Polymerization with Fischer-Tropsch Olefins – A New Challenge in Polymer Science

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Summary: Co- and ter-polymerization of ethylene with Fischer-Tropsch derived olefins having odd carbon number and branched olefins are investigated. A method of preparation of a robust, high productivity Ziegler-Natta catalyst suitable for ethylene co-polymerization with Fischer Tropsch olefin is reviewed. In supporting titanium tetrachloride, an attempt was made to control the titanium oxidation state. The resulting experimental data were fitted to a sub-sites model that associates titanium oxidation state with catalyst activity.

Keywords: Fischer-Tropsch Olefins; polymerization; Ziegler-Natta catalysis

Introduction

For more than half a century both science and industry have witnessed the unprecedented growth of the polyolefin industry. The discovery of polymerization of ethylene and propylene on transition metal catalysts was a turning point in the successful history of polyolefins. This success was driven continuously by advances in catalyst and process technology, and by affordable olefin resources and versatile market application.

The early work of Natta and his co-workers opened a new era in polyolefin technology. The development of a multitude of heterogeneous catalysts that followed this work made polyolefins the leading polymer family of our times. This was succeeded by a host of homogeneous catalysts. Metallocenes and the “late transition metal catalysts” resulted in further effervescence in polymer science and technology. Process development witnessed numerous solution, slurry and gas phase technologies, combinations of these, and, most recently, the emergence of bi-modal processes.

Oil is the main source for ethylene and propylene while α-olefin comonomers, 1-butene, 1-hexene and 1-octene were produced historically mainly by ethylene oligomerization. A more complex pool is available from the Fischer-Tropsch process. This option is gaining popularity as a major comonomer market source since access to oil is becoming less

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affordable. The route to olefins is shorter and a complex mixture of hydrocarbon rich in olefins is obtained. The Fischer-Tropsch process offers the polyolefin industry, in addition to the currently known even carbon number olefins, some less explored possibilities such as odd carbon number olefins and branched olefins, making possible new routes to new polymers such as:

i. Ethylene co-polymers with odd carbon number olefins
ii. Propylene co-polymers with odd carbon number olefins
iii. Ethylene ter-polymers with even and odd carbon number olefins
iv. Ethylene co-polymers with branched olefins
v. Ethylene ter-polymers with linear and branched olefins.

Ethylene Polymers with Fischer-Tropsch Olefins

A large number of new polymers with Fischer-Tropsch olefins have been obtained in our laboratories. However, this work is only a beginning in this rather challenging field. The focus of this paper is on ethylene co-polymers with Fischer Tropsch olefins obtained by slurry polymerization of ethylene with Fischer-Tropsch derived olefins using standard polymerization conditions. [1-6] Application properties of some of these polymers having molecular weight and polydispersity index similar to commercial polymers are here reviewed.

Ethylene/1-pentene co-polymers are well known. Data are also available in the literature including some of our investigations. [1-2] They have certainly a good balance of properties between ethylene co-polymers with 1-butene and 1-hexene. In the application margins they are at the lower limit where clusters may be identified by NMR techniques.

Ethylene/1-heptene co-polymers have balanced properties between those of ethylene co-polymers with 1-hexene and 1-octene. Co-polymerization rate, branch distribution and crystallizable sequence length average in this class of higher α-olefin make the co-polymer attractive for applications that cover a large field.

Synthesis and application of ethylene co-polymers with 1-heptene have been previously described. [3] Performance range for some of these polymers is here summarised:

- Izod Notched Impact Strength $I > 10[C_7]$
- Tensile Strength @ Yield (MD) $J > -4.4[C_7] + 17$

- Modulus $E > -275[C_7] + 850$
- Hardness $H > -10[C_7] + 56$

Ethylene/1-nonene co-polymers are somewhat at the upper margins of application due to their lower co-polymerization rate. However, they have the highest impact strength of ethylene copolymers with C3-C9 α-olefins. Synthesis and application of ethylene co-polymers with 1-nonene have been previously described [3] and performance range is here summarised:

- Izod Notched Impact Strength $I > 13.3[C_9]$
- Tensile Strength @ Yield (MD) $J > -16.67[C_9] + 25$
- Modulus $E > -667[C_9] + 1100$
- Hardness $H > -30[C_9] + 65$

Ter-polymers are a higher step in comonomer application. This was illustrated for co-polymers of ethylene with 1-pentene and other olefins.[1] Synthesis and application of ethylene ter-polymers with 1-pentene and other α-olefins have been previously described.[4-5] Performance is here summarised for some of the polymers described:

- Impact Strength > 60 g
- Tear Strength (MD) > 12 $g{\cdot}\mu m^{-1}$
- Tear Strength (TD) > 3 $g{\cdot}\mu m^{-1}$
- Tensile Strength @ Break (MD) > 25 MPa
- Tensile Strength @ Break (TD) > 25 MPa
- Tensile Strength @ Yield (MD) > 15 MPa
- Tensile Strength @ Yield (TD) > 14 MPa

Ter-polymers of ethylene with branched and linear α-olefins are even more diverse, and this diversity increases further when two branched olefins are employed as co-monomers. Synthesis and application of ethylene ter-polymers with branched and linear α-olefins have been previously described.[6] Performance is here summarised for ethylene ter-polymers with 4- Methyl-Pentene-1 and 3-Methyl-Pentene-1:

- Tensile Strength @ Yield (MD) $J > 240\ \rho - 212.4$
- Modulus $E > 700/0.6\rho - 10\ 500$
- Impact Strength > 50

Catalysts Used in Fischer-Tropsch Olefin Polymerization

Fischer-Tropsch olefins can be polymerized practically with all known catalysts that polymerise ethylene. However, as for all other catalysts employed in olefin polymerization, it is desirable for the catalyst to have high productivity, easy architecture and polydispersity control, resistance to poisoning and easy incorporation of higher α-olefins. A method of preparing such a catalyst was previously described[7]. A particular support was prepared from partially hydrated magnesium chloride. In supporting titanium tetrachloride, an attempt was made to control the titanium oxidation state. The preparative steps are reviewed:

Step 1 - Ether

- 0.3 to 3 moles per mol $MgCl_2$
- total number of carbon atoms greater than 8

Step 2 – Alkyl Aluminium

- 1 to 6 moles per mol $MgCl_2$
- total number of carbon atoms between 1 and 10

Step 3 – Alcohol

- 0.4 top 4 moles per mol $MgCl_2$
- total number of carbon atoms between 2 and 10

Step 4 – $TiCl_4$

- 0.5 to 20 moles per mol $MgCl_2$
- wash with saturated hydrocarbons

Catalyst Properties

- Aluminium content: 0.1 to 6 wt%
- Magnesium content: 3 to 15 wt%
- Titanium content: 3 to 15 wt%

Given the complexity of such systems, it is important to develop a fundamental understanding of the catalyst behavior before further work on Fishcher-Tropsch olefin can be attempted. The following section describes the attempts to develop a platform from which a model of the system could be developed.

Modelling the Ziegler-Natta Catalyst System

An investigation was conducted into the oxidation state variation of the active titanium centres in this Ziegler-Natta catalyst for the polymerization of ethylene in the slurry phase. It was found that catalyst prepared according to the method described having titanium at different oxidation states exhibits different activities.[8] This is in line with literature data that discuss the relationship between titanium oxidation state and catalyst activity.[9-13] It is therefore believed that by modelling titanium oxidation state, the catalyst activity may be predicted.

The model of catalyst sub-sites developed by Rawatlal and Starzak [14, 15] was employed in fitting experimental data for the slurry phase homopolymerization of ethylene over a catalyst prepared according to the method described earlier. It was found that the model fit the experimental data quite well in terms of magnitude as well as general trend for the polymer yield and average chain length. Two polymerizing sites are required to fit the data accurately, which is consistent with the experimental observations of previous researchers. The rate equation describing primary site dynamics was written according to Hutchinson [13] by lumping the effect of site transformations which occurs by the various reaction mechanisms [14] into a single parameter β_{st}: [13]

$$\beta_{st}^{q_m q_n} = k_{st,Sp}^{q_m q_n} + \sum_i k_{st,M_i}^{q_m q_n}\left[M_i\right] + k_{st,H}^{q_m q_n}\left[H\right] + k_{st,Al}^{q_m q_n}\left[Al\right] + k_{st,E}^{q_m q_n}\left[E\right] \qquad (1)$$

where the $k_{st,i}^{q_m q_n}$ is the rate of transformation from sites of type q_m to q_n as a result of reaction with component-i. Accordingly, the net rate equation on site q_m becomes:

$$\left(\frac{d}{dt}P_*^{q_m}\right)_{rxn} = \sum_n\left(\beta_{st}^{q_n q_m}P_*^{q_n} - \beta_{st}^{q_m q_n}P_*^{q_m}\right) \qquad (2)$$

where $P_*^{q_m}$ is the concentration of catalytic sites of type q_m, usually given on a mol-Ti/g-catalyst basis. Assuming progressive reduction of the sites, this general equation may be re-written in context with the catalyst:

$$\begin{aligned}
\frac{d}{dt}P_*^{4+} &= -\beta_{st}^{4+,3+}P_*^{4+} \\
\frac{d}{dt}P_*^{3+} &= \beta_{st}^{4+,3+}P_*^{4+} - \beta_{st}^{3+,2+}P_*^{3+} \\
\frac{d}{dt}P_*^{2+} &= \beta_{st}^{3+,2+}P_*^{3+} - \beta_{st}^{2+,1+}P_*^{2+}
\end{aligned} \qquad (3)$$

Eq. 3 applies in particular to well-mixed batch reactor systems in which mass transfer effects can be ignored. This result is valuable in the parameter estimation procedure, which typically involves data obtained under batch conditions.

Adopting a model of catalyst sub-sites [14, 15] the distribution around a single oxidation state q_m is given by equation (4) and the overall sub-site distribution by equation (5):

$$g_m(t,s) = \frac{f_m(t)}{\delta_m\sqrt{2\pi}}\exp\left(-\frac{1}{2}\left[\frac{s-q_m}{\delta_m}\right]^2\right) \tag{4}$$

$$g_T(t,s) = \sum_m \frac{f_m(t)}{\delta_m\sqrt{2\pi}}\exp\left(-\frac{1}{2}\left[\frac{s-q_m}{\delta_m}\right]^2\right) \tag{5}$$

where

$$f_m(t) = P_*^{q_m}(t) \Big/ \sum_n P_*^{q_n}(t) \tag{6}$$

s is the sub-sites index, and δ_m is the sub-sites distribution factor. It is assumed that δ_m does not vary from site to site. The propagation rate constant also varies continuously with sub-site index by a normal distribution in the pre-exponential factor. An Arrenhius relationship is assumed between the kinetic rate constant k_p and the temperature. It is suggested that propagation rate constant distribution spread parameter δ_m be identical for all primary site types m and assumed that activation energy, E_m, is independent of sub-site type but dependent on primary site type. The monomer consumption rate may then be determined:

$$\left(\frac{d}{dt}M\right) = n_{Ti}M(t)\int_{-\infty}^{\infty} k_p(t,s)g_T(t,s)ds \tag{7}$$

where the distribution in the propagation rate constant is given by:[16,17]

$$\begin{aligned} k_p(s,T) &= \sum_m\left[\frac{\overline{A}_p^m}{\delta\sqrt{2\pi}}\exp\left(-\frac{1}{2}\left[\frac{s-q_m}{\delta_{m,p}}\right]^2\right)\exp\left(-\frac{E_m}{RT}\right)\right] \\ &= \sum_m\left[\frac{\overline{A}_p^m}{\delta\sqrt{2\pi}}\exp\left(-\frac{1}{2}\left[\frac{s-q_m}{\delta_{m,p}}\right]^2-\frac{E_m}{RT}\right)\right] \end{aligned} \tag{8}$$

In total, there are seven parameters to be estimated, namely three site transformation parameters, β_{st}^{4-3}, β_{st}^{3-2}, β_{st}^{2-1}, the sub-sites distribution parameter δ, pre-exponential factors

A_2, A_3, and the number titanium atoms exposed on the catalyst surface, $n_{Ti,s}$.

These parameters were determined using the data obtained from experiments conducted in a slurry phase reactor system charged with heptane and the catalyst. Homopolymerization runs, employing ethylene as monomer, were conducted at a temperature of 80^0C. Hydrogen was employed as a chain termination agent, and TEA as co-catalyst.

The primary measurable of interest was the polymer yield. This was estimated by removing polymer from the reactor and measuring the mass change. The initial oxidation state composition of the catalyst used was found to be 95.734% Ti^{4+}, 4.159% Ti^{3+}, and 0.107% Ti^{2+}.

Results of the regression performed using the model described earlier are presented below. The regression yielded parameters that lie within acceptable limits outlined in the literature.

Table 1. Parameter List.

Parameter	**Description**	**Value**	**Units**
$n_{Ti}M$	Product of moles of titanium and monomer concentration	$3.4998\text{x}10^{-5}$	mol-Ti . mol-C2.m^{-3}
δ	Subsites distribution variance	0.1237	mol-Ti . mol-C2.m^{-3}
A_1	Pre-exponential factor, 3+ site	6793	mol-Ti^{-1}.s^{-1}
A_2	Pre-exponential factor, 2+ site	254210	mol-Ti^{-1}.s^{-1}
$\beta_{st}^{4\to3}$	Site transformation parameter, Ti 4 to 3+	$7.123\text{x}10^{-3}$	s^{-1}
$\beta_{st}^{3\to2}$	Site transformation parameter, Ti 3 to 2+	$0.4176\text{x}10^{-3}$	s^{-1}
$\beta_{st}^{2\to1}$	Site transformation parameter, Ti 2 to 1+	$0.6278\text{x}10^{-3}$	s^{-1}
β_T^1	Termination parameter, site 3+	$1.900\text{x}10^{-7}$	s^{-1}
β_T^2	Termination parameter, site 2+	$0.4839\text{x}10^{-7}$	s^{-1}

Data fits are shown in Figure 1. It was found the best fit was obtained when two polymerizing primary sites were used with a low sub-sites dispersion. It was expected that two primary sites would be required since it is known that ethylene polymerizes both on the 2+ and 3+ oxidation state of titanium. The low sub-sites dispersion index (0.1237) is understood in the context of the model of catalyst sub-sites,[14,15] to mean that the variation in primary oxidation state, which affects the types of sites that are polymerizing, contributes to shape of the yield profile.

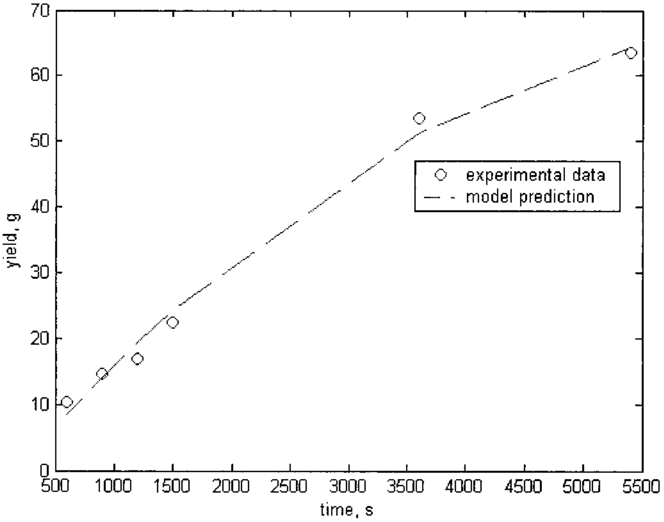

Figure 1. Polymer Yield Profile.

Conclusion

The Fischer-Tropsch process offers the polyolefin industry some less explored possibilities such as odd carbon number olefins and branched olefins, making possible new routes to new polymers. While investigation of these polymers are only at beginning and laborious work is needed to identify all opportunities, work has been initiated in this field by incorporation for a kinetic framework capable of incorporating the effects observed thus far.

The review presented demonstrates that ethylene co-polymers with odd carbon number olefins have in general a balance of properties of the co-polymers obtained with the even carbon number olefins having one carbon unit higher or lower. They extend margin of application of ethylene co-polymers with even carbon number olefin. Ethylene co-polymers and ter-polymers with branched olefins extend the margin of application even more and property change is sharper.

Fischer-Tropsch olefins can be polymerized practically with all known catalysts that polymerise ethylene. A rather robust, high productivity catalyst that is capable of high co-monomer incorporation was developed in this study. A particular support was prepared from partially hydrated magnesium chloride. In supporting titanium tetrachloride, the titanium oxidation state was controlled by the ratio of the alcohol to tri-ethyl-aluminium during catalyst preparation. It is believed that different active centres control olefin incorporation, with titanium oxidation state being associated with catalyst activity. Before incorporating this effect into the co- and ter-polymer systems, an attempt was made to model the homopolymerization of ethylene using a sub-sites model. This kinetic framework developed provides a platform for future studies in this interesting field.

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