Low Pressure Polymerization of Propylene: Kinetics

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Synopsis

Kinetic studies on low pressure polymerization of propylene using the catalyst system $VOCl_3$ + $AlEt_3$ and Et_2AlCl are reported. Effect of various parameters such as the [Al]/[V] ratio, catalyst concentration, reaction time, temperature, solvents, and additives on rate of the reaction, yield, and % conversion were studied. Each of these parameters had a profound effect on the yield and rate of the reaction for both the systems. Triethylamine was found to increase the yield and the rate of polymerization. We also found that aliphatic hydrocarbons acted as a better polymerization medium than aromatic ones.

INTRODUCTION

Ziegler–Natta polymerization reactions have been the subject of extensive kinetic studies and a number of attempts have been made to account for their kinetic behavior. All these attempts have necessitated the adoption of assumptions concerning the nature of many of the fundamental processes, both physical and chemical, which are involved in these fascinating yet complex polymerization systems. A kinetic phenomena exists, which is the result of a delicate interplay between a number of operational factors such as cocatalyst to catalyst ratio, catalyst concentration, temperature, etc. that can be controlled during the synthesis of catalyst and its use in polymerization. Although enough literature is available regarding the kinetics, extensive and systematic studies are available only for systems mostly based on titanium. Moreover, what is learned from a study of one catalyst may not necessarily be applicable to understanding of another.

Though vanadium follows titanium in the periodic table and meets all the requirements to act as one of the components in a system of catalyst and cocatalyst, its compounds have not received enough attention. Our main motivation to work with $VOCl_3$ sprang from this aspect. In this paper, we report an extensive study carried out for low pressure polymerization of propylene using $VOCl_3$ in combination with triethylaluminium (TEAL) and diethylaluminium chloride (DEAC). The study carried out included variation of cocatalyst to catalyst ratio, catalyst concentration, aging time of catalyst, reaction time, temperature of polymerization, and effect of solvents and additives.

EXPERIMENTAL

$VOCl_3$ was synthesized from V_2O_5 and $SOCl_2$ following the reported[1] procedure and its purity was confirmed spectroscopically. TEAL and DEAC was

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TABLE I
Variation of Cocatalyst to Catalyst Ratio (System A)[a]

Sample no.	[Al]/[V]	[Alkyl] (mol L^{-1})	Yield (g)	Rate $R_s \times 10^2$ (g polymer/g $VOCl_3$ h)
1	0.51	1.33	Negligible	—
2	1.02	2.66	0.205	0.76
3	1.19	3.11	0.570	2.09
4	1.36	3.55	1.521	5.59
5	1.42	3.73	0.284	1.04
6	1.70	4.44	0.164	6.01
7	2.04	5.33	0.0986	0.36

[a] *n*-Hexane = 30 mL, [$VOCl_3$] = 0.0759 mol L^{-1}, reaction time = 90 min, reaction temperature = 30°C, flow rate of propylene gas = 50 mL min^{-1}.

TABLE II
Variation of Cocatalyst to Catalyst Ratio (System B)[a]

Sample no.	[Al]/[V]	[Alkyl] (mol L^{-1})	Yield (g)	Rate $R_s \times 10^2$ (g polymer/g $VOCl_3$ h)
1	1.33	3.48	1.681	6.18
2	1.59	4.17	1.709	6.29
3	1.86	4.87	2.098	7.72
4	2.02	5.29	1.678	6.17
5	2.23	5.85	1.620	5.96
6	2.82	7.36	1.018	3.74

[a] Other conditions are same as in Table I.

TABLE III
Variation of Catalyst Concentration (System A)[a]

Sample no.	Catalyst concentration $\times 10^2$ (mol L^{-1})	Yield (g)	Rate $R_s \times 10^2$ (g polymer/g $VOCl_3$ h)
1	10.70	0.984	3.62
2	7.59	1.521	5.59
3	4.79	1.562	5.75
4	3.08	1.983	7.29
5	2.49	1.036	3.81
6	1.68	0.543	1.98
7	1.27	0.393	1.44

[a] [TEAL] = 3.55 mol L^{-1}. Other conditions are same as given in Table I.

obtained as a 20% solution in versol from Polyolefins Industries Ltd. (Bombay); concentration of these alkyls was determined iodometrically.[2] *n*-Hexane, all other solvents and additives used were of AR grade (from B.D.H. Chemicals,

TABLE IV
Variation of Catalyst Concentration (System B)[a]

Sample no.	Catalyst concentration × 10^2 (mol L^{-1})	Yield (g)	Rate R_s × 10^2 (g polymer/g $VOCl_3$ h)
1	10.90	1.023	3.76
2	7.70	2.099	7.72
3	4.84	2.235	8.22
4	3.10	2.699	9.93
5	2.51	1.263	4.64
6	1.69	0.684	2.51

[a] [DEAC] = 4.87 mol L^{-1}. Other conditions are same as in Table I.

Bombay) and purified following the reported procedures.[3] Propylene gas was obtained from BOC (U.K.) and argon was obtained from IOL Ltd. (Bombay).

POLYMERIZATION

Polymerization was carried out in an all-glass double-walled assembly of about 200 mL capacity with provisions for gas inlet and gas outlet and thermometer pocket. Water was circulated using a water pump from a thermostat (with necessary accessories) maintained at the required temperature (± 0.1°C).

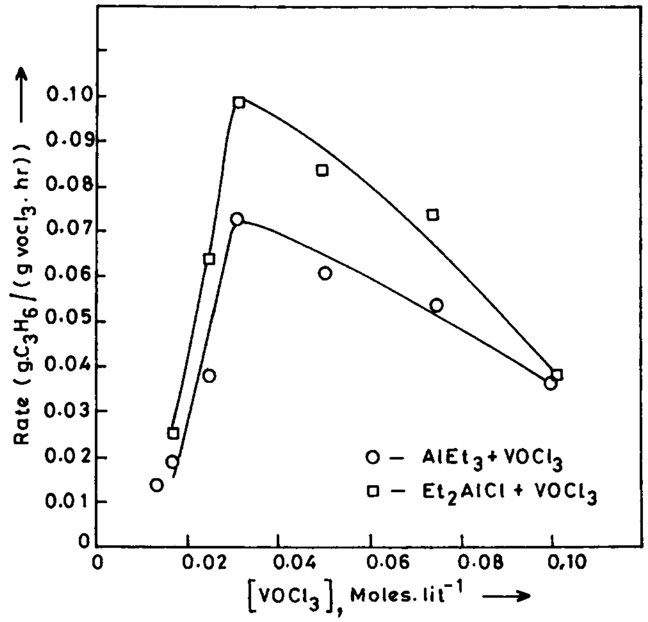

Fig. 1. Rate vs. catalyst concentration.

TABLE V
Variation of Aging Time (System A)[a]

Sample no.	Aging time (min)	Yield (g)	Rate $R_s \times 10^2$ (g polymer/g $VOCl_3$ h)
1	5	0.744	2.73
2	10	1.521	5.59
3	20	1.221	4.49
4	30	1.003	3.69
5	40	0.329	1.20
6	60	0.123	4.53

[a] [TEAL] = 3.55 mol L^{-1}. Other conditions are same as in Table I.

The reaction vessel was dried at 140–150°C for 4–5 h. The catalyst was handled in a glove box under nitrogen blanket. The order of addition of components were slurry liquid (*n*-hexane), alkyl, $VOCl_3$, and the additive (if added). After allowing an aging time of say 10 mins, the flask was taken out of the glove box and maintained at 30°C (or the required temperature) with continuous stirring on a magnetic stirrer. Then, propylene gas was passed at a flow rate of 50 mL min^{-1}, maintained constant by the addition of propylene throughout the polymerization. Upon completion of the run, 10–20 mL of isopropanol with 0.5*M* HCl (to deactivate the catalyst) was used. The polymer was allowed to stand for 24 h and then washed with methanol, dried, and weighed to determine the polymer yield. In each run two to three reaction vessels were used to allow an estimate of the precision of the data (precision = ± 5%).

RESULTS AND DISCUSSION

Various parameters were studied to get more of an idea about the behavior of $VOCl_3$ and aluminium alkyls (with or without additives), i.e., effect of [Al]/[V] ratio, catalyst concentration, aging time, reaction time, temperature, solvents, and additives.

TABLE VI
Variation of Aging Time (System B)[a]

Sample no.	Aging time (min)	Yield (g)	Rate $R_s \times 10^2$ (g polymer/g $VOCl_3$ h)
1	5	1.853	6.81
2	10	2.099	7.72
3	20	1.746	6.42
4	30	1.411	5.19
5	40	1.193	4.39
6	60	0.994	3.65

[a] [DEAC] = 4.87 mol L^{-1}. Other conditions are same as given in Table I.

TABLE VII
Variation of Reaction Time (System A)[a]

Sample no.	Reaction time (min)	Yield (g)	Rate $R_s \times 10^2$ (g polymer/g $VOCl_3$ h)
1	40	0.463	1.71
2	60	0.968	3.56
3	90	1.521	5.60
4	120	1.463	5.39
5	150	1.363	5.02
6	180	1.301	4.79
7	210	1.292	4.75

[a] [TEAL] = 3.55 mol L^{-1}. Other conditions are same as in Table I.

Cocatalyst to Catalyst Ratio

Cocatalyst to catalyst ratio was varied by keeping the amount of $VOCl_3$ constant and varying the amount of TEAL (System A) or DEAC (System B). Tables I and II give the details; from these tables it can be seen that, as the ratio is increased in small steps, in the beginning there is a gradual increase in the gram of polymer obtained, then a maximum, and finally the yield decreases. This shows that the combination of $VOCl_3$ with these alkyls is most active only at a particular [Al]/[V] ratio. These results can also be interpreted on the basis of alkyl concentration. We see a direct correlation between the ratio and alkyl concentration on yield and subsequently on the rate of the reaction. Only at a particular ratio is maximum yield obtained; this may be due to the fact that, at this ratio, the maximum number of active sites are formed which are capable of propagating the polymer chain.

Catalyst Concentration

Tables III and IV illustrate the details of the effect of catalyst concentration on the yield and specific rate of polymerization. Variation of catalyst concentration was carried out by diluting the reaction mixture with the solvent. From

TABLE VIII
Variation of Reaction Time (System B)[a]

Sample no.	Reaction time (min)	Yield (g)	Rate $R_s \times 10^2$ (g polymer/g $VOCl_3$ h)
1	40	0.612	2.25
2	60	1.510	5.56
3	90	2.699	9.93
4	120	2.721	1.00
5	150	2.693	9.99
6	180	2.589	9.53
7	210	2.560	9.42

[a] [DEAC] = 4.87 mol L^{-1}. Other conditions are same as given in Table I.

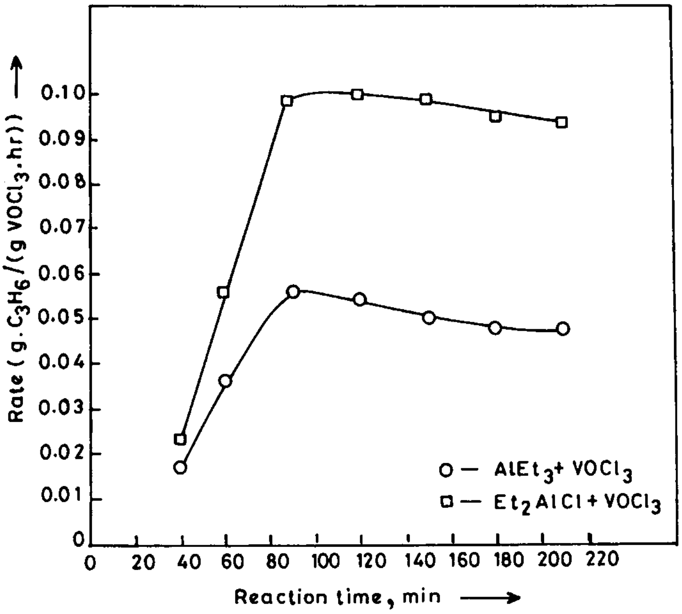

Fig. 2. Rate vs. reaction time.

TABLE IX
Variation of Reaction Temperature (System A)[a]

Sample no.	Temperature (K)	Yield (g)	Rate $R_s \times 10^2$ (g polymer/g $VOCl_3$ h)
1	303	1.521	5.59
2	308	1.762	6.48
3	313	1.269	4.67
4	323	1.162	4.27
5	328	1.001	3.68

[a] [TEAL] = 3.55 mol L^{-1}. Other conditions are same as given in Table I.

TABLE X
Variation of Reaction Temperature (System B)[a]

Sample no.	Temperature (K)	Yield (g)	Rate $R_s \times 10^2$ (g polymer/g $VOCl_3$ h)
1	303	2.099	7.72
2	308	2.331	8.58
3	313	1.669	6.14
4	323	1.371	5.04
5	328	1.305	4.80

[a] [DEAC] = 4.87 mol L^{-1}. Other conditions are same as given in Table I.

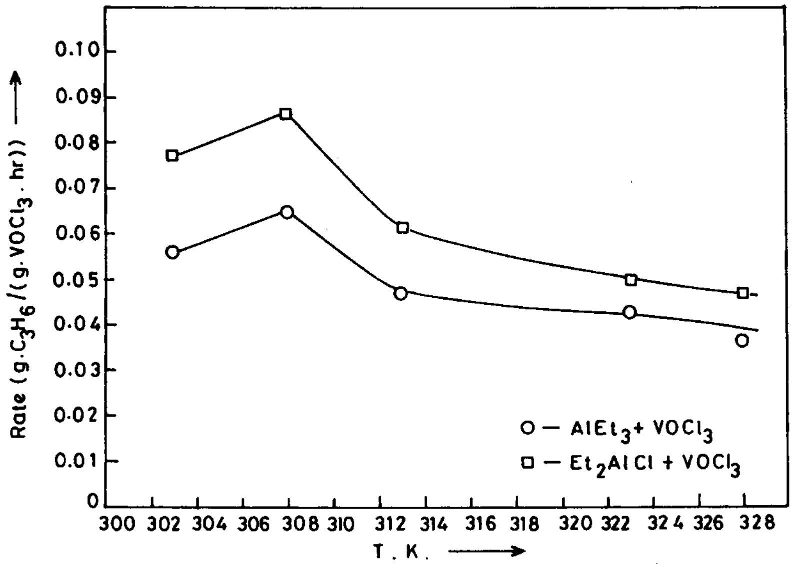

Fig. 3. Rate vs. reaction temperature.

TABLE XI
Variation of Reaction Medium (System A)[a]

Sample no.	Solvent (mL)	Yield (g)	% Conversion
1	*n*-Hexane	1.521	30.0
2	Cyclohexane	1.462	28.8
3	*n*-Heptane	1.410	29.5
4	Benzene	0.371	7.3
5	Toluene	0.430	8.4

[a] mL of each solvent = 30, [TEAL] = 3.55 mol L^{-1}. Other conditions are same as in Table I.

TABLE XII
Variation of Reaction Medium (System B)[a]

Sample no.	Solvent (mL)	Yield (g)	% Conversion
1	*n*-Hexane	2.099	41.4
2	Cyclohexane	1.938	38.2
3	*n*-Heptane	1.968	38.8
4	Benzene	0.747	14.7
5	Toluene	0.547	10.7

[a] mL of each solvent = 30, [DEAC] = 4.87 mol L^{-1}. Other conditions are same as in Table I.

Tables III and IV and figure 1, it can be seen that even at a narrow range of catalyst concentration there is a profound effect on the rate and the yield obtained. As more quantity of *n*-hexane is used, it had the effect of increasing

TABLE XIII
Variation of Additives (System A)[a]

Sample no.	Additives (mL)	Yield (g)	% Conversion
1	Triethylamine	1.849	36.4
2	Hexamine	1.788	35.2
3	Diisopropyl ether	0.517	10.1
4	Chloroform	1.303	25.7

[a] [TEAL] = 3.55 mol L^{-1}; additive = 0.125 mL. Other conditions are same as in Table I.

the effective concentration of propylene, an effect similar to increase in pressure.[4] We also feel that, when the system is more dilute, agglomerates of catalyst particles may break up and hence diffusion of the incoming monomer becomes easier and sites are more accessible. However, at very low concentration of the catalyst, the concentration of active centers is low and hence a direct effect is seen on the yield and hence the rate.

Aging Time

The aging time of the catalyst system was varied from 5 min to 1 h. Results are given in Tables V and VI. From these tables, it can be seen that, as we increase the aging time from 5 min to 1 h, yield and rate of the reaction decrease. This inverse relationship can be explained on the basis of activity and stability of the catalyst systems used for the experiments and can be attributed to the decay of active centers. However, for both the systems, an optimum aging time was required for their best activity.

Reaction Time

Reaction time was varied from 40 to 210 min. Details are given in Tables VII and VIII. It can be seen from the above tables and Figure 2 that, as the reaction time was increased from 40 to 210 min, for both the systems, a decay-type curve is obtained. The initial increase in the reaction rate can be attributed to the formation of active sites. At 90 min, maximum potential active sites are formed. It can also be said that, as more and more reaction time lapses, the formed polymer chain forms a covering around the catalyst surface and thus

TABLE XIV
Variation of Additives (System B)[a]

Sample no.	Additive (mL)	Yield (g)	% Conversion
1	Triethylamine	2.855	56.3
2	Hexamine	1.731	34.1
3	Diisopropyl ether	1.680	33.1
4	Chloroform	0.801	15.8

[a] [DEAC] = 4.87 mol L^{-1}; additive = 0.125 mL. Other conditions are same as in Table I.

makes it difficult for the incoming monomer molecules to react with these centers. As a result, the reaction may become more diffusion-controlled.

Reaction Temperature

Reaction temperature was varied between 303 and 328 K. Details are furnished in Tables IX and X and Figure 3. When the reaction temperature was varied from 303 to 328 K, yield as well as the rate of the reaction decrease. The temperature for optimum activity of the catalyst was between 303 and 308 K. At higher temperature the activity is reduced due to the deactivation of the centres, and also may be due to the fact that solubility of the gas is reduced and hence yield and rate decreases.

Solvent Effect

Aliphatic hydrocarbon solvents and aromatic solvents were used as polymerization medium. Results obtained are tabulated in Tables XI and XII. From the tables, aliphatic hydrocarbon solvents seem to be a better polymerization medium than the aromatic ones. It may be possible that aromatic solvents may be interacting with the catalyst components and reducing the activity of the system. However, various other results can be seen in the literature.[5]

Additives

Apart from the catalyst and cocatalyst certain electron donor molecules were added to the system to check their effect on the efficiency of the catalyst system and thus on the yield and % conversion. Details are given in Tables XIII and XIV. From the above tables, it can be seen that, under similar conditions, yield improved with amines. Many such cases have been reported in the literature.[6] A detailed analysis showed that the sequence of addition of the additive and its concentration had an effect on yield. Hexamine was taken for the study. It was noticed that best results were obtained when it was added after the addition of catalyst and cocatalyst and when 0.125 mL (0.0300 g in 1 mL chloroform) of it was added.

CONCLUSION

The kinetic studies revealed that the optimum [Al]/[V] ratio was 1.36 for $Et_3Al + VOCl_3$ and 1.86 for $Et_2AlCl + VOCl_3$ and aging time was 10 min. With increasing dilution, yield was found to increase till a catalyst concentration of 3.0×10^{-2} mol L^{-1}. With increasing temperature and reaction time, the activity of the catalyst system was found to decrease. Hexamine and triethylamine additives improved the efficiency of the catalyst system and, finally, aliphatic hydrocarbon solvents were found to be a better polymerization medium than aromatic solvents.

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