Variations of Polymer Structure with Catalyst Composition in Ziegler Type Polymerizations

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Introduction

The discovery of the Ziegler catalyst (4) for polymerizing olefins, particularly ethylene, created intense academic and industrial interest. Prior to this discovery, polymers of ethylene consisted of oils prepared by Lewis acid catalyzed polymerizations or solid low-density polyethylene prepared at very high pressures using traces of oxygen as a free radical catalyst.

A typical Ziegler catalyst can be prepared by coreacting mole for mole, an aluminum alkyl and a metal halide such as titanium tetrachloride in a hydrocarbon forming an intensely colored heterogeneous solid catalyst. Polymerization of ethylene at room temperature and at atmospheric pressure is rapid (5).

The polymerization of ethylene by these heterogeneous catalysts was not easily explained by a free radical mechanism. Ziegler (1) suggested that the polymerization may occur by an anionic mechanism. Furthermore, the catalyst component ratio can be varied and still yield solid polyethylene suggesting that the catalyst structure may vary and may have an effect on the structure of the polymer. A detailed study of selected catalyst ratios was undertaken to obtain more information about the catalyst and to discover a possible mechanism of the polymerization.

Titanium tetrachloride is a Lewis Acid capable of initiating a cationic polymerization reaction, while triisobutyl aluminum, an organometal, is capable of initiating some anionic polymerizations. Therefore, if in the preparation of a Ziegler catalyst, an excess of either component is used above the stoichiometric amount required to prepare the catalyst, it may be possible for the resulting system to function either as a pseudocationic or a pseudo-anionic system.

The variation of catalyst structure over a selected ratio should affect polymer structure and yield, catalyst efficiency, monomer absorption rate, and should indicate the most efficient ratio for optimum polymer yield.

After establishing the Al/Ti ratio for ethylene, this data may be applied to other olefins to determine whether the change in composition of catalyst would indeed influence the structure of the polymer.

Ethylene is symmetrical and will not yield a polymer having stereospecific structure, but yield oligomers in the presence of Lewis Acids (2). However, propylene can produce polymers having three stereo-

specific conformations depending upon the type of polymerization catalyst. With Lewis Acids, atactic oligomers are usually obtained while with anionic catalysts, isotactic, syndiotactic, or atactic forms of polypropylene can be obtained. Similarly, the structure of the polyisoprenes are determined by the composition of the initiator yielding hard resinous cationic polymers, or rubbery polyisoprene with anionic catalysts. This should also hold true for Ziegler catalysts if their ionic character changes with composition.

Experimental

Ethylene

The following general procedure of Experiment No. 1 was used for all experiments using catalyst ratios listed in Table 1.

TABLE I
Mole Ratio of Catalyst Reactants for Ethylene Polymerization

Experiment No.	Millimoles AlR_3	Millimoles $TiCl_4$	Ratio Al/Ti
1	10.1	50.5	1:5
2	10.1	40.4	1:4
3	10.1	30.3	1:3
4	10.1	20.2	1:2
5	10.1	10.1	1:1*
6	10.1	0	—
7	0	10.1	—
8	20.2	10.1	2:1
9	30.3	10.1	3:1
10	40.4	10.1	4:1
11	50.5	10.1	5:1

* This catalyst ratio yields a catalyst having the composition indicated by the equation: $R_3Al + TiCl_4 \rightarrow R + R_2AlCl + TiCl_3$.

Into a two-liter autoclave containing 400 ml. of freshly distilled dry n-heptane was placed 5.55 ml. (50.5 mmoles) of titanium tetrachloride and 5.0 ml. (10.1 mmoles) of triisobutyl aluminum under a nitrogen blanket forming a typical Ziegler catalyst. The autoclave was flushed with nitrogen, stirring was started and the catalyst was aged for twenty-four hours at 60°.

Ethylene was then pressured to the autoclave at 300 psi with the stirrer off; stirring was resumed and the reaction was continued for twelve hours. Pressure drops were noted and recorded. Upon completion of the reaction, the autoclave was cooled, the excess gas vented, the autoclave opened under a nitrogen blanket, and the color of the reaction mass noted. The contents of the autoclave were poured into 200 ml. of methanol containing 1% of hydroquinone as an antioxidant. The solids were stirred in methanol for several hours prior to filtering, washing, and drying to afford 4.87 g. of polyethylene which melted at 125°.

The methanol and heptane layers were separated using a separatory funnel, and each layer was concentrated under a vacuum and the residues distilled.

The heptane layer yielded 0.74 g. of a viscous oily residue, while the methanol layer yielded 2.5 g. of an oil distilling between 30-60° at 5 mm. and 1.0 g. of a tarry solid which when charred, yielded inorganic salts.

The results of these reactions are summarized in Table II.

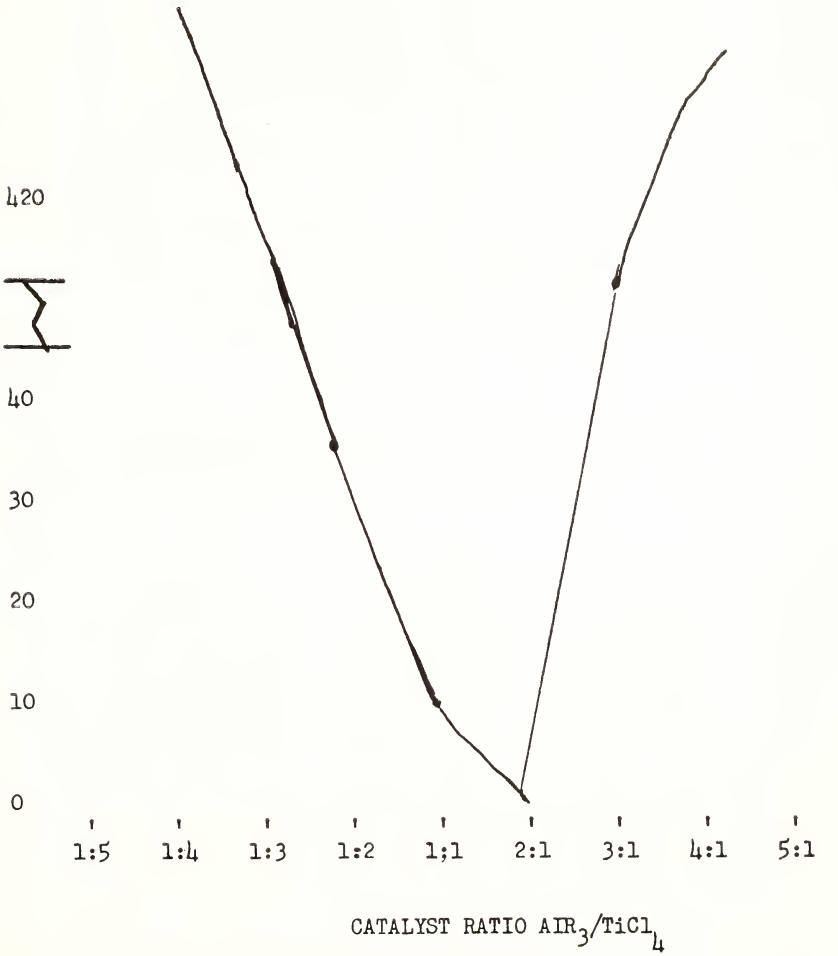

Figure 1. Disappearance of ethylene monomer with time.

The rate of disappearance of the monomer was noted on the basis of its variation with catalyst mole ratio, and the data obtained is listed in Table III and Figure 1.

TABLE II

Results of the Ethylene Polymerizations Using Various Al/Ti Ratios in Catalyst

Experiment No.	Al/Ti in Catalyst Ratio[a]	Color of Reaction Mass	Weight of Solid Polymer(g)	M.P.(°C) of Polymer	Weight of Product in Heptane[b](g)	Weight of Product in Methanol[c](g)
1	1:5	purple	4.87	125	0.74 oil	2.55 oil b.p. 30–60° 5mm 1.0 tar
2	1:4	purple	9.55	126.5	3.19 oil	1.0 tar
3	1:3	red-purple	14.6	131-132	1.10 oil	5.67 oil b.p. 70–72° 9.56 tar
4	1:2	dark-brown	16.11	124-125	1.41 oil	3.92 oil b.p. 70–72° 5.29 tar
5	1:1	light-brown	15.7	136-136.5	0.96 tar	8.78 oil b.p. 70–72° 2.8 tar
6	1:0	colorless	0.0	.....	0.26 tar	.....
7	0:1	colorless	0.0	.....	2.1 tar	.....
8	2:1	grey	15.6	137-138	1.35 oil	9.62 tar
9	3:1	black	16.0	138-139	0.69 tar	6.62 oil 1.42 tar
10	4:1	black	15.1	133-134	0.53 oil	6.42 tar
11	5:1	black	13.8	136-137	.....	1.3 tar

a. The catalyst ratio is the ratio of triisobutyl aluminum to titanium tetrachloride in millimoles per liter.
b. The product obtained after concentrating the heptane layer.
c. The product obtained after concentrating the methanol layer.

TABLE III
Disappearance of Ethylene Monomer as Function of Catalyst Composition

Experiment No.	Minutes required for 0 pressure	Al/Ti Ratio[a]
1	more than 960 min	1:5
2	960	1:4
3	420	1:3
4	34	1:2
5	9	1:1
8	2	2:1
9	37	3:1
10	420	4:1
11	420	5:1

a. The ratio of triisobutyl aluminum to titanium tetrachloride.

Disappearance of the Monomer

Catalyst Efficiency

The catalyst efficiency calculated as the amount of polymer obtained per gram of catalyst is shown in Table IV. The maximum catalyst efficiency occurs at the 1:1 ratio of catalyst components.

TABLE IV
Catalyst Efficiency for Ethylene Polymerization

Al/Ti ratio in Catalyst[a]	Catalyst Weight(g)	Polymer Yield(g)	Catalyst Efficiency
1:5	11.6	4.87	0.42
1:4	9.7	9.55	0.99
1:3	7.8	14.6	1.86
1:2	5.8	16.0	2.76
1:1	3.9	15.4	3.93
2:1	4.9	11.6	2.37
3:1	7.9	16.0	2.06
4:1	9.9	15.1	1.52
5:1	11.9	13.8	1.16

a. The catalyst ratio is the ratio of triisobutyl aluminum to titanium tetrachloride.

Propylene

The procedure used for the polymerization of propylene was the same as that used for ethylene and is described above with the exception of the propylene was pressured to 100 psi.

The results of these experiments are listed in Table V.

TABLE V

Results of the Propylene Reactions using Catalyst Ratios

Experiment No.	Catalyst Ratio[a]	Color of Reaction Mass	Weight of Solid Polymer(g)	M.P.(°C) of Polymer	Weight of Product in Heptane[b](g)	Weight of Product in Methanol[c](g)
1	1:5	red-brown	....	.....	5.56 oil	28.37 dark oil
2	1:4	reddish	....	.....	9.35 oil	19.01 viscous oil
3	1:3	dark-brown	....	.....	8.21 oil	5.8 tar
4	1:2	brown	....	.....	10.1 oil	10.41 dark oil
5	1:1	mud-brown	5.7	159-161	0.42 wax	5.91 solids and tar
6	1:0	colorless	....	.....	0.21 oil	6.64 oil, b.p. range 72-85
7	0:1	colorless	....	.....	3.0 (ml) waxy oil	2.38 dark oil
8	2:1	black	7.37	110	.....	7.57 tar
9	3:1	black	1.56	155	1.54	6.66 tar
10	4:1	black	0.21	145-146	0.09 tacky solid	0.09 solid (Al_2O_3) 21.13 tar
11	5:1	black	0.19	145-146	0.32 tacky solid	16.76 tar

a. The catalyst ratio is the ratio of triisobutyl aluminum to titanium tetrachloride.
b. The product obtained after concentrating the heptane layer.
c. The product obtained after concentrating the methanol layer.

Isoprene

The procedure used for the polymerization of isoprene is the same as that used for ethylene with the exception that 10 ml. of distilled liquid isoprene was added. The results are listed in Table VI.

TABLE VI
Results of the Isoprene Polymerization Reactions Using Various Catalyst Ratios

Al/Ti Ratio Catalyst[a]	Color of Reduction Mass	Weight of Solid Polymer(g)	Weight of Product in Heptane(g)[b]	Weight of Product in Methanol[c](g)
1:5	purple	0.22	3.21 resin	12.39 black tar
1:4	red-purple	.....	4.40 resin	8.32 black tar
1:3	red-brown	3.38	0.23 resin	15.01 black tar
1:2	red-brown	0.19	3.86 resin terpene odor	4.87 black tar
1:1	red	latex 6.8	.....	.....
1:0	colorless	.....	terpene oil	.....
0:1	colorless	resin	.....	.....
2:1	black	0.91 rubber	3.71 oil	.....
1:3	black	0.79 rubber	1.73 terpene oil	tar
4:1	black	0.36 rubber	0.5 terpene oil	tar
5:1	black	trace	trace terpene oil	tar

a. The catalyst ratio is the ratio of triisobutyl aluminum to titanium tetrachloride.
b. The product obtained after concentrating the heptane layer.
c. The product obtained after concentrating the methanol layer.

In order to complete and extend the study, the soluble portion of the Ziegler catalyst prepared at the Al/Ti 1:1 ratio was used to polymerize propylene and isoprene. At this ratio, dialkyl aluminum chloride would be present and should yield products typical of cationic initiation. Using the procedure outlined for ethylene, an oil was obtained with propylene and a short-rubber characteristic of a cationic initiation was obtained from isoprene.

Discussion

Ethylene

Several changes are noted when ethylene is polymerized using different Al/Ti ratios in the preparation of Ziegler catalysts.

The maximum rate of disappearance of monomer occurs at a catalyst component ratio of 1:1. Polyethylene yield and catalyst efficiency also approach a maximum at this ratio. The decrease in activity of the catalyst over or under Al/Ti ratio of 1:1 may indicate that the nature of the catalyst is being changed with an excess of either aluminum alkyl or titanium tetrachloride. The amount of heptane soluble oil

was higher when excess titanium tetrachloride was used (Al/Ti ratio 1:4) than when excess aluminum alkyl was used. (Al/Ti ratio 4:1)

Changes in the color of the reaction mass were noted. As the catalyst composition increased in aluminum alkyl content, the color changed from purple to brown to black and remained black above an Al/Ti ratio of 2:1. This indicates that the solid phase of the catalyst changes in titanium trichloride content and above a Al/Ti ratio of 2:1 is predominantly titanium dichloride.

Propylene

The results of the propylene experiments are very much in accord with the proposal that a pseudo-anionic or pseudo-cationic mechanism may be operating depending upon the ratio of catalyst components. Particularly significant is the complete change in the nature of the product at an Al/Ti ratio of 1:1, which corresponds to the polymers obtained by known anionic systems. The melting point of polypropylene obtained at a ratio of 1:1 (159-161°C) is in agreement with the melting point of isotactic polypropylene.

Although the yields are not as well defined as those in the polyethylene case, the general trend toward a decrease in the yield of solid polymer with increasing Al/Ti ratio above 1:1 ratio is in general agreement with the data for ethylene.

Another point of general agreement is the color of the catalyst and the fact that above a ratio of 1:1 of Al/Ti a black color indicative of the formation of titanium dichloride, is obtained for each monomer. This may be explained by the reduction of the initial $TiCl_3$ (purple) to $TiCl_2$ (black) by excess aluminum alkyl. This was also shown by sodium reduction of $TiCl_4$ and sodium reduction of $TiCl_3$ (2).

Isoprene

The results obtained with isoprene are consistent with the theory developed using ethylene and propylene.

One interesting fact is the almost complete absence of rubber above a Al/Ti ratio of 2:1 is reached and the appearance of terpene oils. This may be explained by the appearance of a black catalyst as the ratio of catalyst components exceeds 1:1 and indicates the formation of titanium dichloride, which in the presence of triisobutyl aluminum was shown to be an inactive catalyst (2).

The change in the nature of the product from a resin to a rubber at Al/Ti ratio of 1:1 is in agreement with previous results obtained with propylene and indicates the ratio which yields the most active catalyst. At a catalyst component ratio of 1:1, Saltman (3) obtained rubber in high yields containing essentially cis 1,4 polyisoprene.

Conclusion

The data obtained by polymerizing ethylene propylene and isoprene at different Al/Ti ratios, indicates that the nature of the respective polymers obtained depends to a high degree on the component ratio.

Ziegler (4) reported that when solid and liquid phases of the catalyst were separated neither component was capable of initiating

polymerization. This was confirmed by the present authors and by Saltman (3) who obtained similar results and showed that when the components were recombined catalyst activity was restored. This would indicate that both components, the organo-metal and the metal halide, are necessary for catalyst activity.

However, in these studies since some solid polymers were obtained by varying the Al/Ti ratio in the catalyst composition, it should be possible to prepare solid polyethylene from strictly ionic catalysts without the use of organo-metals.

A study of organo-metal free catalysts will be presented in the next paper.

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