
4	0.0254	6.002	22.09
5	0.0171	4.316	15.89
6	0.0143	4.168	15.34
7	0.0122	3.902	14.36

[DEAC] = 4.876 mol L<sup>-1</sup>; other conditions are the same as in Table II.

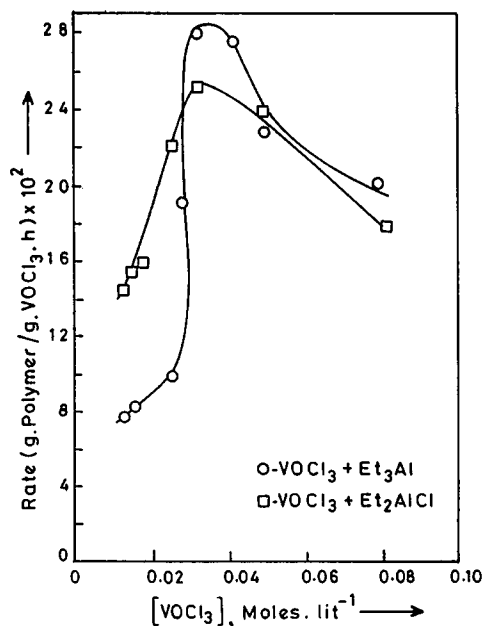


Figure 1 Rate vs. catalyst concentration.

that at higher dilution the agglomerates of the catalyst particles may breakdown and more surface area is created and, moreover, the diffusion of monomer to the active sites is made easier due to the large volume available.

### Aging Time

Aging time of the catalyst was varied from 5 min to 1 h. Results are given in Tables V and VI.

From Tables V and VI it can be seen that the kinetic activity decreases rapidly as a function of the time elapsed from the preparation of the catalyst to its use and, hence, a decrease in the yield and

Table V Variation of Aging Time

Sample No.	Aging Time (min)	Yield (g)	Rate $\times 10^2$ (g PE/g VOCl <sub>3</sub> h)
1	5	4.010	14.76
2	10	5.464	20.11
3	15	5.003	18.42
4	20	3.125	11.50
5	30	3.088	11.37
6	40	2.969	10.93
7	60	2.165	7.97

[TEAL] = 2.232 mol L<sup>-1</sup>; other conditions are the same as in Table I.

Table VI Variation of Aging Time

Sample No.	Aging Time (min)	Yield (g)	Rate $\times 10^2$ (g PE/g VOCl <sub>3</sub> h)
1	5	1.601	5.89
2	10	4.876	17.95
3	15	1.996	7.35
4	30	1.959	7.21
5	50	1.431	5.27
6	70	1.248	4.59

[DEAC] = 4.876 mol L<sup>-1</sup>; other conditions are the same as in Table II.

rate of the reaction. Two different kinds of active centers have been proposed by many authors.<sup>12,13</sup> For our system, it is also possible that two different types of centers are present. One may be short-lived and the other may be long-lived and less active. However, for both the systems, a particular aging time is required for their best activity, since at no aging time was the yield obtained almost negligible.

### Reaction Time

Reaction time was varied from 15 to 210 min. Details are given in Tables VII and VIII and Figure 2.

It can be seen from the above tables that for both systems there is an initial increase in the rate and

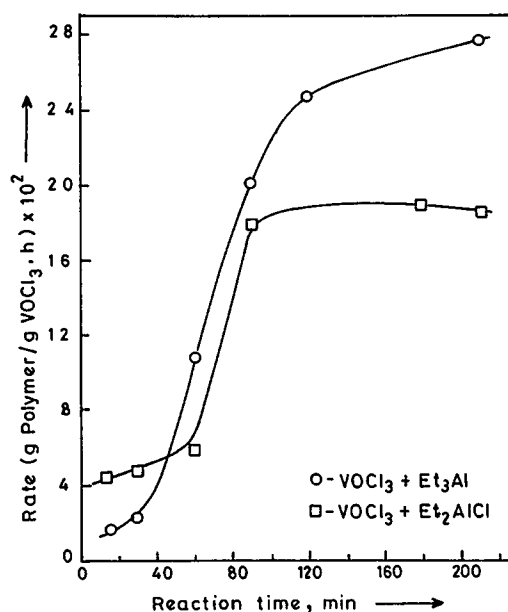


Figure 2 Rate vs. reaction time.

**Table VII Variation of Reaction Time**

Sample No.	Reaction Time (min)	Yield (g)	Rate $\times 10^2$ (g PE/gVOCl <sub>3</sub> h)	$M_v \times 10^{-5}$
1	15	0.457	1.68	0.82
2	30	0.633	2.33	—
3	60	2.924	10.76	1.26
4	90	5.451	20.07	2.72
5	120	6.712	24.71	—
6	180	7.584	27.20	2.84
7	210	7.504	27.63	2.85

Other conditions are the same as in Table I.

**Table VIII Variation of Reaction Time**

Sample No.	Time (min)	Yield (g)	Rate $\times 10^2$ (g PE/g VOCl <sub>3</sub> h)	$M_v \times 10^{-5}$
1	15	1.176	4.33	—
2	30	1.296	4.77	0.77
3	60	1.610	5.93	1.26
4	90	4.875	17.95	2.66
5	180	5.120	18.85	2.70
6	210	5.012	18.45	2.72

[DEAC] = 4.876 mol L<sup>-1</sup>; other conditions are the same as in Table II.

**Table IX Variation of Reaction Temperature**

Sample No.	Temperature (K)	Yield (g)	Rate $\times 10^2$ (g PE/g VOCl <sub>3</sub> h)	$M_v \times 10^{-5}$
1	303	5.478	20.17	2.72
2	313	6.169	11.67	2.04
3	323	2.563	9.44	1.04

Other conditions are the same as in Table I.

**Table X Variation of Reaction Temperature**

Sample No.	Temperature (K)	Yield (g)	Rate $\times 10^2$ (g PE/g VOCl <sub>3</sub> h)	$M_v \times 10^{-5}$
1	303	4.870	17.95	2.66
2	313	2.219	8.17	1.67
3	323	1.981	7.29	1.20

[DEAC] = 4.876 mol L<sup>-1</sup>; other conditions are the same as in Table II.

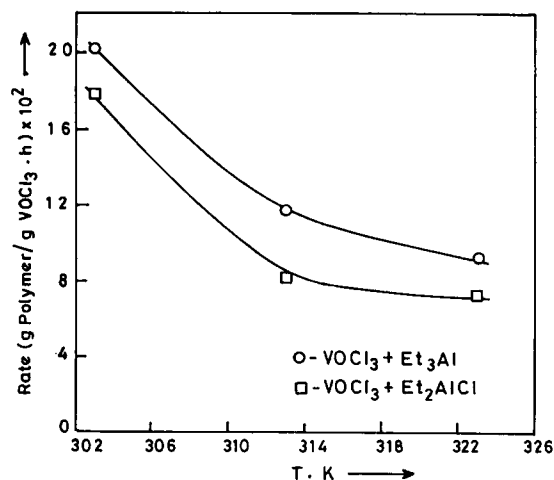


Figure 3 Rate vs. reaction temperature.

then the steady-state condition is reached. Many authors<sup>1,14</sup> have explained this on the basis of the covering of the active centers by the polymer formed, thus preventing the incoming monomer to react with the active sites, i.e., as time lapses, the reaction becomes diffusion controlled. At higher reaction times, probably more long-living and less reactive sites are present and, hence, the yield obtained almost remains constant. This fact is also illustrated by the molecular weight data.

### Reaction Temperature

Reaction temperature was varied between 303 and 323 K. Details are given in Tables IX and X and Figure 3.

When the reaction temperature was varied from 303 to 323 K, yield as well as the rate of the reaction decreases. Decrease in the rate may be attributed to the fact that at higher temperatures the potential polymerization centers may be partially deactivated.

Table XI Variation of Solvents

Sample No.	Solvent	Yield (g)	Rate × 10 <sup>2</sup> (g PE/g VOCl <sub>3</sub> h)
1	<i>n</i> -Hexane	5.481	20.18
2	<i>n</i> -Heptane	5.512	20.29
3	Benzene	4.993	18.38
4	Toluene	4.201	15.46
5	Xylene	3.988	14.68
6	Chlorobenzene	2.104	7.74

[TEAL] = 2.232 mol L<sup>-1</sup>; other conditions the same as in Table I.

Table XII Variation of Solvents

Sample No.	Solvent	Yield (g)	Rate × 10 <sup>2</sup> (g PE/g VOCl <sub>3</sub> h)
1	<i>n</i> -Hexane	4.876	17.95
2	<i>n</i> -Heptane	4.013	14.77
3	Cyclohexane	3.956	14.56
4	Benzene	3.063	11.28
5	Toluene	3.163	11.64

[DEAC] = 4.876 mol L<sup>-1</sup>; other conditions are the same as in Table II.

Also, at higher temperatures, the solubility of ethylene in *n*-hexane is considerably reduced and, hence, the decrease in the yield and a fall in the reaction rate is observed. An inverse relationship between temperature of polymerization and molecular weight is observed.<sup>15</sup>

### Solvents and Additives

Aliphatic and aromatic solvents were used as the polymerization medium. It can be seen from Tables XI and XII that aliphatic solvents are better polymerization mediums than are aromatic ones. Poor solubility of ethylene in the aromatic solvents and probably some interaction of these solvents with the catalyst components may be the reasons for lower yield and, hence, the lower rate in the aromatic medium. However, various other results can be cited in the literature.<sup>16,17</sup> Apart from the catalyst and co-catalyst, certain electron donors were added to the system to check their effect on the catalyst system.

From Tables XIII and XIV it can be seen that additives certainly improve the yield. However, this was seen when a particular sequence of addition was followed, i.e., solvent, alkyl, VOCl<sub>3</sub>, and, finally, the additive.

Table XIII Variation of Additives

Sample No.	Additive	Yield (g)	Rate × 10 <sup>2</sup> (g PE/g VOCl <sub>3</sub> h)
1	Triethylamine	5.831	21.47
2	Hexamine	4.318	15.90
3	Chloroform	5.612	20.66
4	Diisopropyl ether	3.101	11.42

[TEAL] = 2.232 mol L<sup>-1</sup>; additive = 0.125 mL; other conditions are the same as in Table I.

**Table XIV** Variation of Additives

Sample No.	Additive	Yield (g)	Rate $\times 10^2$ (g PE/g $\text{VOCl}_3$ h)
1	Triethylamine	5.924	21.81
2	Hexamine	5.059	18.62
3	Chloroform	2.556	9.41
4	Diisopropyl ether	2.454	9.03

[DEAC] = 4.876 mol L<sup>-1</sup>; additive = 0.125 mL; other conditions are the same as in Table II.

## CONCLUSION

From the kinetic studies, the following points were noticed within our experimental limits: (1) optimum [Al]/[V] ratio was 0.86 for Et<sub>3</sub>Al + VOCl<sub>3</sub> and 1.86 for Et<sub>2</sub>AlCl + VOCl<sub>3</sub> systems; (2) with increasing dilution, yield was found to increase until a catalyst concentration in the range 2.5–3.2  $\times 10^{-2}$  mol L<sup>-1</sup>; (3) with increasing reaction time and temperature, the catalyst activity was impaired; (4) triethylamine as an additive increased the catalyst efficiency to some extent; (5) aliphatic hydrocarbon solvents were found to be a better polymerization medium than were the aromatic ones; (6) reaction time and temperature had an effect on the molecular weight of the samples.

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