

Ethylene Oligomerisation Beyond Schulz-Flory Distributions

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Supporting Information Placeholder

ABSTRACT: The oligomerisation of ethylene produces α -olefin distributions ranging from Schulz-Flory distributions to alternating and selective oligomer distributions which can be mathematically analysed and characterised by recurrence relations.

The oligomerisation of ethylene is an important industrial process for the production of linear α -olefins (LAOs).¹⁻³ More than 3 million tonnes of linear α -olefins are produced each year and used as intermediates for the production of detergents, lubricants and as comonomers in polyethylene. Several different LAO processes exist, for example the *Shell Higher Olefin Process (SHOP)*,⁴ which generates a range of α -olefins from C₄ (1-butene) to C₂₀₊ (see Chart 1).⁵ More selective oligomerisations are, for example the titanium-based IFP/Sabic Alphabutol[®] process for ethylene dimerisation to 1-butene,⁶⁻¹¹ and the Sabic/Linde Alpha-SABLIN[®] process based on zirconium for C₄-C₁₀ α -olefins.^{2,9} A chromium-based ethylene trimerisation process to 1-hexene is operated by Chevron-Phillips and a chromium-based ethylene tetramerisation process to 1-octene was recently announced by Sasol.^{5,12-14}

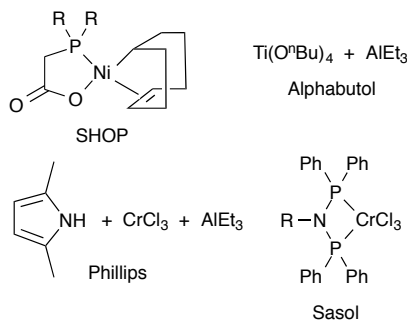


Chart 1. Industrially applied oligomerisation systems.

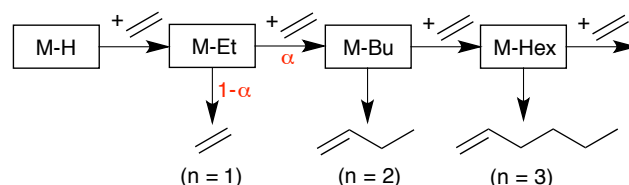
Following on from the groundbreaking treatise 80 years ago by Schulz and Flory,^{15,16} we present here a novel mathematical approach using recurrence relations to analyse olefin distributions, from the well-known simple Schulz-Flory distribution to more complicated

alternating and selective oligomer distributions. This approach provides a straightforward method to analyse and characterise LAO distributions, while demonstrating how selective trimerisations and tetramerisations can be understood as distributions beyond Schulz-Flory.

Simple α -Olefin Distributions

Chain growth in ethylene oligomerisation can occur via different mechanisms. Late transition metal oligomerisation catalysts generally operate by a linear chain growth alkene insertion mechanism (Cossee mechanism).¹⁷ A metal hydride species [M-H] undergoes successive coordination and single insertions of ethylene with a given probability of propagation α to give longer metal alkyl species [M-Et], [M-Bu] etc. (Scheme 1). Termination of chain growth occurs via competing β -H elimination with probability $1-\alpha$, resulting in a distribution of linear α -olefins that follows an exponential decay function (a Schulz-Flory distribution).^{15,16}

Scheme 1: Ethylene Oligomerisation via a Cossee mechanism



This distribution can be mathematically described as a *first order linear homogeneous recurrence relation with constant coefficients*.¹⁸ Each oligomer fraction is related to the previous fraction, $T_{n+1} = \alpha T_n$, where T_n describes the molar amount of each oligomer n (n is the number of ethylene units in the oligomer, e.g. $n = 1$ is ethylene, $n = 2$ is 1-butene etc.) and α is the probability of chain propagation (sometimes referred to as K value). The general solution to this relation takes the form $T_n = cr^n$, whereby in this case $r = \alpha$ and the constant c is the ratio of chain termination and propagation probabilities $(1-\alpha)\alpha^{-1}R$ ($R = \Sigma T_n$, total moles of olefins produced in a given time).

This provides the standard Schulz-Flory formula: $\text{mol}\%(n) = T_n/R = (1-\alpha)\alpha^{n-1}$ (see Supporting Information for detailed derivations).

Several oligomerisation catalysts based on early transition metals, in particular chromium-based catalysts, are known to operate *via* a different chain growth mechanism involving the formation of metallacycles. The active catalyst [M] generated from the pre-catalyst and the co-catalyst is in a lower oxidation state and undergoes oxidative addition upon coordination of ethylene. Further additions and insertions of ethylene lead to expansion of the metallacycle, as illustrated in Scheme 2. Elimination of the olefinic product occurs via β -H transfer to the chain end. The Cossee and metallacyclic mechanisms can be experimentally differentiated by coligomerisation of equimolar mixtures of C_2H_4 and C_2D_4 , as has been shown in a number of cases.¹⁹⁻²² Oligomer distributions from a simple metallacyclic mechanism follow a Schulz-Flory distribution, as shown in Figure 1 for bis(benzimidazole)pyridine chromium catalyst **1**. An α -olefin distribution with $\alpha = 0.84$ was obtained, which can be determined by fitting the experimental data to the Schulz-Flory formula or from a plot of $\ln[\text{mol}\%(n)]$ versus n (see inset Figure 1).²¹

Scheme 2: Ethylene oligomerisation via a metallacyclic mechanism

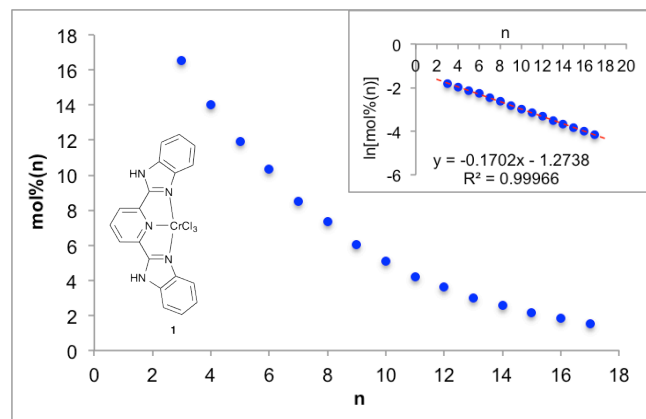
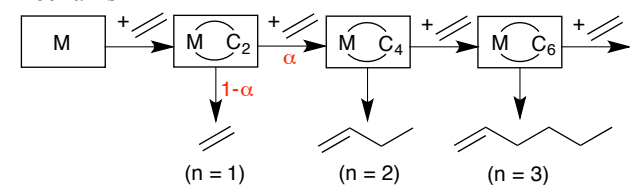


Figure 1. Schulz-Flory α -olefin distribution as $\text{mol}\%(n)$ versus n (units of ethylene) obtained with catalyst **1** (1 μmol). Conditions: 4 bar ethylene pressure, 30 $^\circ\text{C}$, co-catalyst MAO (8 mmol), toluene, 70 min. Inset: $\ln[\text{mol}\%(n)]$ versus n , $\alpha = e^{-0.1702} = 0.84$. Data used from ²¹.

Alternating Distributions

A remarkable chromium-based oligomerisation catalyst was discovered by Tomov et al. in 2006, which produces an alternating distribution of α -olefins *via* a metallacyclic mechanism.²³ The olefins obtained from an odd number of ethylene units ($n = 1, 3, 5$ etc.) are significantly less abundant than those from an even number such as 1-butene, 1-octene, 1-dodecene etc., as shown for the bis(benzimidazole)methylamine (BIMA) chromium catalyst **2** in Figure 2.

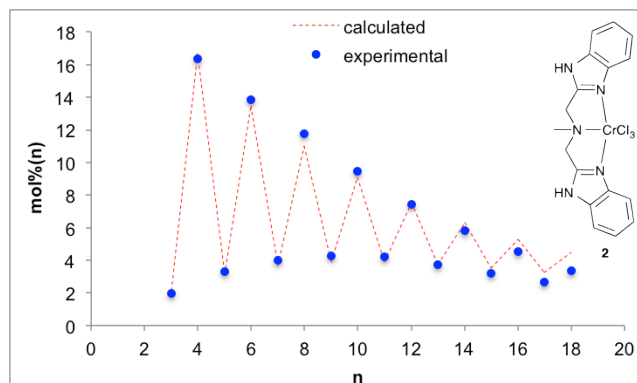
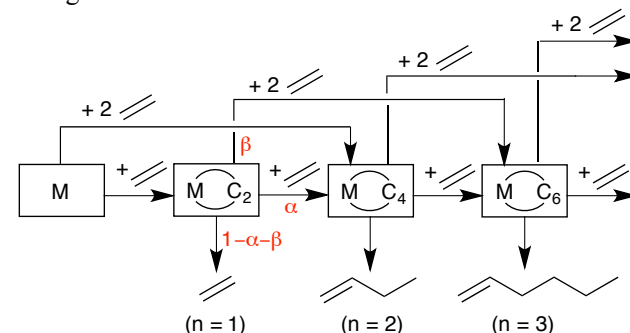


Figure 2. Alternating α -olefin distribution as $\text{mol}\%(n)$ versus n (units of ethylene) obtained with chromium BIMA catalyst **2** (32 nmol). Conditions: 4 bar ethylene pressure, 50 $^\circ\text{C}$, co-catalyst MAO (7 mmol), toluene 200 mL, 1 hour. Calculated: $\text{mol}\%(n) = 12.68(0.94)^n + 13.57(-0.85)^n$ (goodness of fit: $R^2 = 0.988$). Data used from ²³.

An alternating distribution can be described as a *second order linear homogeneous recurrence relation with constant coefficients*, $T_{n+2} = \alpha T_{n+1} + \beta T_n$. Each oligomer fraction is related to the previous fraction and the one before and the parameters α and β are in this case the probability of propagation via single ethylene coordination (α) and via double ethylene coordination (β). The term $1-\alpha-\beta$ represents the probability of termination, as illustrated in Scheme 3.

Scheme 3: Ethylene oligomerisation resulting in alternating distributions



The solution to this second order recurrence relation is more complicated and takes the general form $T_n = c_1 r_1^n$

+ $c_2r_2^n$, whereby the terms $c_{1,2}$ and $r_{1,2}$ are related to α and β as shown in Table 1. This relation can be explained as an exponential decay function $c_1r_1^n$ with decay parameter r_1 , combined with an alternating function $c_2r_2^n$ with a negative and thereby alternating parameter r_2 , as is graphically illustrated in Figure S1 (see Supporting Information).

Analysis of the oligomerisation results in Figure 2 is achieved by fitting the experimental data to the general formula $T_n = c_1r_1^n + c_2r_2^n$, which provides the equation $\text{mol}\%(n) = 12.68(0.94)^n + 13.57(-0.85)^n$ for this particular distribution. The probabilities for single and double coordination are determined as $\alpha = 0.09$ and $\beta = 0.79$ and the probability for termination is $1-\alpha-\beta = 0.12$. Small deviations at the tail end of the distribution are most likely due to some precipitation of the higher olefins.

Table 1: Overview of oligomer distributions

	Schulz-Flory Distribution	Alternating Distribution
Relation type	<i>First order homogeneous recurrence relation with constant coefficients</i>	<i>Second order homogeneous recurrence relation with constant coefficients</i>
Relation	$T_{n+1} = \alpha T_n$	$T_{n+2} = \alpha T_{n+1} + \beta T_n$
General solution	$T_n = cr^n$ $r = \alpha, c = \frac{(1-\alpha)R}{\alpha}$ $\alpha = \text{propagation probability}$ $1-\alpha = \text{termination probability}$ $R = \text{total moles of product produced during reaction time}$	$T_n = c_1r_1^n + c_2r_2^n$ $r_{1,2} = \frac{\alpha \pm \sqrt{\alpha^2 + 4\beta}}{2}$ $c_1 = \frac{(1-\alpha-\beta)[R_1(\alpha-r_2)+R_2]}{r_1(r_1-r_2)}$ $c_2 = \frac{(1-\alpha-\beta)[R_1(\alpha-r_1)+R_2]}{r_2(r_2-r_1)}$ $\alpha/\beta = \text{propagation probability by single/double coordination}$ $1-\alpha-\beta = \text{termination probability}$ $R_1 + R_2 = \text{total moles of product produced during reaction time}$
Final equation:	$\text{mol}\%(n) = cr^n/R = (1-\alpha)\alpha^{n-1}$	$\text{mol}\%(n) = \frac{c_1r_1^n + c_2r_2^n}{R_1 + R_2}$

The formation of alternating distributions relies on a mechanism that involves both single and double coordination of ethylene prior to insertion. A related mechanism was first proposed by Lemos based on kinetic studies in Ziegler-Natta catalysis,²⁴ has been implicated in other oligomerisation reactions.²⁵ Both single ethylene coordination followed by insertion and double ethylene coordination with subsequent sequential insertion of two ethylene monomers, operate simultaneously. This mechanism is related but

mechanistically distinct from the “trigger mechanism” proposed by Ystenes,²⁶ where the insertion of the first ethylene monomer is triggered by an incoming (but not completely coordinated) second monomer. The first monomer will not insert as long as a second monomer is not interacting with the metal centre. We have previously shown that the single and double coordination mechanism also operates in selective oligomerisation reactions such as the chromium-catalysed ethylene tetramerisation to 1-octene,²⁷ and the relation between these systems will be discussed in the next section.

Selective Oligomerisations

Di-, tri- and tetramerisation of ethylene are examples of selective oligomerisation reactions, which can be regarded as further variations within the distributions landscape. Dimerisation of ethylene via a Cossee mechanism can be easily understood and described as a Schulz-Flory distribution with a very high probability for chain termination (low α value).¹⁰ Selective tri- and tetramerisation reactions to 1-hexene and 1-octene, as observed with certain Cr/PNP catalysts, occur via a metallacyclic mechanism. For example, ethylene oligomerisation with chromium PNP catalyst **3** (PNP = Ph₂PN(ⁱPr)PPh₂) shown in Figure 3, results in a very high selectivity for 1-octene (≈ 70 mol%), together with approximately 16 mol% 1-hexene, 3 mol% C₁₀₊ α -olefins and various coproducts of which methyl cyclopentane and methylene cyclopentane are the major components (≈ 4 mol% each).^{12,20} Coproducts in the C₁₀-C₁₄ fractions are a result of co-trimerisation and co-tetramerisation of ethylene with 1-hexene and 1-octene resulting in various isomers.²⁷⁻³⁰

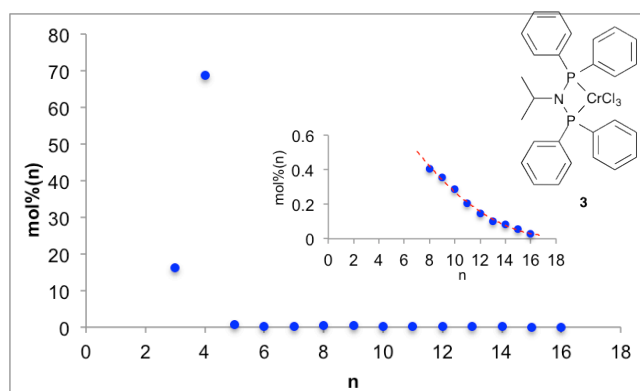


Figure 3: Selective α -olefin distribution as $\text{mol}\%(n)$ versus n (units of ethylene) obtained with Cr/PNP/MAO catalyst **3** (10 μmol). Conditions: toluene, MAO (3 mmol), 30°C, 30 bar, 30 min. Inset: Expanded $\text{mol}\%(n)$ versus n for the C₁₆-C₃₂ fraction; $\alpha = 0.80$ ($R^2 = 0.986$). Data used from ²⁷.

The high selectivity to 1-octene is the result of a distribution generated according to Scheme 3 where the probabilities for propagation α and β , and consequently termination ($1-\alpha-\beta$), are no longer *constant* for all metallacyclic intermediates. The differences are most pronounced early on in the oligomerisation process. Termination from a metallacyclopentane to give 1-butene is very unfavourable and therefore $\alpha+\beta \approx 1$, with β much larger than α as judged from large 1-octene/1-hexene ratios of 8/1 and 4.4/1 in Figures 2 and 3 respectively. Termination from the subsequent metallacycloheptane and -cyclononane intermediates is much more favourable, such that >95 mol% of the total oligomeric product has been generated at this point in the oligomerisation sequence. The probability of double coordination (β) is high for the metallacyclopentane intermediate, but rapidly decreases for larger metallacycles. From the inset in Figure 3 it can be seen that the tail end of the α -olefin distribution (approximately 3 mol%) from C₁₆-C₃₂ ($n = 8-16$) can be described by a Schulz-Flory distribution with $\alpha = 0.80$ (and consequently $\beta = 0$). The differences between the individual metallacycles become negligible for larger metallacycles, and their termination probabilities converge to a constant value of $1-\alpha-\beta = 0.2$.

The varying propagation and termination probabilities for the different metallacycles are believed to be a result of the different stabilities of the various metallacycles in these particular PNP chromium catalysts. Our recent computational studies on the related PNP* chromium catalyst system (where (PNP* = Me₂PN(Me)PMe₂) provided a barrier of +20.8 kcal/mol for termination from a metallacyclopentane intermediate to give 1-butene, which decreases to +13.9 and +11 kcal/mol for the metallacycloheptane and -cyclononane intermediates, respectively.²⁷ In addition, the formation of a metallacyclopentane complex with two coordinated ethylene units is a downhill process by -9.2 kcal/mol, whereas a doubly coordinated metallacycloheptane is uphill by +8.5 kcal/mol. The difference may be attributable to steric reasons. Selective oligomerisation reactions such as ethylene tetramerisation and trimerisation to 1-hexene with related PNP chromium catalysts, can be described as distributions generated according to Scheme 3 where the probabilities for propagation and termination vary during the oligomerisation process. These distributions can be mathematically described as a *recurrence relation with variable coefficients*, but such relations are not easily solved.

In conclusion, α -olefin distributions generated from metal-catalysed ethylene oligomerisation can be mathematically described by recurrence relations. A Schulz-Flory distribution, generated by a Cossee or a metallacyclic mechanism, is a *first order homogeneous*

recurrence relation with constant coefficients and is the simplest olefin distribution. Alternating α -olefin distributions, generated by a metallacyclic mechanism via single and double ethylene coordination, are described by *second order homogeneous recurrence relations with constant coefficients*. Selective oligomerisations such as ethylene trimerisation and tetramerisation to 1-hexene or 1-octene are oligomer distributions that follow *recurrence relations with variable coefficients*. The analysis of oligomer distributions shown here for the three selected catalysts **1-3** can also be applied to other distributions and other monomers. Further explorations of the fascinating oligomer distributions landscape are underway, as well as mathematical developments to analyse and model their underlying mechanisms.

Acknowledgement. Financial support from INEOS Technologies is kindly acknowledged. We thank the Australian Research Council for financial support through grant FT100100609 to D.S.M and the University of Tasmania for Visiting Scholars funding to G.J.P.B.

Supporting Information Available: Mathematical derivations and solutions for the recurrence relations.

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