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Linear Alpha-Olefins by Catalytic Oligomerization of Ethylene

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SUMMARY

This paper describes a new catalytic process for linear alpha-olefins by oligomerization of ethylene using a soluble alkyl aluminum chloride-titanium tetrachloride catalyst. Important catalytic and polymerization variables, such as catalyst activity, selectivity to linear products, and molecular weight, are discussed. An ionic mechanism is proposed to explain the unusual features of this new process.

INTRODUCTION

Low molecular weight olefins have been synthesized by polymerization of ethylene using combinations of alkyl metals and transition metal compounds as catalysts [1-4]. These products were highly branched oils and semisolids, which were useful as lubricating oils, greases, and pour point depressants. Some linear alpha- and internal-olefins were produced, but the major products were 2-alkyl-1-olefins.

Ethylene has been dimerized to butene-1 by a variety of methods, but the higher molecular weight linear alpha-olefins have not been obtained previously in high purity or selectivity by catalytic oligomerization of ethylene. Present commercial processes for making C_{4-20} linear alpha-olefins are based on the Ziegler high pressure growth reaction on aluminum triethyl followed by low pressure displacement [5], or dehydration of natural alcohols [6].

The former yields low purity olefins above C_{20}, and the latter is limited by the availability of natural alcohols.

RESULTS AND DISCUSSION

Despite the enormous amount of research that has been done using Ziegler-type catalysts, there are no reports in the literature in which ethylene polymerization has produced high purity linear alpha-olefins. In the course of this investigation, combinations of critical catalyst and reaction variables which led to this result were discovered. The most important variables include catalyst composition, ethylene concentration, reaction temperature, and catalyst solvation. Although proper interaction of all these variables is required to obtain linear olefins rather than Ziegler polyethylene or branched oils, each variable will be discussed separately to illustrate its effects.

Catalyst Compositions

The catalyst is a soluble reaction product obtained by mixing an alkyl aluminum chloride with titanium tetrachloride under conditions that prevent decomposition of the alkylated titanium product to the conventional, reduced, heterogeneous Ziegler catalyst. If reduction occurs, one obtains the expected high molecular weight Ziegler polyethylene. A soluble catalyst is a necessary, but not sufficient, condition for ethylene oligomerization. The aluminum component, after alkylating the titanium, must be a strong Lewis acid. This requires that at least part of the aluminum component be either alkyl aluminum dichloride or aluminum trichloride. If, after alkylation of titanium, only dialkyl aluminum chloride or aluminum trialkyl is present, the heterogeneous Ziegler catalyst will be formed. Even with the proper catalyst compositions, it is necessary to use mild temperatures and low catalyst concentrations to prevent decomposition of the alkyl titanium trichloride to insoluble titanium trichloride.

The effect of aluminum alkyl acidity is shown in Table 1. At a 12/1 mole ratio ($Al/TiCl_4$), both $AlEtCl_2$ and aluminum sesquichloride gave only liquid olefins. $AlEt_2Cl$ gave predominantly polyethylene plus a small amount of oligomer from the $AlEtCl_2$ produced during alkylation of the titanium. However, when the catalyst consisted of equimolar amounts of $AlEt_2Cl$ and $TiCl_4$, the alkylation reaction converted $AlEt_2Cl$ into $AlEtCl_2$, and only liquid olefins were obtained.

Table 1. Effect of Aluminum Alkyl Acidity
(500 ml solvent; -20°C; 150-165 psia C_2H_4; 1 hr)

Al alkyl	$Al/TiCl_4$	Diluent	Yield (g) Liquid olefins	Solid polymer
$AlEtCl_2$	12/1	C_6H_5Cl	7	0
$AlEt_{1.5}Cl_{1.5}$	12/1	C_6H_5Cl	16	0
$AlEt_2Cl$	12/1	C_6H_5Cl	3	48[a]
$AlEt_2Cl$	2/2	Xylene	13	0

[a] Viscosity molecular weight = 1,670,000.

Ethylene Concentration

High ethylene concentrations are required to obtain pure linear alpha-olefins. Table 2 illustrates the results from a series of runs made at comparable conditions in which ethylene pressure was varied from atmospheric pressure to 500 psia. Olefin purity, measured on the C_{12-20} fraction, increased sharply with increasing ethylene pressure above 50 psia, and reached 90-100% above ~100 psia.

Copolymerization of the product olefins with ethylene would lead to branched products. The high ethylene concentration suppresses copolymerization since both molar concentration and reactivity are higher than those of the product olefins. Therefore, it is evident that higher ethylene concentrations are needed in order to maintain the same olefin purity when oligomer concentration increases with time.

Reaction Temperature

An unusual feature of this system is that the product molecular weight decreases with decreasing temperature (Table 3). This is directly opposite to the general effect of temperature on polymerizations including those using conventional Ziegler catalysts. Obviously, chain transfer to monomer must become more favorable relative to propagation at low temperatures. This suggests that beta-hydride abstraction becomes more facile in the alkyl titanium species complexed with ethylene. Hydride abstraction should become more favorable with increasing positive charge on the titanium. Since ion pairs and ions are favored by stronger solvation at lower temperatures, the temperature effect on molecular weight is taken as good evidence for ionic, catalytic species.

Table 2. Effect of Ethylene Pressure
(500 ml chlorobenzene; -20°C)

Catalyst: $\overset{A}{AlEt_2Cl}/\overset{B}{AlEtCl_2}/\overset{C}{TiCl_4}/\overset{D}{t\text{-}BuOH}$

A/B/C/D (mmoles)[a]	Time (hr)	C_2H_4 (psia)	% Linear olefins in C_{12-20}
12/12/2/2	1	15[b]	67
12/12/2/2	1	55	70
6/6/1/1	1	165	97
3/3/0.5/0.5	2	250	99
12/12/2/2	0.5	500	100

[a] The t-butanol and $AlEt_2Cl$ were mixed 5 min in 100 ml chlorobenzene, the $AlEtCl_2$ was added, and the mixture was added to the reactor containing the $TiCl_4$ in 400 ml chlorobenzene at -20°C.

[b] Gaseous ethylene bubbled continuously through the diluent at atmospheric pressure.

Table 3. Effect of Reaction Temperature
(500 ml solvent; 1 hr)

A/B/C/D (mmoles)[a]	Solvent	C_2H_4 (psia)	Temp. (°C)	Total product $\overline{M}_n$
6/6/1/1	C_6H_5Cl	150	0	137
6/6/1/1	C_6H_5Cl	150	-20	109
6/6/1/1	C_6H_5Cl	150	-30	100
4/4/2/0	Xylene	120	0	148
4/4/2/0	Xylene	120	-20	111

[a] See footnote a in Table 2.

Solvent

Increasing catalyst solvation increases catalyst activity (Table 4) and decreases product molecular weight (Table 5). Both results are consistent with ionic catalyst species as discussed in the section on mechanism.

The effect of solvent on molecular weight holds directionally for other catalyst compositions and for other conditions of temperature and pressure. However, it is apparent from the preceding sections that one can get lower molecular weights with any solvent by increasing catalyst acidity or decreasing temperature. By choosing the proper combinations of the major variables, it is possible to achieve any desired $\bar{M}_n$ between ~70 and 300.

Table 4. Effect of Solvent on Activity
(500 ml solvent; -20°C.; 160 psia)

Solvent	A/B/C/D (mmoles)[a]	Activity (g/g $TiCl_4$/hr)
Xylene	4/4/2/2	87
Chlorobenzene	4/4/2/2	217
Xylene	6/6/1/1	90
Chlorobenzene	6/6/1/1	147

[a] See footnote a in Table 2.

Table 5. Effect of Solvent on $\bar{M}_n$
(500 ml solvent; -20°C.; 300 psia)

Solvent	$\bar{M}_n$[a]
n-Heptane	High polymer
Xylene/heptane (1/1)	>300
Xylene	150
Chlorobenzene	125
o-Dichlorobenzene	120

[a] Correlated data using $6AlEt_2Cl/6AlEtCl_2/TiCl_4$/t-BuOH.

Reaction Time

In the absence of poisons the catalyst is active for many hours when used under conditions which maintain the catalyst in its soluble form. Product concentration increases with time and eventually leads to some branched products from copolymerization as shown in Table 6. There is no significant change of molecular weight with increasing reaction time except when solvent polarity changes appreciably due to the increase in olefin concentration.

Table 6. Effect of Reaction Time
(Xylene; 0°C; 525 psia)
Catalyst: $AlEt_2Cl/2AlEtCl_2/2TiCl_4$

Time (hr)	Product conc. (wt.%)[a]	Product (g)/ catalyst (g)[a]	$\bar{M}_n$	% Linear olefins in $C_{12\text{-}20}$
1	9.6	61	123	100
2	15.1	101	123	100
3	20.3	146	123	100
4	25.1	191	123	100
5	29.9	244	123	99.7
6	33.5	287	123	99.5[b]

[a] Exclusive of volatility losses and insoluble waxes.

[b] Gas chromatography analysis on a 100-ft capillary column gave 96.5% purity by better resolution of trace impurities than was obtained on the 4-ft column.

Mechanism

The experimental observations which must be satisfied by a proposed mechanism are:

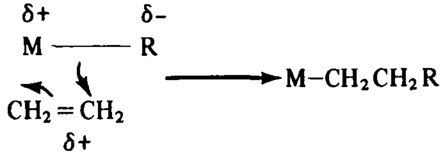
1) The rate of chain transfer is high relative to propagation under mild conditions.

2) Catalyst activity increases with increasing solvation or solvent polarity.

3) Molecular weight decreases with decreasing temperature and with increasing solvent polarity.

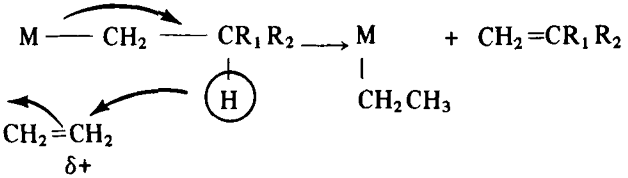
The conventional growth and displacement reactions with pi-complexed ethylene at a metal alkyl bond appear to be operating in this system:

Growth:



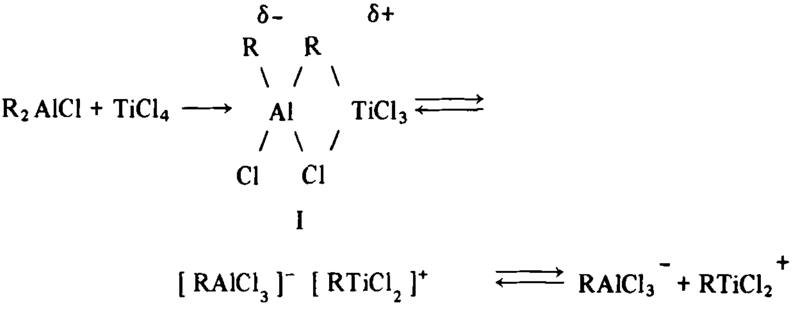
$$\begin{array}{c}\overset{\delta+}{M}\text{———}\overset{\delta-}{R}\\ \underset{\delta+}{CH_2=CH_2}\end{array}\longrightarrow M{-}CH_2CH_2R$$

Displacement:



In the displacement reaction, abstraction of the beta-hydride is favored by alkyl substitution on the beta-carbon that stabilizes the incipient carbonium ion. With a linear alkyl group, displacement is more difficult since it involves abstraction of a secondary hydride; therefore a greater driving force is required to displace linear alkyls than branched alkyls. The bond polarizations shown above suggest that displacement would become more favorable if ethylene were polarized more strongly upon complexation with the metal, M. This would be the case if the metal itself possessed some positive charge in a polarized complex, an ion pair, or especially a free cation.

All of the experimental observations are consistent with catalyst species having appreciable ionic character as shown in the following equilibria:

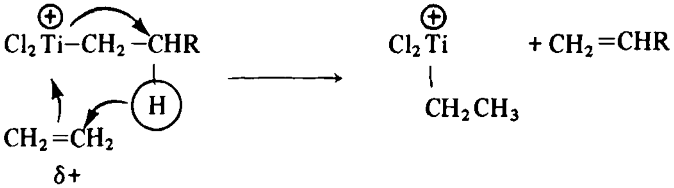


I

II

III

The equilibria are shifted from I toward III with increasing solvent polarity, increasing solvation at lower temperatures, and increasing Lewis acidity of the aluminum moiety. Likewise the displacement reaction occurs more readily in the same order because of the greater positive charge on the titanium and the correspondingly greater polarization of the complexed ethylene:



Ionic catalyst species similar to those above were also postulated by Bestian and Clauss [4] to explain their ethylene oligomerization results. They used $CH_3TiCl_3.CH_3AlCl_2$ catalyst in chlorinated hydrocarbon solvents at -70°C and obtained mixtures of alpha-olefins, branched olefins, and internal olefins. In toluene they obtained slow growth and little displacement. In heptane they reported no reaction after 4 hr. Thus, the effects of solvent polarity on activity and on the displacement reaction were directionally the same as in this work and were interpreted similarly.

Presumably, polymerization could take place on all three species (I-III). Activity probably increases from I to III because of the ability of the increasingly positive titanium to complex ethylene. This would be analogous to anionic polymerization by alkali metal alkyls [7] and carbonium ion polymerization of isobutylene [8], in which propagation can occur from both ion pairs and free ions; however, the latter are far more active. For Ziegler catalysts, Uelzmann [9] proposed ion pairs in which $TiCl_n^{\oplus}$ cation complexed and polarized the monomer but the growing carbanion was attached to an aluminum alkyl anion.

The cationic aspects of Ziegler-Natta catalysts were reviewed in 1964 [10] but there was no discussion of catalyst mechanism involving polymerization on an alkyl transition metal cation. Several Russian papers [11-13] related ethylene polymerization activity in heptane/benzene and in dichloroethane to the electrical conductivity of $(C_5H_5)_2TiCl_2.Al(CH_3)_2Cl$ catalyst and suggested that the active particles were positive ions such as $(C_5H_5)_2TiR^{\oplus}$. However, the product was polyethylene rather than oligomer. D'Yachkovskii [14] studied this catalyst by electrodialysis and found that the positive ion contained titanium, but that it was only active for polymerization when an aluminum alkyl compound was present to form a complex which acted as a normal Ziegler catalyst. Previous electrolytic studies [15] on the $AlR_3 + TiCl_4$ catalyst showed that the titanium was in a complex anion containing aluminum. It appears quite likely that the ethylene oligomerization catalysts are different in kind from conventional Ziegler catalysts.

EXPERIMENTAL SECTION

Titanium tetrachloride (Fisher) and ethyl aluminum chloride catalysts (Ethyl Corp.) were used without purification. For convenience, 1 M stock solutions were prepared in n-heptane and stored in a nitrogen dry box.

Solvents were percolated through Alcoa F-5 alumina and stored over sodium ribbon or calcium hydride.

Ethylene (Matheson C.P.) at 1000 psig was passed over supported, reduced copper oxide at 220°C to remove oxygen and finally through 3A molecular sieves to remove water.

General Reaction Procedure

All operations involving catalysts were carried out in a nitrogen dry box. The ethylene oligomerizations were performed in a 1-liter stainless steel autoclave with a magnetic stirrer and a dip tube for removing liquid samples during the reactions.

Solutions of the catalyst components were added separately to the reactor under a dry nitrogen blanket and aged at various temperatures, times, and concentrations prior to the addition of ethylene. The reactor gas phase was evacuated briefly at polymerization temperature and purified ethylene was pressured in rapidly from a large reservoir. Pressure was maintained by adding ethylene as needed. Samples (5-10 ml) were taken periodically for analysis by gas chromatography (GC) (F&M, Model 720, 4 ft 1/4 in. column 5% SE30 on Chromosorb W; He 50 cc/min, injected at 390°C, t/p 7.5°/min to 390°C). The reactions were terminated by pressuring the total reactor contents into alcoholic NaOH. Solutions were water-washed twice and dried over K_2CO_3 for GC analysis. A typical GC pattern is shown in Fig. 1.

Product Yield

Product concentrations and yields were determined directly by GC analyses. These values are 5-10% low due to loss of butene, hexene, and octene which occurred during flashing of ethylene, and because some of the higher molecular weight solid olefin products were either insoluble in the GC sample or were retained on the column. For the same reasons, the polymerization rates and catalyst efficiencies are also low.

Product Purity

Alpha-olefin purity was measured (GC) for the C_{12-20} fraction to avoid any corrections due to volatility or insolubility. Branched olefins separated readily from the linear olefins in this carbon range. Results are given as mole % linear in the C_{12-20} fraction. The C_{4-10} olefins are more linear and the C_{22+} olefins are slightly less linear than the C_{12-20} fraction. Infrared analyses of total samples and of single carbon cuts agreed with the GC analyses and confirmed that only trace amounts of internal olefins were

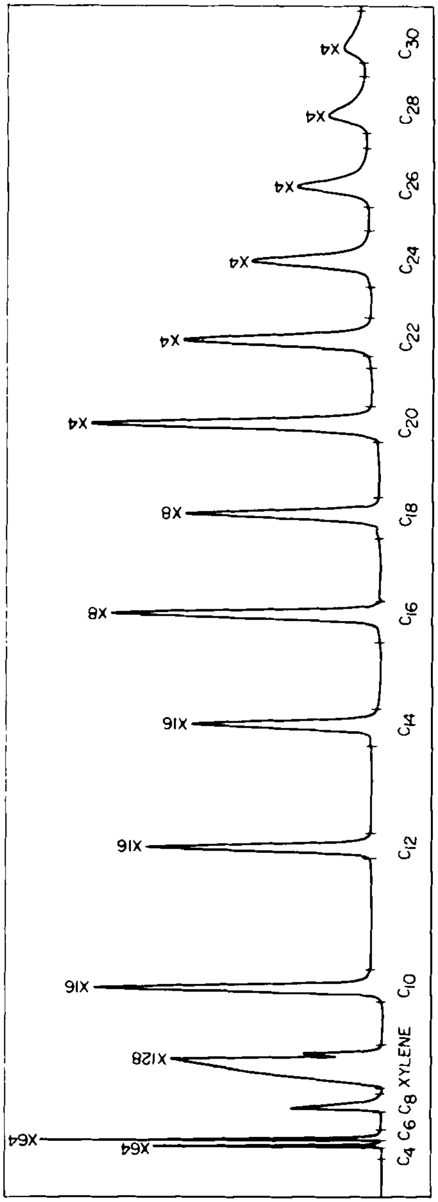


Fig. 1. Gas chromatography pattern of ethylene oligomerization total product.

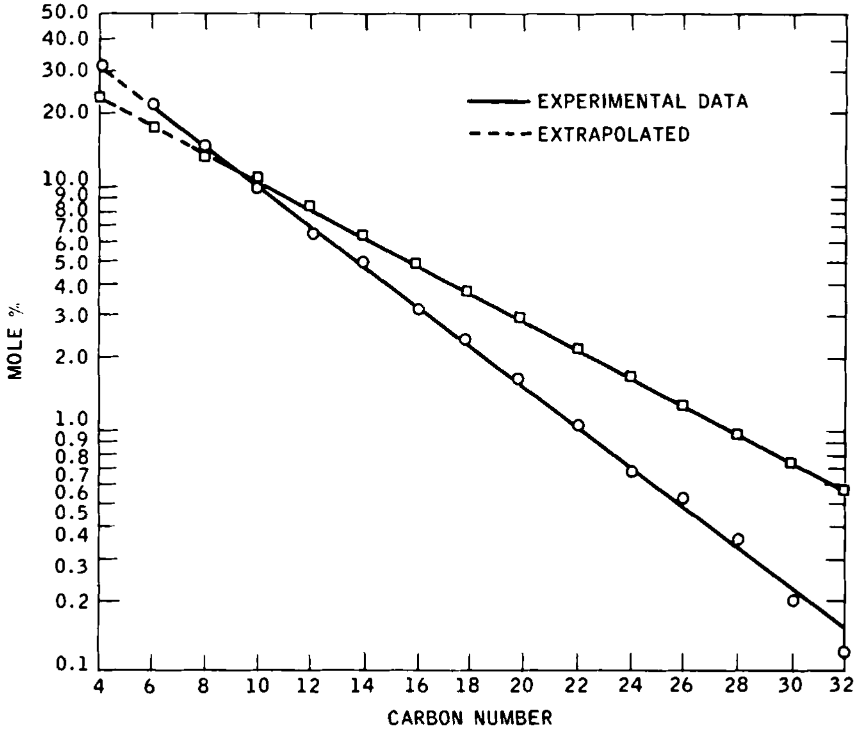


Fig. 2. Catalytic oligomerization process yields simple exponential product distribution. (○), 113 $\bar{M}_n$; (□), 147 $\bar{M}_n$.

present. Therefore, the linearity of the total product is higher than that shown for the C_{12-20} fraction because the C_{4-10} fraction is a major portion of the total product in most of the experiments.

Product Molecular Weight

Except for volatility and insolubility losses, the GC data show that the reaction product has the expected simple exponential product distribution for catalytic oligomerization with random growth and chain transfer. This distribution produces a straight line on a plot of log mole % vs degree of polymerization. For oligomerizations which give high purity alpha-olefins, the experimental data fall on a straight line (Fig. 2). The slope of the line (p) is related to the propagation and chain transfer reactions by the equation

$$p = \frac{P_{\text{propagation}}}{P_{\text{propagation}} + P_{\text{chain transfer}}}$$

where P = probability (or rate). For this distribution, the number-average molecular weight ($\overline{M}_n$) of the total product is calculated from the slope of the line by the equation

$$\overline{M}_n = \frac{28}{1 - p} + 28$$

where 28 is the molecular weight of the monomer. Experimentally, the number-average molecular weight for each reaction product was calculated from the slope of the line drawn through the points obtained from the C_{10}-$_{20}$ GC data.

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