Ethylene Oligomerization beyond Schulz–Flory Distributions

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Ⓢ *Supporting Information*

ABSTRACT: The oligomerization of ethylene produces α-olefin distributions ranging from Schulz–Flory distributions to alternating and selective oligomer distributions that can be mathematically analyzed and characterized by recurrence relations.
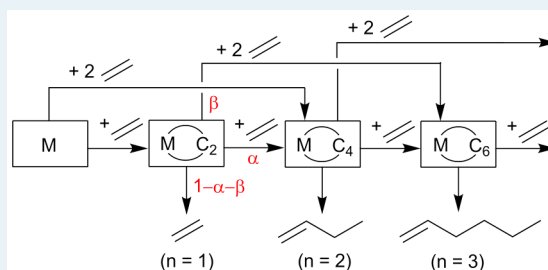
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The oligomerization of ethylene is an important industrial process for the production of linear α-olefins (LAOs).[1−3] More than 3 million tons of linear α-olefins are produced each year and used as intermediates for the production of detergents and lubricants and as co-monomers in polyethylene. Several different LAO processes exist, for example, the shell higher-olefin process (SHOP),[4] which generates a range of α-olefins from C_4 (1-butene) to C_{20+} (see Chart 1).[5] More selective

## Chart 1. Industrially Applied Oligomerization Systems
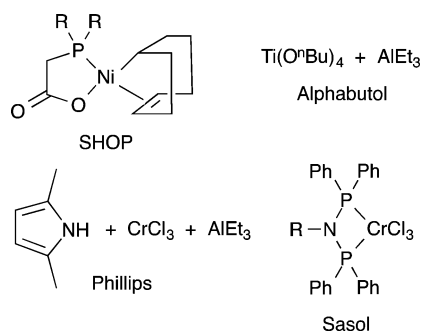
oligomerizations are, for example, the titanium-based IFP/Sabic Alphabutol process for ethylene dimerization to 1-butene[6−11] and the Sabic/Linde Alpha-SABLIN process based on zirconium for C_4–C_{10} α-olefins.[2,9] A chromium-based ethylene trimerization process to 1-hexene is operated by Chevron-Phillips, and a chromium-based ethylene tetramerization process to 1-octene was recently announced by Sasol.[5,12−14]

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 analyze olefin distributions, from the well-known simple Schulz–Flory distribution to more complicated alternating and selective oligomer distributions. This approach provides a straightforward method for analyzing and characterizing LAO distributions, while demonstrating how selective trimerizations and tetramerizations can be understood as distributions beyond Schulz–Flory.

■ SIMPLE α-OLEFIN DISTRIBUTIONS

Chain growth in ethylene oligomerization can occur via different mechanisms. Late transition metal oligomerization 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 insertion 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 Oligomerization via a Cossee Mechanism
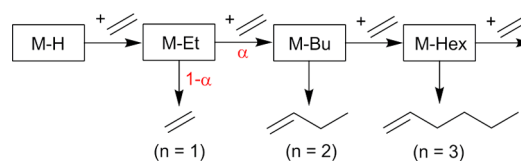
This distribution can be mathematically described as a first-order linear homogeneous recurrence relation with constant coefficients.[18] Each oligomer fraction is related to the previous fraction, $T_{n+1} = \alpha T_n$, where T_n describes the molar amount of each oligomer n (n is the number of ethylene units in the oligomer, e.g., $n = 1$ for ethylene, $n = 2$ for 1-butene, etc.) and α is the probability of chain propagation (sometimes termed the 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 relates to the ratio of chain termination and propagation probabilities $(1-\alpha)\alpha^{-1}R$ ($R = \sum T_n$, total moles of olefins produced in a given time). This provides the standard Schulz−Flory formula: mol $\%(n) = T_n/R = (1-\alpha)\alpha^{n-1}$ (see the Supporting Information for detailed derivations).

Several oligomerization 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 precatalyst and the cocatalyst 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.

Scheme 2. Ethylene Oligomerization via a Metallacyclic Mechanism
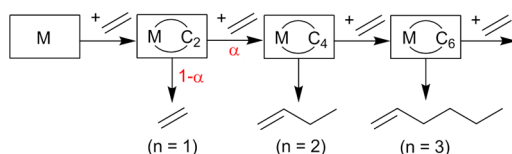
Elimination of the olefinic product occurs via β-H transfer to the opposite chain end. The Cossee and metallacyclic mechanisms can be experimentally differentiated by co-oligomerization of equimolar mixtures of C_2H_4 and C_2D_4, as has been shown in a number of cases.[19−22] Oligomer distributions from 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−
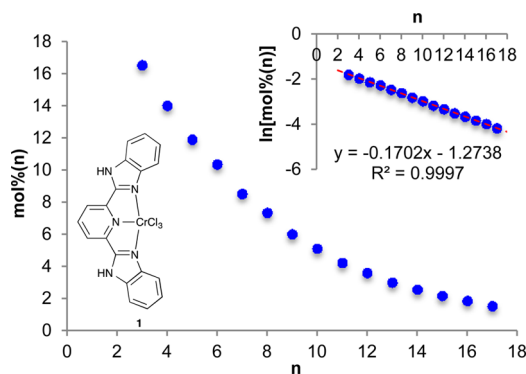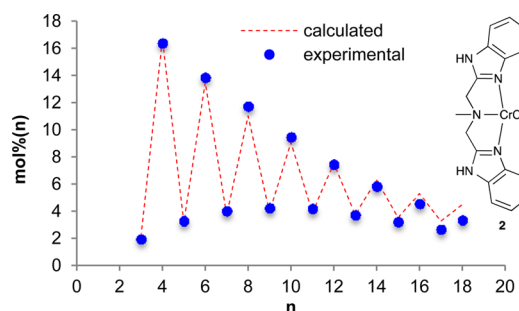

Figure 1. Schulz−Flory α-olefin distribution as mol % (n) vs n (units of ethylene) obtained with catalyst **1** (1 μmol). Conditions: 4 bar of ethylene pressure, 30 °C, cocatalyst MAO (8 mmol), toluene, 70 min. The inset shows ln[mol %(n)] vs n, where $\alpha = e^{-0.1702} = 0.84$. Data from ref 21 used.

Flory formula or from a plot of ln[mol %(n)] versus n (see the inset of Figure 1).[21]

ALTERNATING DISTRIBUTIONS

A remarkable chromium-based oligomerization 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 mol %(n) vs n (units of ethylene) obtained with chromium BIMA catalyst **2** (32 nmol). Conditions: 4 bar of ethylene pressure, 50 °C, cocatalyst MAO (7 mmol), 200 mL of toluene, 1 h. Calculated: mol %(n) = $12.68(0.94)^n + 13.57(-0.85)^n$ (goodness of fit, $R^2 = 0.988$). Data from ref 23 used.

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 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 Oligomerization Resulting in Alternating Distributions
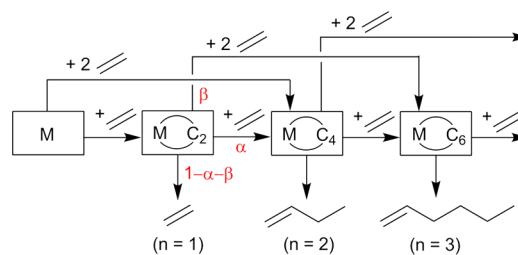
The solution to this second-order recurrence relation is more complicated and takes the general form $T_n = c_1 r_1^n + c_2 r_2^n$, whereby the terms $c_{1,2}$ and $r_{1,2}$ are related to α and β as shown in Table 1. This relation can be explained as an exponential decay function $c_1 r_1^n$ with decay parameter r_1, combined with an alternating function $c_2 r_2^n$ with a negative and thereby alternating parameter r_2, as is graphically illustrated in Figure S3 of the Supporting Information.

Analysis of the oligomerization results in Figure 2 is achieved by fitting the experimental data to the general formula $T_n = c_1 r_1^n + c_2 r_2^n$, which provides the equation mol %(n) = $12.68(0.94)^n +$

Table 1. Overview of Oligomer Distributions

|	Schulz−Flory distribution	alternating distribution
relation type	first-order homogeneous recurrence relation with constant coefficients	second-order homogeneous recurrence relation with constant coefficients
relation	$T_{n+1} = \alpha T_n$	$T_{n+2} = \alpha T_{n+1} + \beta T_n$
general solution	$T_n = cr^n$	$T_n = c_1 r_1{}^n + c_2 r_2{}^n$
	$r = \alpha, \; c = \dfrac{(1-\alpha)R}{\alpha}$	$r_{1,2} = \dfrac{\alpha \pm \sqrt{\alpha^2 + 4\beta}}{2}$
	α = propagation probability	$c_1 = \dfrac{(1-\alpha-\beta)[R_1(\alpha - r_2) + R_2]}{r_1(r_1 - r_2)}$
	$1-\alpha$ = termination probability	$c_2 = \dfrac{(1-\alpha-\beta)[R_1(\alpha - r_1) + R_2]}{r_2(r_2 - r_1)}$
	R = total moles of product produced during reaction time	α/β = propagation probability by single/double coordination $1-\alpha-\beta$ = termination probability $R_1 + R_2$ = total moles of product produced during reaction time
final equations	$\mathrm{mol}(n) = cr^n = (1-\alpha)\alpha^{n-1}R$	$\mathrm{mol}(n) = c_1 r_1{}^n + c_2 r_2{}^n$
	$\mathrm{mol}\,\%(n) = cr^n/R = (1-\alpha)\alpha^{n-1}$	$\mathrm{mol}\,\%(n) = \dfrac{c_1 r_1{}^n + c_2 r_2{}^n}{R_1 + R_2}$

$13.57(-0.85)^n$ for this particular distribution. The probabilities for single and double coordination are determined as $\alpha = 0.09$ and $\beta = 0.79$, respectively, 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.

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 of Ziegler−Natta catalysis[24] and has been implicated in other oligomerization 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 center. We have previously shown that the single- and double-coordination mechanism also operates in selective oligomerization reactions such as the chromium-catalyzed ethylene tetramerization to 1-octene,[27] and the relation between these systems will be discussed in the next section.

■ SELECTIVE OLIGOMERIZATIONS

Di-, tri-, and tetramerization of ethylene are examples of selective oligomerization reactions, which can be regarded as further variations within the distributions landscape. Dimerization 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 tetramerization reactions to 1-hexene and 1-octene, as observed with certain Cr/PNP catalysts, occur via a metallacyclic mechanism. For example, ethylene oligomerization with chromium PNP catalyst **3** [PNP = $Ph_2PN(^iPr)PPh_2$], shown in Figure 3, results in a very high selectivity for 1-octene ($\approx$70 mol %), together with approximately 16 mol % 1-hexene, 3 mol % C_{10+} α-olefins, and various coproducts of which methyl cyclopentane and methylene cyclopentane are the major
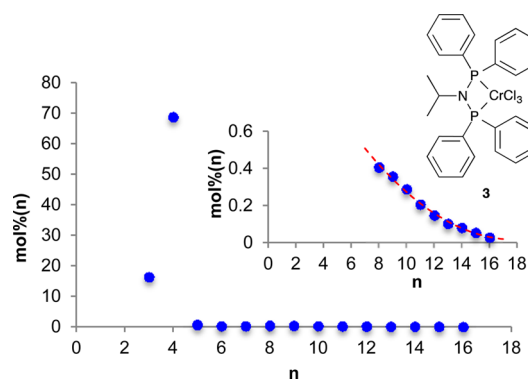
Figure 3. Selective α-olefin distribution as mol %(n) vs n (units of ethylene) obtained with Cr/PNP/MAO catalyst **3** (10 μmol). Conditions: toluene, MAO (3 mmol), 30 °C, 30 bar, 30 min. The inset shows an expanded plot of mol %(n) vs n for the $C_{16}-C_{32}$ fraction; $\alpha = 0.80$ ($R^2 = 0.986$). Data from ref 27 used.

components ($\approx$4 mol % each).[12,20] Coproducts in the $C_{10}-C_{14}$ fractions are a result of cotrimerization and cotetramerization of ethylene with 1-hexene and 1-octene resulting in various isomers.[27−30]

The high selectivity for 1-octene is the result of a distribution generated according to Scheme 3 in which 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 in the oligomerization process. Termination from a metallacyclopentane to give 1-butene is very unfavorable, and therefore, $\alpha + \beta \approx 1$, with β being much larger than α as judged from high 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 favorable, such that >95 mol % of the total oligomeric product has been generated at this point in the oligomerization sequence. The probability of double coordination (β) is high for the metallacyclopentane intermediate but rapidly decreases for larger metallacycles. From the inset of Figure 3, it can be seen that the tail end of the α-olefin distribution (approximately 3 mol %) from C_{16} to C_{32} ($n = 8-16$) can be described by a Schulz−Flory distribution

with α = 0.80 (and consequently β = 0). The differences between the individual metallacycles become negligible for larger metallacycles, and their termination probabilities converge to a constant $1-\alpha-\beta$ value of 0.20.

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 of the related PNP* chromium catalyst system [where PNP* = $Me_2PN(Me)PMe_2$] provided a barrier of +20.8 kcal/mol for termination from a metallacyclopentane intermediate to give 1-butene, which decreases to +13.9 and +11.0 kcal/mol for the metallacycloheptane and -cyclononane intermediates, respectively.[27] Single and double coordination of ethylene to a metallacyclopentane intermediate are both downhill processes by −5.8 and −3.4 kcal/mol, respectively. In contrast, whereas single coordination of ethylene to a metallacycloheptane intermediate is downhill by −3.0 kcal/mol, coordination of a second ethylene is significantly uphill by +8.5 kcal/mol, which suggests that double coordination is rather unfavorable in this case. The difference may be attributable to steric reasons. Selective oligomerization reactions such as ethylene tetramerization to 1-octene and trimerization to 1-hexene with related PNP chromium catalysts can be described as distributions generated according to Scheme 3, in which the probabilities for propagation and termination vary during the oligomerization process. These distributions can be mathematically described as recurrence relations with variable coefficients, but such relations are not easily solved.

In conclusion, α-olefin distributions generated from metal-catalyzed ethylene oligomerization can be mathematically described by recurrence relations. A Schulz−Flory distribution, generated by a Cossee or a metallacyclic mechanism, is a first-order linear 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 linear homogeneous recurrence relations with constant coefficients. Selective oligomerizations such as ethylene trimerization and tetramerization to 1-hexene or 1-octene are oligomer distributions that follow linear homogeneous 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 distribution landscape are underway, as well as mathematical developments for analyzing and modeling their underlying mechanisms.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b02203.

    Mathematical derivations and solutions for the recurrence relations (PDF)

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Notes

The authors declare no competing financial interest.

REFERENCES

(1) Forestière, A.; Olivier-Bourbigou, H.; Saussine, L. *Oil Gas Sci. Technol.* **2009**, *64*, 649.

(2) Olivier-Bourbigou, H.; Forestière, A.; Saussine, L.; Magna, L.; Favre, F.; Hugues, F. *Oil Gas Eur. Mag.* **2010**, *36*, 97.

(3) Belov, G. P.; Matkovsky, P. E. *Pet. Chem.* **2010**, *50*, 283.

(4) Keim, W. *Angew. Chem., Int. Ed.* **2013**, *52*, 12492.

(5) van Leeuwen, P. W. N. M.; Clément, N. D.; Tschan, M. J.-L. *Coord. Chem. Rev.* **2011**, *255*, 1499.

(6) Commereuc, D.; Chauvin, Y.; Gaillard, J.; Léonard, J.; Andrews, J. *Hydrocarb. Process.* **1984**, *63*, 118.

(7) Al-Sa'doun, A. W. *Appl. Catal., A* **1993**, *105*, 1.

(8) Al-Jarallah, A. M.; Anabtawi, J. A.; Siddiqui, M. A. B.; Aitani, A. M.; Al-Sa'doun, A. W. *Catal. Today* **1992**, *14*, 1.

(9) Breuil, P.-A. R.; Magna, L.; Olivier-Bourbigou, H. *Catal. Lett.* **2015**, *145*, 173.

(10) Suttil, J. A.; McGuinness, D. S. *Organometallics* **2012**, *31*, 7004.

(11) Robinson, R.; McGuinness, D. S.; Yates, B. F. *ACS Catal.* **2013**, *3*, 3006.

(12) Bollmann, A.; Blann, K.; Dixon, J. T.; Hess, F. M.; Killian, E.; Maumela, H.; McGuinness, D. S.; Morgan, D. H.; Neveling, A.; Otto, S.; Overett, M. J.; Slawin, A. M. Z.; Wasserscheid, P.; Kuhlmann, S. *J. Am. Chem. Soc.* **2004**, *126*, 14712.

(13) McGuinness, D. S. *Chem. Rev.* **2011**, *111*, 2321.

(14) Agapie, T. *Coord. Chem. Rev.* **2011**, *255*, 861.

(15) Schulz, G. V. *Z. Phys. Chem. (B)* **1935**, *30*, 379.

(16) Flory, P. J. *J. Am. Chem. Soc.* **1936**, *58*, 1877.

(17) Cossee, P. *J. Catal.* **1964**, *3*, 80.

(18) Rosen, K. H.; Michaels, J. G. *Handbook of discrete and combinatorial mathematics*; CRC Press: Boca Raton, FL, 2000.

(19) Agapie, T.; Schofer, S. J.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2004**, *126*, 1304.

(20) Overett, M. J.; Blann, K.; Bollmann, A.; Dixon, J. T.; Haasbroek, D.; Killian, E.; Maumela, H.; McGuinness, D. S.; Morgan, D. H. *J. Am. Chem. Soc.* **2005**, *127*, 10723.

(21) Tomov, A. K.; Chirinos, J. J.; Jones, D. J.; Long, R. J.; Gibson, V. C. *J. Am. Chem. Soc.* **2005**, *127*, 10166.

(22) Tomov, A.; Gibson, V. C.; Britovsek, G. J. P.; Long, R. J.; van Meurs, M.; Jones, D. J.; Tellmann, K. P.; Chirinos, J. J. *Organometallics* **2009**, *28*, 7033.

(23) Tomov, A.; Chirinos, J. J.; Long, R. J.; Gibson, V. C.; Elsegood, M. R. J. *J. Am. Chem. Soc.* **2006**, *128*, 7704.

(24) Marques, M. M.; Dias, A. R.; Costa, C.; Lemos, F.; Ramôa Ribeiro, F. *Polym. Int.* **1997**, *43*, 77.

(25) Kelly, W. M.; Wang, S.; Collins, S. *Macromolecules* **1997**, *30*, 3151.

(26) Ystenes, M. *J. Catal.* **1991**, *129*, 383.

(27) Britovsek, G. J. P.; McGuinness, D. S.; Wierenga, T. S.; Young, C. T. *ACS Catal.* **2015**, *5*, 4152.

(28) Bowen, L. E.; Wass, D. F. *Organometallics* **2006**, *25*, 555.

(29) Bowen, L. E.; Charernsuk, M.; Hey, T. W.; McMullin, C. L.; Orpen, A. G.; Wass, D. F. *Dalton Trans.* **2010**, *39*, 560.

(30) Do, L. H.; Labinger, J. A.; Bercaw, J. E. *Organometallics* **2012**, *31*, 5143.