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**(ⁿBuCp)₂ZrCl₂-catalyzed Ethylene-4M1P Copolymerization:
Copolymer Backbone Structure, Melt Behavior, and Crystallization****Muhammad Atiqullah**

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The judicious design of methylaluminoxane (MAO) anions expands the scope for developing industrial metallocene catalysts. Therefore, the effects of MAO anion design on the backbone structure, melt behavior, and crystallization of ethylene-4-methyl-1-pentene (E-4M1P) copolymer were investigated. Ethylene was homopolymerized, as well as copolymerized with 4M1P, using (i) MAO anion A (unsupported [MAOCl₂][−]) premixed with dehydroxylated silica, (ⁿBuCp)₂ZrCl₂, and Me₂SiCl₂; and (ii) MAO anion B (Si-O-Me₂Si-[MAOCl₂][−]) supported with (ⁿBuCp)₂ZrCl₂ on Me₂SiCl₂-functionalized silica. Unsupported Me₂SiCl₂, opposite to the supported analogue, acted as a co-chain transfer agent with 4M1P. The modeling of polyethylene melting and crystallization kinetics, including critical crystallite stability, produced insightful results. This study especially illustrates how branched polyethylene can be prepared from ethylene alone using particularly one metallocene-MAO ion pair, and how a compound, that functionalizes silica as well as terminates the chain, can synthesize ethylene- α -olefin copolymers with novel structures. Hence, it unfolds prospective future research niches in polyethylene synthesis.

Keywords: metallocene catalyst, ethylene-4-methyl-1-pentene copolymerization, 1,2 versus 2,1 insertion, inter- and intra-chain composition distributions, pseudo-tandem branched polyethylene, lamellar thickness distribution, melt behavior, nonisothermal crystallization kinetics

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Introduction

Metallocenes are a modern innovation in the family of polyolefin catalysts. Here, the [metallocenium]⁺[cocatalyst][−] ion pair is the active catalytic species, which applies to supported as well as unsupported metallocenes. The partial alkylation and abstraction of the chloride σ -ligand (attached to the transition metal) by the methylaluminoxane (MAO) cocatalyst form the above catalytic ion pair.^{1–10} This is how the metallocene precatalyst is activated. In this area, the scope to modify the non-coordinating MAO anion, for a selected metallocene, is very wide. The functionalization of the support; introduction of a spacer; use of additional anions, Lewis acids and phase transfer catalysts; etc. partially list the various approaches that we can apply to prepare different MAO anions. The supported catalyst is the prerequisite to achieve the desired polyolefin particulate morphology, using slurry and gas phase fluid bed polymerization processes. These two polyolefin-making processes are industrially most prevalent. We summarize below how the MAO anion relates to the development of the copolymer backbone and the resulting thermal properties.

Metallocene-catalyzed olefin polymerization is an example of a typical addition polymerization. Therefore, it characteristically consists of the following three elementary steps: initiation (activation), propagation, and termination. However, these steps differ from those of a conventional free-radical polymerization. We already reported the first step above. Reversible complex formation^{11–15} with the transition metal active site, as per the *trigger mechanism* of Ystenes,¹⁶ makes the propagation step. According to Ystenes, the coordination site is never free; it is always occupied by a monomer. This complexed monomer gets inserted into the

growing polymer chain as soon as another incoming monomer is ready to complex through expansion of the coordination sphere. This associates two monomers with the active center in the form of a transition state.¹⁰ The termination step is completed through various chain transfer reactions, which have been detailed elsewhere in the literature.¹⁷ The propagation step determines the catalyst activity and dictates the copolymer inter- and intra-chain composition distributions. On the other hand, the relative rate between chain propagation and chain termination controls the molecular weight distribution and its average. Independently, the chain termination introduces various chain end unsaturations, such as vinyl, vinylidene, and trans-vinylene groups. This is how the MAO anion—the noncoordinating component of the catalyst active species—indirectly influences the architecture of the resulting polyethylene backbone.

The incorporation of the α -olefin comonomer affects the catalyst-mediated copolymer backbone. It introduces structural/enchainment defects (which varies from backbone to backbone) and partially disrupts the crystal package of the polyethylene chains. The distribution of ethylene sequence (between the pendant side chains), that is, the *equilibrium crystal length* characterizes this crystal package disruption. The structural defects and *equilibrium crystal length* are basic factors that influence the copolymer thermal behavior which is reflected during melting and cooling (crystallization). The latter aspects relate to polymer processing and making the desired end-products.

Metallocene-catalyzed copolymerization of ethylene with various substituted pentenes, including 4-methyl-1-pentene (4M1P) (a sterically hindered α -olefin), is a versatile approach to making new grades of linear low density polyethylenes

(LLDPEs). Mitsui's ULTZEX[®] and BP's Innovex[®] grades are selected examples of commercial E-4M1P copolymers.^{18,19} These LLDPEs have a lot of applications in power, control, optical, telephone, and signal cables. However, we note that the contributions to this area are far less in the literature than those related to ethylene-1-hexene copolymerization. So far as metallocenes are concerned, we can summarize research in this area as follows. Several groups worked on E-4M1P solution copolymerization to investigate catalyst structure-activity relationship, influence of polymerization conditions, comonomer effect, and copolymer microstructure (as appropriate).^{18,20–25} On the other hand, Awudza and Tait²⁶ show to be the only group that studied E-4M1P slurry copolymerization, using supported silica/MAO/Cp₂ZrCl₂ catalyst, where Cp₂ZrCl₂ stands for bis(cyclopentadienyl) zirconium dichloride. They primarily investigated comonomer effect. However, none of these studies investigated E-4M1P copolymerization from the significantly coherent view point of MAO anion design, polymer backbone structure, and melt and crystallization behavior, which we summarized earlier. This motivated us to undertake this study, which we, therefore, design as follows.

- i. Investigate how the proposed differing MAO anions, with a defined metallocene precatalyst, affect E-4M1P copolymer backbone structure (molecular weight distributions and averages; and the copolymer inter- and intra-chain composition distributions, and averages).
- ii. Evaluate the potential of a silane, such as supported and unsupported Me₂SiCl₂ (a secondary chlorosilane), to influence the elementary copolymerization reactions and thereby synthesize ethylene- α -olefin copolymers with prospective novel structures and properties.

- iii. Study the influence of the above copolymer backbone inter- and intra-chain composition distributions on the resulting melt and crystallization behavior, including the crystal package disruption, critical crystallite stability, and crystallization kinetics, through appropriate modeling and experiments.

We shall investigate the above using *pseudo*-homogeneous polymerization (developed in our laboratory) and the typical slurry-heterogeneous polymerization. Both polymerization modes overcome reactor fouling and thermal runaway problems, and are likely to ensure, under the same impeller speed, reaction volume, feed rate, etc. approximately comparable hydrodynamics and macromixing, which are very important. By macromixing we mean mixing at the scale of the impeller and the reactor vessel among molecules having varying residence times, particularly with reference to a semi-batch stirred reactor.²⁷ In *pseudo*-homogeneous polymerization, an equivalent amount of the dehydroxylated support, functionalizing agent (optional), metallocene, and cocatalyst are instantaneously premixed, preferably in a common solvent such as toluene (density = 0.8623 g/mL at 25 °C). Then the resulting mixture, monomer, and comonomer immediately feed the reactor containing the polymerization diluent, namely *n*-hexane (density = 0.6548 g/mL at 25 °C). Toluene (an aromatic compound) and *n*-hexane (an aliphatic compound), because of density difference, are immiscible. MAO—the most widely used cocatalyst—is soluble in toluene and insoluble in *n*-hexane. Therefore, they are likely to form, strictly and theoretically speaking, a two-phase microemulsion that contains the active catalytic species, effecting the polymerization. Hence, the polymerization primarily occurs in this microemulsion phase because of very prompt premixing and the afore-said mode

of reactor feeding, which are stringent prerequisites to the currently defined *pseudo*-homogeneous polymerization. On the other hand, the slurry-heterogeneous polymerization feeds the solid catalyst particles, impregnating the catalyst components, directly into the reactor. Here, the catalyst particles and the liquid polymerization medium, under vigorous mixing, make a slurry. The polymerization occurs on the suspended solid catalyst particles. We shall use (i) the commercially available $(^n\text{BuCp})_2\text{ZrCl}_2$ bis(*n*-butyl cyclopentadienyl) zirconium dichloride (an *aspecific* C_{2v} symmetric metallocene, (ii) Me_2SiCl_2 to functionalize the silica, and (iii) the following two differing anions, unsupported $[\text{MAOCl}]^-$ (MAO anion A) and supported $\text{Si-O-SiMe}_2-[\text{MAOCl}]^-$ (MAO anion B). The synthesis of these MAO anions has been illustrated through Scheme 1 that shows the major relevant reactions which have been reported in References 28 and 29 and the citations therein. We shall pursue the modeling work using Flory equation,^{30,31} Gibbs-Thompson (GT) lamellar thickness equation,^{31–35} and a new nonisothermal Avrami-Arofeev crystallization model that we published in 2013.³⁶

We trust that this study will hopefully add new insight to metallocene-catalyzed ethylene homo- and copolymerization and broaden our comprehension.

Experimental

Materials

Silica PQ 3030 having surface area of $322 \text{ m}^2/\text{g}$, an average pore volume of $3.00 \text{ cm}^3/\text{g}$, and a pore size of $374 \text{ \AA}$ was used as the catalyst support.

$(^n\text{BuCp})_2\text{ZrCl}_2$ and MAO (30 wt% in toluene) were bought from Chemtura, Germany. Analytical grade toluene, *n*-hexane (both 99.999 % pure), molecular

sieves, 0.05 w/v% 2,6-di-*tert*-butyl-4-methyl phenol (BHT), 1,2,4 trichlorobenzene (TCB) (analytical grade and deuterated), triisobutylaluminum (TIBA), dimethyl dichlorosilane (Me_2SiCl_2), and 4-methyl-1-pentene (4M1P)—all were purchased from Sigma-Aldrich. Ethylene (99.999 % pure) was procured from a local vendor; and oxygen trap (OT-4-SS) and moisture absorber (500CC 316-SS), from Agilent and Parker, respectively.

Synthesis of the supported catalyst

The supported catalyst—silica/ Me_2SiCl_2 /MAO/($^n\text{BuCp}$) $_2\text{ZrCl}_2$ —was synthesized as follows by doing all the manipulations under argon, using standard Schlenk technique. Toluene was dried using 4A activated molecular sieve, and it was used in each step.

The required amount of silica was dehydroxylated at 250 °C for 4 h using a Thermocraft furnace equipped with a vertical quartz glass tube, a digital temperature indicator and a controller, a gas flow meter, and a vacuum pump. The silica was continuously fluidized during dehydroxylation using nitrogen. Upon dehydroxylation, it was stored in an inert glove box.

The required amounts of dehydroxylated silica, Me_2SiCl_2 , and the dried toluene were slurried in a specially designed Schlenk flask. The resulting mixture was refluxed at the boiling point of toluene for 20 h to functionalize silica with Me_2SiCl_2 . After that, the functionalized silica was vacuum dried to free-flowing particles.

Next, a calculated volume of MAO was added drop by drop to a given amount of functionalized silica-toluene slurry under argon using constant stirring at room temperature. Then this was heated for several hours for complete impregnation.

Following this, the mixture was cooled to room temperature, and a calculated amount of $(^n\text{BuCp})_2\text{ZrCl}_2$ was added to it and heated at 80 °C for 1 h. This final catalyst was dried under vacuum to free-flowing particles and saved in a glove box. The following compositions—Si (wt%), Al (wt%), Zr (wt%), and Al:Zr molar ratio—were calculated from mass balance. These turned out to be 79.98, 18.68, 1.34, and 47.2, respectively.

Polymerization trials

Ethylene was homo- and copolymerized using a computer-interfaced, AP Miniplant laboratory-scale reactor set up. It consists of a fixed top head and a one-liter jacketed Büchi glass autoclave. The glass reactor was baked for 2 h at 120 °C. Then, it was purged with nitrogen four times at the same temperature. The reactor was cooled from 120 °C to 40 °C. About 200 ml of dried *n*-hexane was transferred to the reactor. Then, 1.0 ml of 1.0 M TIBA was added to scavenge the impurities that may poison the catalyst, and the mixture was stirred for 10 min. *n*-hexane was dried by contacting it with activated 4A molecular sieves at room temperature over night that decreased the moisture level to less than 10 ppm. The molecular sieve was activated at 230 °C. At this stage, for the copolymerization, 15 mL 4M1P was added. The resulting mixture was stirred at 50 rpm for 10 min. For the homopolymerization, no 4M1P was used.

The slurry-heterogeneous polymerization was conducted as follows. An estimated amount of the supported catalyst was slurried in 50 ml of *n*-hexane. The whole volume was siphoned into the reactor under mild argon flow. No MAO cocatalyst was separately added to the reactor. Ethylene was passed through oxygen- and moisture-removing columns. Then it fed the reactor at a constant flow rate of

5000 NmL/min to maintain approximately the same level of macromixing. The polymerization temperature and stirrer speed were set at 50 °C and 700 rpm, respectively. An anchor stirrer (impeller) was used. The trial was continued for 1 h. The polymerization was terminated by closing the ethylene flow and venting the post-polymerization ethylene (in the reactor) to the atmosphere. Then, the data acquisition was stopped; the stirrer speed was reduced to about 100 rpm; and the reactor was gradually cooled to room temperature.

During *pseudo*-homogeneous polymerization, the amounts of silica, Me_2SiCl_2 , MAO, and $(^n\text{BuCp})_2\text{ZrCl}_2$, which corresponded to the Si, Al, and Zr content of the above supported catalyst, were first pre-contacted in dried toluene. Toluene is a common solvent for MAO and $(^n\text{BuCp})_2\text{ZrCl}_2$. Next, the resulting mixture, ethylene, and 4M1P comonomer were immediately introduced to the reactor. The rest of the above slurry polymerization procedures were repeated.

After conducting a polymerization trial, the reactor was opened; the resulting polyethylene was dried under ambient condition in a hood, and the dried polymer was weighed to determine the yield. The polymer yield was subsequently used to determine the corresponding catalyst productivity which has been reported in Table 1. Using each polymerization mode (*pseudo*-homogeneous and slurry-heterogeneous polymerization) and MAO anion, one homo- and one E-4M1P copolymer were prepared.

Molecular weights and polydispersity indices

The synthesized polyethylenes were characterized in terms of molecular properties [weight average molecular weight (M_w) and polydispersity index (PDI)] using a Waters 200 gel permeation chromatography (GPC) instrument. The column

temperature was set at 135 °C. Polyethylene sample (about 1.0 mg), taken in a 1 mL vial, was dissolved in 1.0 mL Santanox R-stabilized 1,2,4 trichlorobenzene (TCB) as follows. The vial was shaken in the warming compartment of the GPC instrument at 135 °C for about 5 h to completely dissolve the sample.

Before injecting the samples, the differential refractive index (DRI) detector was purged for 4 h using TCB (1 mL/min) to obtain stable baseline. Also, the inlet pressure (IP) and the differential pressure (DP) outputs were purged for 1 h. The flow rate of TCB was 1.0 mL/min and each sample was analyzed for 35 min.

The instrument was calibrated using nine polystyrene standards whose peak molecular weights ranged from 580 to 3.79 million. The polystyrene calibration curve was converted into the corresponding polyethylene calibration curve using the Mark-Houwink constants of both polymers.³⁷ Table 1 reports the measured average molecular weights and the polydispersity indices.

Thermal properties, density, and copolymer melt fractionation

The thermal properties of the as-synthesized polyethylenes were measured in terms of peak melting (T_{pm}) and crystallization (T_{pc}) temperatures, and % crystallinity (X_c) using a differential scanning calorimeter (DSC Q2000, Texas Instrument). The instrument was calibrated using indium. The experimental procedure reported in the literature was followed.^{38–40} The data were acquired for each cycle and handled using the TA explorer software. The measured X_c was subsequently used to calculate the polymer material density ρ_{polym} , following the rule of additivity of volumes of polyethylene amorphous and crystalline phases:¹⁷ $X_c = (1/\rho_{polym} - 1/\rho_a)/(1/\rho_c - 1/\rho_a)$; where ρ = density; a = amorphous phase; c = crystalline phase; and $polym$ = polymer.

For polyethylene, $\rho_c = 1.004$ g/mL and $\rho_a = 0.853$ g/mL. Next, the amorphous volume fraction ϕ_a was estimated using the relation $\phi_a = (\rho_c - \rho)/(\rho_c - \rho_a)$. Table 1 reports the above thermal properties, densities, and amorphous volume fractions of the as-synthesized polyethylenes.

The synthesized copolymers were thermally fractionated using the above DSC instrument, and following the successive self-nucleation and annealing (SSA) experimental procedure reported in the literature.^{41–47} Seven annealing steps (160, 125, 119, 114, 111, 107, and 103 °C) were applied. Details are available in Reference 47.

Copolymer composition distribution

The composition distribution of the as-synthesized copolymers was determined using Polymer Char CRYSTAF 100 instrument. The fractionation principle of this technique is already published in the literature.^{48–50} The sample solution of concentration 0.1% (w/w) was prepared in 1, 2, 4 trichlorobenzene (TCB) at 160 °C under stirring for 60 min. The solution was equilibrated at 95 °C for 45 min. This was subsequently crystallized at a cooling rate of 0.2 °C/min from 95 °C to 35 °C.

The qualitative differential composition distribution ($\frac{dw}{dT}$ versus T) was obtained by numerical differentiation of the integral analogue.

Copolymer microstructure and ethylene sequence length distribution

The microstructural parameters, including average ethylene and 4M1P mole% in the synthesized copolymers, were determined using ^{13}C NMR spectroscopy. For this, a Bruker 600 MHz AVANAC III spectrometer (Bruker BioSpin, Rheinstetten, Germany) was used. The details of this instrument and the NMR operating conditions

and procedure are available in one of our earlier publications.⁴⁰ The spectra were recorded using DEPT (distortionless enhancement by polarization transfer) 135 pulse sequence, and they were analyzed applying Bruker Topspin 2.1 software (Bruker BioSpin, Rheinstetten, Germany). The receiver gain was set at 203. Exponential line broadening of 1 Hz was applied before Fourier transformation. DEPT was used because of its prioritized advantages that include enhanced ¹³C signal sensitivity; superior spectral editing; and capability to distinguish methyl CH₃, methylene CH₂, and methine CH sites, and identify branches.

First, the mole fractions of the E-4M1P copolymer, triad sequences were calculated following the procedure published by Kimura et al.⁵¹ Next, the monad and diad mole fractions, and the copolymer microstructural parameters of the present interest were calculated using the relations reported in References 52 and 53. Table 2 lists the triad and monad mole fractions (average copolymer compositions), and the copolymer microstructural parameters.

The thermodynamically predicted theoretical distribution of ethylene sequence length (between the pendant *i*-butyl side chains), that is, the *equilibrium crystal length* was calculated using the Flory equation.^{30,31} According to this, the normalized weight fraction W_n of the sequence of n ethylene units (bounded at either end by 4M1P) is related to the ethylene perpetuation probability p , that is, the probability that a crystallizable unit is succeeded by another such unit, through the following expression:

$$W_n = n(1-p)^2 p^{n-1} \quad (5)$$

where p is also called sequence propagation probability.

For a statistical copolymer with very long chains, p is related to the experimental reactivity ratio product $\langle r_E r_C \rangle$ and ethylene mole fraction X_E as follows:^{31,54}

$$p = 1 - \frac{1 - [1 - 4(1 - \langle r_E r_C \rangle)X_E(1 - X_E)]^{1/2}}{2(1 - \langle r_E r_C \rangle)X_E} \quad \langle r_E r_C \rangle \neq 1 \quad (6)$$

blocky and alternating

$$p = X_M = X_E \quad \langle r_E r_C \rangle = 1 \quad \text{random} \quad (7)$$

where X_M is the mole fraction of the monomer. Note that the perpetuation probability p shows the aliased interaction of $\langle r_E r_C \rangle$ and X_E . Therefore, varying combinations of $\langle r_E r_C \rangle$ and X_E may give the same value of p . Consequently, the definition of block copolymer for $p > X_E$ and alternating copolymer for $p < X_E$ ^{55,56} may be misleading. See Reference 57 for the details.

The ethylene perpetuation probability p can be used to study copolymer melt behavior and crystallization by calculating the critical (limiting) sequence number $n^*(T)$ of the stable crystallite, that equilibrates with the melt at a given temperature, using the following equation.^{30,32,58}

$$n^*(T) = \frac{-1}{\theta + \ln p} \left[\ln \left(\frac{DX_E}{p} \right) + 2 \ln \left(\frac{1-p}{1-e^{-\theta}} \right) \right] \quad (8)$$

where

$$\theta = \frac{\Delta H_u}{R} \left(\frac{1}{T} - \frac{1}{T_m^0} \right) \quad \text{and} \quad D = e^{-2\sigma_e a_o / RT}$$

In Equation 8, T_m^0 is the melting point for polyethylene perfect crystal, ΔH_u is the heat of fusion for a C_2H_4 repeat unit, σ_e is the polyethylene basal surface energy, and a_o is the cross-sectional area of a polyethylene chain. The parameters θ and D measure the level of undercooling and crystal surface free energy effect, respectively.

For a constant cooling rate nonisothermal crystallization process in a typical DSC experiment, it evaluates the temperature-dependent dynamic critical crystallite stability.

Only ethylene sequences, greater than $n^*(T)$, form stable crystals in copolymers. With increasing temperature, the crystals melt and $n^*(T)$ increases, and $n^* \rightarrow \infty$ represents the thickest possible crystals.⁵⁸ A particular feature of Equation 8 is that it includes p which is a function of $\langle r_{ERC} \rangle$ and X_E . Catalyst mediates $\langle r_{ERC} \rangle$ and X_E . Therefore, this equation indirectly investigates the effect of catalyst on copolymer melt behavior and crystallization.

Using $X_E = p = 1$, the series expansion of $\ln(1 - p)$ for $p \rightarrow 1$, and $(1 - 1/2 + 1/3 - 1/4 + 1/5 - \dots) = \ln 2$, we derived the following expression for a homopolymer:

$$n^*(T) = -\frac{1}{\theta} \ln \frac{D}{4(1 - e^{-\theta})^2} \quad (9)$$

Modeling of Polymer Crystallization Kinetics

A new nonisothermal crystallization model³⁶ for crystalline polymer using the Avrami-Erofeev equation was published by us in 2013. This model, with detailed assumptions and mathematical derivation, and experimental evidence, is reported in the above reference. Here, a summary is provided as follows.

The *nonisothermal* Avrami-Erofeev polymer crystallization rate can be written as:

$$\frac{d\alpha}{dT} = \frac{k_0}{\beta} \times \exp \left[-\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right] \times n(1 - \alpha) [-\ln(1 - \alpha)]^{\frac{n-1}{n}} \quad (10)$$

where we define the following:

$$f(\alpha) = n(1-\alpha)[-\ln(1-\alpha)]^{\frac{n-1}{n}} \quad (11)$$

$$k'(T) = k_0 \times \exp\left[-\frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \quad (12)$$

$$E_a = (\text{apparent crystallization energy}) = E_{\text{grow}} - E_{\text{nucl}} \quad (13)$$

$$k_0 = \left(\frac{k_s N_0}{V_0}\right) \frac{k_{\text{grow},0}}{k_{\text{nucl},0}} \quad (14)$$

$$k_{\text{grow}}(T) = k_{\text{grow},0} \times \exp\left[-\frac{E_{\text{grow}}}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \quad (15)$$

$$k_{\text{nucl}}(T) = k_{\text{nucl},0} \times \exp\left[-\frac{E_{\text{nucl}}}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \quad (16)$$

In the above equations, $f(\alpha)$ is called Avrami-Erofeev nonisothermal crystallization function. n is the dimension of the growing crystal. N_0 is the number of germ nuclei, that is, the potential nucleus formation sites/defects. V_0 is the initial volume of the molten polymer. K_s is the shape factor for the growing nuclei. $k_{\text{grow},0}$ and E_{grow} are the frequency factors and activation energy of crystal growth, respectively. $K_{\text{nucl},0}$ and E_{nucl} represent the corresponding terms for nucleation, respectively. T_0 is the centering temperature.

The Avrami index n , in Equation 10, illustrates two aspects—the crystal dimension and the nature of nucleation process. Therefore, n is written in terms of the following two components:⁵⁹

$$n = n_d + n_n \quad (17)$$

where n_d shows the dimension of the growing crystals. Theoretically speaking, n_d can be only integers—1, 2, and 3—that correspond to one-, two-, and three-dimensional crystals formed, respectively; and n_n represents the time dependence of the nucleation process. In principle, it should be 0 or 1, where 0 refers to instantaneous (athermal/heterogeneous) nucleation; and 1, to sporadic (thermal/homogeneous) one. For many systems, the model-predicted n turns out to be a non-integer which is attributed to $0 \leq n_n \leq 1$. This means that the nucleation process is intermediate between instantaneous and sporadic.⁶⁰ A balance between thermodynamic and kinetic factors influences the value of n_n .⁵⁵

α is related to the corresponding weight fraction relative crystallinity $\alpha_w(T)$ through the following expression:³⁶

$$\alpha = \frac{\alpha_w}{\alpha_w + \frac{\rho_c}{\rho_a}(1 - \alpha_w)} \quad (18)$$

where ρ_c and ρ_a are the densities of the crystalline and amorphous phases, respectively. For polyethylene, the values of ρ_c and ρ_a have been reported earlier.

α_w can be calculated from a typical constant cooling rate nonisothermal DSC experiment by using Equation 19:

$$\alpha_w = \frac{\Delta H(T)}{\Delta H_{total}} = \frac{\int_{T_0}^T \left(\frac{dH}{dT} \right) dT}{\int_{T_0}^{T_\infty} \left(\frac{dH}{dT} \right) dT} \quad (19)$$

where ΔH_{total} is the maximum enthalpy value reached at the end of the nonisothermal crystallization process and $\Delta H(T)$ is the enthalpy evolved as a function of

crystallization temperature T . T_o and T_∞ represent the start and completion temperatures of crystallization, respectively. ΔH_{total} and $\Delta H(T)$ both can be acquired through the software of a standard differential scanning calorimeter (DSC). Using Equation 18, the DSC-generated α_w can be converted to the corresponding volume fraction α .

The experimental confirmation of the above new non-isothermal crystallization model is available in one of our recent publications.⁶¹

Results and Discussion

Copolymer inter-chain composition distribution and copolymerization micromixing/segregation effects

Here, we evaluate how the lack of molecular level mixing (micromixing), or the occurrence of segregation effect influences the as-synthesized E-4M1P copolymer inter-chain differential composition distribution, measured by *Crystaf*. Note that it is copolymer composition distribution that is particularly sensitive to micromixing/segregation effects.^{62–64} We specifically discourse the effects of unsupported $[\text{MAOCl}_2]^-$ and Me_2SiCl_2 versus supported $\text{Si-O-Me}_2\text{Si-}[\text{MAOCl}_2]^-$ on ethylene and 4M1P insertions.

Figure 1 shows that MAO anion A (*pseudo*-homogeneous polymerization) and MAO anion B (slurry-heterogeneous polymerization without separate feeding of MAO) synthesized highly broad composition distribution E-4M1P copolymers. Also, see the root mean square crystallization temperature $T_{\sigma \text{Crystaf}}$ values in Table 1. This composition distribution broadness demonstrates the presence of significant

micromixing/segregation effect.^{62–64} This result can be ascribed to the three-dimensional MAO cage structures that feature the following:^{4,5,7–9,65–67}

- i. Each MAO structure comprises n different MAO $[-(\text{AlOMe})_n-]$ repeat units; and
- ii. The above MAO structures have preferably one type of defined strong active Lewis acid catalyst site that can be attributed to the $-\text{AlO}_2\text{Me}-$ environment.⁸ Accordingly, different active site ion-pairs $[\text{Zr}]^+[\text{MAO}]_n^-$, in the presence of $(^n\text{BuCp})_2\text{ZrCl}_2$, are likely to prevail. This subject—metallocene active center distribution—has been particularly detailed in some of our recent publications.^{29,40}

Despite the above commonality of composition distribution broadness, the *Crystaf* curve of Copolymer B (slurry-heterogeneous polymerization without separate feeding of MAO) strikingly differed from that of Copolymer A (*pseudo*-homogeneous polymerization with premixed feeding of dehydroxylated silica, $(^n\text{BuCp})_2\text{ZrCl}_2$, MAO anion A, and Me_2SiCl_2). To explain this finding better, we plotted, in parallel, the *Crystaf* curves of Homopolymer A and Homopolymer B. Highly interesting results follow. Homopolymer A showed a sharp monomodal composition distribution around 90 °C. This means that it practically comprised linear polyethylene backbones, essentially devoid of branching. However, Homopolymer B (unlike Homopolymer A) and Copolymer A, during *Crystaf* cooling, successively crystallized from ethylene-rich branched backbones (at around 78 °C), with minor α -olefin incorporation, to crystallizable E- α -olefin backbones till 38 °C without any amorphous/rubbery E- α -olefin soluble fraction. In this context, α -olefin means

4M1P for Copolymer A, and very likely several unsaturated hydrocarbon oligomers for Homopolymer B. Hence, Homopolymer B and Copolymer A may be considered as a catalyst-mediated *in-situ* reactor blend of fairly ethylene-rich backbones and crystallizable E- α -olefin backbones, without E- α -olefin soluble fraction. Therefore, Homopolymer B is a branched polyethylene formed *via* polymerization of ethylene alone. Note that its Crystaf curve fairly resembles that of Copolymer A. The SSA-induced fractionation of Homopolymer B, which alternatively confirms branching, will be addressed at a later section. On the other hand, the Copolymer B *Crystaf* curve did not show the ethylene-rich backbones. It demonstrated (i) only crystallizable E-4M1P backbones and E-4M1P soluble fraction (0.0018), and (ii) very low crystallinity and density. See Table 1. In other words, Copolymer B contained much more backbone structural defects than Copolymer A and Homopolymer B. In conclusion, we remark that Homopolymer B and Copolymer B have unusual branched backbone structures. What does make these observed striking differences? We categorically address this question as follows.

The synthesis of branched backbones in Homopolymer B, particularly *via* a single ethylene feed, can be attributed to a *pseudo*-tandem oligomerization-cum-copolymerization process in the presence of $[(^n\text{BuCp})_2\text{ZrMe}]^+\text{Si-O-Me}_2\text{Si-}[\text{MAOC}_2]^-$ (MAO anion B). Because of the conceptual and mechanistic similarity, we can use, as an example, the trimerization of ethylene to 1-hexene (which is an isomer of 4M1P) and its concerted copolymerization with ethylene to illustrate the above finding. See Scheme 2 which has been extracted from a review of the relevant literature.^{68–71} The mechanism of ethylene trimerization, as shown in Scheme 2, follows a metallacyclic route.

Accordingly, two ethylene molecules are added to the metal, followed by insertion of another ethylene unit, which yields a higher order metallacycle (zirconacycloheptane). Reductive β -hydride transfer then releases 1-hexene and regenerates the active metal species. The resulting 1-hexene gets incorporated into the growing polyethylene chain through 1,2 insertion and synthesizes the branched polyethylene.^{68–71} The literature mostly reports a typical tandem process that involves two different transition metal precatalysts with one cocatalyst^{68–71} as well as one zirconocene precatalyst with two different cocatalysts.⁷² However, $[(^n\text{BuCp})_2\text{ZrMe}]^+\text{Si-O-Me}_2\text{Si-}[\text{MAOCl}_2]^-$ shows that a tandem copolymerization can also be achieved using a single precatalyst-cocatalyst ion pair. Our result is, therefore, unprecedented.

Now, we discuss the unusual branched backbone structure of Copolymer B from the perspective of ethylene versus 4M1P insertion. The active catalytic species in Copolymerization A (*pseudo*-homogeneous polymerization) and Copolymerization B (slurry-heterogeneous polymerization) are the following two ion pairs: (i) $[(^n\text{BuCp})_2\text{ZrMe}]^+[\text{MAOCl}_2]^-$ and (ii) $[(^n\text{BuCp})_2\text{ZrMe}]^+\text{Si-O-Me}_2\text{Si-}[\text{MAOCl}_2]^-$, respectively. See Scheme 1. This shows that MAO anion B ($\text{Si-O-Me}_2\text{Si-}[\text{MAOCl}_2]^-$) is much bulkier than MAO anion A ($[\text{MAOCl}_2]^-$). Therefore, the former exerted over all more steric than the latter. This affected the metallocene-MAO ion-pair gap,^{3,29,73–76} electronic effect, and coordination environment (at the Zr^+ metal center of $(^n\text{BuCp})_2\text{ZrCl}_2$) in such a manner that did not adequately favor the exclusive formation of ethylene-rich homopolymer backbones in Copolymer B. This indicates very slow insertion of ethylene, presumably during early part of polymerization. However, ethylene and 4M1P later on co-inserted into the Zr^+-C bond of the propagating copolymer backbone chain. $(^n\text{BuCp})_2\text{ZrCl}_2$, being a

moderately electrophilic 16-electron Group IV B metallocene precatalyst with arched ⁿBuCp ligand, the insertion of 4M1P preferably happened *via* the thermodynamically favored 1,2 primary insertion^{77,78} than the 2,1 secondary insertion. See Scheme 3 and the [EEE] triad values reported in Table 2. For nonmetallocene precatalysts, depending on the metal-ligand relation, predominantly secondary^{79,80} or, both primary and secondary^{81,82} insertions may occur. However, in Copolymer A, the exclusive formation of ethylene-rich homopolymer backbones, in addition to the co-insertion of ethylene and 4M1P, prevailed. Here, during the early part of polymerization, the insertion of ethylene seems to be rapid. Therefore, the E-4M1P backbone-building propagation mechanism significantly differed between unsupported MAO anion A (*pseudo*-homogeneous polymerization) and supported anion B (slurry-heterogeneous polymerization).

The above discussion on *Crystaf* curves illustrates how the crystallinity and density of an ethylene- α -olefin copolymer are affected particularly by the formation of ethylene-rich linear homopolymer backbones during copolymerization reaction. The copolymer composition distribution shows to be a better representative factor than the average composition. This is an insightful finding.

Polymer molecular weight and chain transfer effect

We discuss in this section the chain transfer/termination effect, particularly with reference to Me₂SiCl₂ and 4M1P, as reflected by the measured molecular weight distributions (MWDs) and their averages. MAO anion A is unsupported [MAOCl₂][−]. It is premixed with dehydroxylated silica, Me₂SiCl₂ and (ⁿBuCp)₂ZrCl₂, and it refers to *pseudo*-homogeneous polymerization. On the other hand, MAO anion B is supported Si–O–Me₂Si–[MAOCl₂][−]. It is impregnated with (ⁿBuCp)₂ZrCl₂ on

Me₂SiCl₂-functionalized silica, and it relates to slurry-heterogeneous polymerization (without separate feeding of MAO). They show the following results. First, we discuss the homopolymer molecular weights and their distributions. Homopolymer B (slurry-heterogeneous polymerization) has less weight average molecular than Homopolymer A (*pseudo*-homogeneous polymerization), and it is shifted toward the left. However, the molecular weight distributions are comparable but the concentration of higher molecular weight backbones in Homopolymer B is less than that in Homopolymer A. See Table 1 and Figure 2. This argues why Homopolymer B has less weight average molecular weight than Homopolymer A, which is attributed to the following. MAO anion B shows greater chain transfer rate than MAO anion A; the former is bulkier than the latter. Now, we focus on Copolymer A and Copolymer B. Me₂SiCl₂ and 4M1P decreased the weight average molecular weight of Homopolymer A by $\approx 23\%$. On the contrary, the extent of decrease in Homopolymer B is $\approx 1\%$. Also, the copolymer molecular weight distribution (MWD) here shifted toward the left more than the corresponding homopolymer MWD, generating a fair amount of low molecular weight backbones. The slurry-heterogeneous polymerization showed a surprisingly interesting result. It, unlike the *pseudo*-homogeneous polymerization, differently affected the chain transfer due to Me₂SiCl₂ and 4M1P. The homo- and copolymerization MWDs and PDIs turned out to be fairly comparable.

Now, we re-visit the above findings from the mechanistic view point. In the present context of copolymerization of ethylene with 4M1P, the related chain transfer reactions include the following:

- i. **Route A:** With ethylene as the last inserted unit, β -hydrogen transfer to Zr⁺ and/or to ethylene or 4M1P;

- ii. **Route B:** With ethylene as the last inserted unit, 2, 1 misinsertion of 4M1P, followed by β -hydrogen elimination to the Zr^+ active sites;
- iii. **Route C:** With ethylene as the last inserted unit, 1, 2 insertion of 4M1P; and
- iv. **Route D:** Silanolytic chain transfer in the presence of Me_2SiCl_2 that simultaneously controls molecular weight and makes silyl-terminated polyethylene backbone.^{83,84}

The first three routes, with the concerned kinetic rate expressions, have been schematically detailed in one of our recent publications.¹⁷

In *pseudo*-homogeneous polymerization, Me_2SiCl_2 —a silane Lewis acid (electron-pair acceptor) with reactive labile Cl ligand—is freely available in the polymerization medium. Therefore, as stated above, this potentially acted as a co-chain transfer agent with 4M1P. However, Me_2SiCl_2 has no vinyl unsaturation. Hence, the concerned chain transfer mechanism differs from the afore-said well-known ethylene- α -olefin chain transfer reactions.¹⁷ Me_2SiCl_2 end-capped the growing polymer chains following an *in-situ* ($^n\text{BuCp}$)₂ZrCl₂-mediated catalytic cycle that presumably proceeds through concerted bond cleavage and formation *via* four-centered σ -bond metathesis transition states.^{83–85} See the postulated Scheme 4, which is supported by references cited in this context. This work mentions a case of potential activation of Si–Cl bond thru σ -bond metathesis using a chlorosilane, particularly applicable to ethylene- α -olefin copolymerization. Such an example, to the best of our knowledge, has not been widely reported in the literature. The incorporation of silane provides scope for post-synthesis reactive modification of polymers.

The consecutive immobilization of Me_2SiCl_2 and MAO on silica produced $\text{Si-O-Me}_2\text{Si-}[\text{MAOCl}_2]^-$. Therefore, $\text{Si-O-Me}_2\text{Si-}[\text{MAOCl}_2]^-$, a sandwich of Me_2SiCl_2 between bulky MAO and silica, provided much more steric encumbrance than the unsupported Me_2SiCl_2 to silanolytic as well as 4M1P-mediated chain transfers. Consequently, the concerned chain termination reactions were significantly suppressed. However, the following reactions¹⁷ related to ethylene homopolymerization chain termination appeared to be active, which explains the Figure 1 findings:

- i. β -H transfer to the active metal center and ethylene;
- ii. Chain isomerization followed by β -H transfer to ethylene; and
- iii. The re-insertion of an ethylene macromer into the growing polyethylene chain, followed by β -H transfer to ethylene monomer and/or to the catalyst transition metal Zr^+ .

The above results evaluate the scope of silanolytic chain transfer, applicable to supported zirconocene olefin polymerization catalysts. Also, we illustrate the role played by ion-pairing in affecting the chain propagation (Figure 1) and termination (Figure 2) in metallocene-catalyzed ethylene–4M1P copolymerization.

The overall findings revealed by Figures 1 and 2 illustrate how a compound, that functionalizes silica as well as acts as a chain terminator, can synthesize ethylene– α -olefin copolymers with novel structural backbones (branched to highly branched). This unfolds niche for prospective future research and areas of new applications for ethylene– α -olefin copolymers.

Copolymer intra-chain microstructure and copolymer types

Here, we discuss the effects of 4M1P insertion and MAO anion type on the resulting copolymer intra-chain microstructures. The copolymer microstructure, in this context, will be described in terms of the following:

- i. ^{13}C NMR-determined average ethylene sequence/block length $n_{E\text{ NMR}}$; and
- ii. The Flory distribution of ethylene sequence/block length between the pendant branched *i*-butyl short side chains, and its most probable value $n_{E\text{ MPNMR-Flory}}$ (number of ethylene units corresponding to the peak of the distribution).

First, we discuss the average copolymer composition in the as-synthesized E-4M1P copolymers, and correlate it to the corresponding monomer and comonomer reactivity ratios. ^{13}C NMR shows the following: $[\text{E}]_{\text{Copolymer A}} > [\text{E}]_{\text{Copolymer B}}$; $[\text{4M1P}]_{\text{Copolymer A}} < [\text{4M1P}]_{\text{Copolymer B}}$; $r_{E\text{ Copolymer A}} > r_{E\text{ Copolymer B}}$; $r_{C\text{ Copolymer A}} \ll r_{C\text{ Copolymer B}}$; and $\langle r_E r_C \rangle_{\text{Copolymer A}} < \langle r_E r_C \rangle_{\text{Copolymer B}}$, where C means 4M1P. The above orders of average ethylene and 4M1P mole fractions and reactivity ratios conform to the previously reported *Crystaf* results that relate to ethylene-rich linear homopolymer backbone, crystallizable E-4M1P backbone, and amorphous/rubbery E-4M1P soluble fraction. However, the average reactivity ratio product shows that Copolymer B is much blockier than Copolymer A,^{53,86} which matches the order of average ethylene sequence length $n_{E\text{ NMR}}$. The $n_{E\text{ NMR}}$ of Copolymer B is greater than that of Copolymer A. This means that the former has a greater tendency to generate ethylene homosequence in the copolymer backbone than the latter.

The immobilization of the Me_2SiCl_2 chain transfer agent and the variance in the design of the MAO anion (characterized with different electronic and steric effects

due to $(^n\text{BuCp})_2\text{ZrCl}_2$) and coordination environments affected the above copolymer micro-structural parameters.

Figure 3 compares the Flory sequence length distributions (SLDs) of the as-synthesized copolymers. For each copolymer, two curves have been plotted. One refers to the experimental copolymer SLD that was calculated using the ^{13}C NMR-determined $\langle r_E r_{4M1P} \rangle$ and average ethylene mole fraction X_E . The other corresponds to the reference copolymer SLD where $\langle r_E r_{4M1P} \rangle = 1$ with the same X_E . Therefore, the reference copolymer assumes the synthesis of a random copolymer having the average ethylene mole fraction as same as that of the experimental copolymer. We introduced this comparison to evaluate to what extent the positioning of ethylene and 4M1P along the copolymer backbone deviates from the situation when the probability of inserting ethylene equals that of 4M1P for a given precatalyst-cocatalyst ion pair active center. The reference LTDs of Copolymer A and Copolymer B become indistinguishable when both have the same ethylene perpetuation probability p and average ethylene mole fraction X_E . Under such a situation, the MAO anion type and the mode of copolymerization (*pseudo*-homogeneous versus heterogeneous) will not affect the resulting copolymer LTD. The above figure demonstrates that the sequence length distribution broadened as the copolymer crystallinity and density decreased. Therefore, the Flory equation is shown to qualitatively illustrate the eventual partial disruption of the crystal package of the polyethylene chains due to 4M1P incorporation. We address this as follows.

Copolymer B incorporated more 4M1P units in the polymer backbone than Copolymer A, without having enough ethylene-rich linear population. See Figure 1 and Table 2. As a result, the *i*-butyl side chains (short branches) introduced more

structural defects along Copolymer B backbone. In parallel, the Flory distribution broadened with the increase in the most probable ethylene sequence length $n_{E\ MP\ NMR\ Flory}$. $n_{E\ MP\ NMR\ Flory}$ corresponds to the maximum of the thermodynamically predicted theoretical distribution of ethylene sequence length (between the pendant *i*-butyl side chains), that is, the *equilibrium crystal length*. Table 2 shows that for each copolymer, $n_{E\ MP\ NMR\ Flory}$ well compared with the ^{13}C NMR-determined $n_{E\ av\ NMR}$, which sets a good example of theoretical prediction versus experimental confirmation. This is an intriguing finding. The reference SLD of each copolymer shows that the as-synthesized blocky Copolymer A and Copolymer B significantly deviated from random sequence distributions. They also mutually differed spectacularly. The more $\langle r_{EC} \rangle$ exceeded 1, the greater the Flory distribution broadened. We determined $p_{\text{Copolymer A}} = 0.9778$ and $p_{\text{Copolymer B}} = 0.9795$, using Equation 6. This shows how only a very small difference in the ethylene perpetuation probability p significantly altered the sequence distribution (Figure 3), and influenced the peak melting and crystallization temperatures and %crystallinity (Table 1). We also calculated n^* , applying Equations 8 and 9, to evaluate the critical crystallite stability at room temperature (25 °C). In these calculations, we used $T_m^0 = 418.7\text{ K}$, $\Delta H_u = 8.284\text{ kJ/mol}$, $\sigma_e = 90\text{ mJ/m}^2$, and $a_o = 1.10 \times 10^5\text{ m}^2/\text{mol}$.^{58,87} As per the model prediction, under the same level of undercooling and crystal surface free energy effect, the transition of ethylene sequence from random to blocky did not affect n^* which showed to be higher than that of the corresponding homopolymer. See Table 3.

Melting behavior and bulk crystallinity

In this section, we discuss the E-4M1P copolymer peak melting and crystallization temperatures (T_{pm} and T_{pc}), % crystallinity (X_c), SSA-induced fractionation temperatures (multiple alternate melting and cooling behavior with intervening annealing), and lamellar thickness distributions (LTDs) and their averages; and compare them with the corresponding homopolymer properties. We particularly address the apparent inverse relation between crystallinity and $n_{E\ av\ NMR}$ (or $n_{E\ MP\ NMR\ Flory}$) reported in the earlier section.

In both copolymers, the incorporation of noncrystallizable 4M1P, with reference to the corresponding homopolymers, depressed the T_{pm} , T_{pc} , and X_c . Copolymer B showed the depression of these properties more than that due to Copolymer A. See Table 1.

The above findings are attributed to 4M1P-induced (i) structural/enchainment defects and (ii) the eventual partial disruption of the crystal package of the polyethylene chains, which are reflected in the following properties:

- i. Inter-chain copolymer composition distribution (See Figure 1), and average comonomer composition [C] (See Table 2);
- ii. The thermodynamically predicted Flory distribution of ethylene sequence length (between the pendant branched *i*-butyl side chains), that is, the *equilibrium crystal length*; most probable ethylene sequence length $n_{E\ MP\ NMR\ Flory}$; and average ethylene sequence length $n_{E\ av\ NMR}$; and
- iii. Average and most probable lamellar thicknesses ($L_{wav\ DSC\ GT}$, $L_{MP\ DSC\ GT}$, and $L_{wav\ DSC\ SSA}$), which are affected by inter- as well as intra-chain copolymer composition distributions.

Figure 4 mutually compares the lamellar thickness distributions (LTDs) of the as-synthesized polyethylenes. We calculated them applying Gibbs-Thompson (GT) equation, the related literature expressions,^{31–35,40} and the DSC data. We evaluated the most probable lamellar thickness $L_{MPDSC\ GT}$ from the peak of each lamellar thickness distribution. In these calculations, the following parametric values were used:^{58,87} T_m^0 (equilibrium melting temperature of a perfect crystal) = 145.5 °C, ΔH_f (heat of fusion per unit volume for the perfect crystal) = 290 Jcm⁻³, and σ_e (crystallite specific surface free energy) = 90 mJm⁻². However, $T_{m, copolymer}^0$ (equilibrium melting temperature of the copolymer) was estimated as described in the literature.^{31–35} $L_{MPDSC\ GT}$ was next converted into the most probable ethylene sequence $n_{E\ MPDSC\ GT}$ by dividing it with the length of an ethylene repeat unit (0.254 nm). The weight average lamellar thickness $L_{wav\ DSC\ GT}$ was determined using the LTD. We summarize below the findings of Figure 4 and Table 1.

Considering both MAO anions, $L_{wav\ DSC\ GT}$, $L_{MPDSC\ GT}$, $L_{wav\ DSC\ SSA}$, and $\sigma_{lamellar\ thickness}$ decreased in the following order: Homopolymer A > Copolymer A > Homopolymer B > Copolymer B. The lamellar thickness distribution (LTD) of each copolymer, with respect to the corresponding homopolymer, translated toward the left. Therefore, we can conclude the following. First, the MAO anion types, unsupported [MAOCl₂]⁻ (anion A) versus supported Si–O–SiMe₂–[MAOCl₂]⁻ (anion B), affected these results. The side chains resulting from the incorporation of 4M1P in Copolymers A and B, as well as the in-situ chain branching in Homopolymer B blocked disentanglement processes in the amorphous phase. This resisted crystallization lamellar thickening, and most likely changed intermolecular

topological structure. The linear decrease in weight average lamellar thickness $L_{wav DSC GT}$ as a function of amorphous phase fraction ϕ_a supports this argument. See Figure 5. Hence, we observe the progressively leftward translation of the LTDs (Figure 4) and the above descending order of $\sigma_{lamellar thickness}$, which as well fairly match the positioning of the corresponding Crystaf curves (Figure 1). Second, the Gibbs-Thompson (GT) equation successfully modeled the influence of comonomer-induced (i) structural/enchainment defects and (ii) the eventual partial disruption of the crystal package of the polyethylene chains on the resulting polymer melting behavior.

Figure 6 shows that the % crystallinity X_c of the as-synthesized polyethylenes increased fairly linearly as a function of $L_{wav DSC GT}$; $X_c (\%) = 1.526 \times L_{wav DSC GT} + 29.599$; $R^2 = 0.8731$. Despite variation in MAO anion types and the modes of polymerization (*pseudo*-homogeneous versus slurry-heterogeneous), this linear relation prevailed. This finding has important physical significance. This indicates that the homopolymers and the copolymers, despite having different structural backbones, experienced implicit self-similarity in chain folding behavior. Repulsive energy generated between ethylene sequences and the *i*-butyl branch (that results from the incorporation of 4M1P) increases. Consequently, the sterically hindered *i*-butyl branch inhibited chain folding and made the interlamellar amorphous phase, causing intra-chain phase separation. This means that the structural defect due to 4M1P is excluded from the pure polyethylene-phase crystal lattice. Alternatively, the 4M1P homosequence is not long enough to arrange in a crystal lattice. The [ECC] and [CCC] values (where C = 4M1P) of Table 2 as well as the literature support this conclusion.^{31,88–91} Note that the formation of such amorphous and crystalline phases

influences the copolymer mechanical and various end-use properties. In parallel, Figure 6 summarizes how Gibbs-Thompson (GT) equation successfully modeled the combined influence of 4M1P-induced inter- and intra-chain copolymer composition distributions on the resulting polyethylene bulk crystallinity. The above linear increasing crystallinity relation also holds for $L_{MPDSC\ GT}$ because $L_{wav\ DSC\ GT}$ and $L_{MPDSC\ GT}$ are linearly related; $L_{wav\ DSC\ GT} = 1.0317 \times L_{MP\ DSC\ GT} - 1.4082$; $R^2 = 0.9978$.

Now, we discuss the multiple alternate melting and cooling behavior (with intervening annealing) of the as-synthesized homo- and copolymers, measured by successive self-nucleation and annealing (SSA) DSC technique. Figure 7 compares the SSA curve of Homopolymer B with that of Homopolymer A. The former, unlike the latter, shows multiple peaks (102.0, 107.2, 111.8, 117.0, 121.6, and 125.2 °C). Therefore, we reaffirm that Homopolymer B is branched. See also Figure 1 corresponding Crystaf curve. Interestingly, Copolymer A and Copolymer B displayed the same thermal fractionation melting peaks, namely 100.0, 106.0, 111.0, 115.0, 118.0, and 124.0 °C. However, the corresponding backbone mass fractions differed. See Figure 8. The MAO anion type and the mode of copolymerization (*pseudo*-homogeneous versus slurry-heterogeneous) did not affect this endothermic temperature series. Here, each temperature refers to a defined number of *i*-butyl side chains, which decreased as the fractionation temperature increased. Accordingly, Copolymer B, unlike Copolymer A, has the least mass fraction (~ 0.02) of ethylene-rich backbone with sparsely incorporated 4M1P. Compare Figure 8b with Figure 8a. This complements Figure 1 Copolymer B *Crystaf* finding, which is, therefore, not an

experimental artefact. SSA DSC eventually showed much better peak resolution than *Crystaf*.

The $L_{wav\ SSA\ DSC}$ and the equivalent $n_{Ewav\ SSA\ DSC}$ (which was calculated using the length of an ethylene repeat unit) of Copolymer A fairly match the corresponding $L_{wav\ DSC\ GT}$ and $n_{E\ wav\ DSC\ GT}$. The same can be remarked for Copolymer B. See Tables 1 and 2. These comparable values reflect reproducibility of the estimated melting parameters. $L_{wav\ SSA\ DSC}$ was evaluated applying the above fractionation temperatures and Gibbs-Thompson (GT) equation. $n_{Ewav\ SSA\ DSC}$ measures the length of the effective crystallizable ethylene sequence. For Copolymer A, it approached the related $n_{E\ av\ NMR}$ and $n_{E\ MPNMR\ Flory}$ (the thermodynamically achievable maximum ethylene sequence). However, for Copolymer B, $n_{Ewav\ SSA\ DSC}$ (or $n_{E\ wav\ DSC\ GT}$) is about one-half of $n_{E\ av\ NMR}$ and $n_{E\ MPNMR\ Flory}$. Janicek et al.⁹² reported similar results, who measured the average ethylene sequence length and the average lamellar thickness using ¹³C NMR and X-ray scattering techniques, respectively. We, unlike Janicek et al., determined the average lamellar thickness applying Gibbs-Thompson equation and DSC experiments. In the first case, $n_{Ewav\ SSA\ DSC}$ and $n_{E\ wav\ DSC\ GT}$ (or $n_{E\ av\ NMR}$ and $n_{E\ MPNMR\ Flory}$) correspond with the measured crystallinity (48.41%). In the second case, $n_{Ewav\ SSA\ DSC}$ and $n_{E\ wav\ DSC\ GT}$ also show similar relation with crystallinity (34.85%). However, the relation of $n_{E\ av\ NMR}$ and $n_{E\ MPNMR\ Flory}$ with crystallinity is reverse. This can be addressed as follows.

Here, the *i*-butyl side chains exerted steric hindrance and restricted the whole of the regular ethylene sequences from incorporation into the crystallization lamella. This decreased the crystalline phase and increased the amorphous phase. See amorphous phase fraction (ϕ_a) values in Table 1, and Figure 5. Thus we note that the

presence and absence of predominantly ethylene-rich linear ordered backbones, with minor 4M1P incorporation, can create two different scenarios which refer to Copolymer A and Copolymer B, respectively. The above argument explains why crystallinity and density decrease in a typical ethylene- α -olefin copolymer with the incorporation of the α -olefin comonomer. See Table 1.

Figure 8 shows that the discrete SSA DSC peak temperature distributions of the as-synthesized copolymers differed among themselves. This originates from the catalyst active site, that is, ion-pair distribution (due to the coexistence of multiple MAO structures), and the variation in the design of MAO anion.

Crystallization kinetics of the as-synthesized polyethylenes

In this section, we discuss the crystallization kinetics of the as-synthesized polyethylenes in terms of apparent crystallization activation energy E_a , crystal dimension n_d and time-dependent nucleation mode n_c . We review them from the viewpoint of copolymer composition distribution (*Crystaf* CCD), $n_{E\text{ NMR}}$, and $n_{E\text{ MPNMR Flory}}$, all of which are dictated by MAO anion A unsupported $[\text{MAOCl}_2]^-$ and anion B supported $\text{Si-O-Me}_2\text{Si}-[\text{MAOCl}_2]^-$.

New Avrami-Erofeev nonisothermal crystallization model versus DSC experiment, and estimation of k_o , n , and E_a

We solved Equation 10 numerically, and estimated the model parameters (k_o , n , and E_a) as follows. First, we modified Equation 10 through separation of variables, and integrated the left hand side analytically, and transformed the right hand side into the well-known *temperature integral* $\int \exp\left(-\frac{E_a}{RT}\right) dT$. See Equations 20 and 21.

Next, we transformed the temperature integral into a real part and an exponential

integral part.⁹³ See Equation 22. This is how we addressed the challenge of integrating the temperature integral, which we finally reduced to the non-linear algebraic form. We solved this modified model equation using the *NonLinear ModelFit* of *Mathematica 8.0*. We used the centering temperature $T_o = 370$ K. The LHS of Equation 22, containing $-\ln(1-\alpha)$, has a point of discontinuity at $\alpha_{final}(T) = 1$. We overcame this by approximating $\alpha_{final}(T) \cong 0.9999$. Depending on the cooling rates, we took 30 to 45 experimental data points for kinetic parameter estimation.

$$\int \frac{d\alpha}{n(1-\alpha)[- \ln(1-\alpha)]^{\frac{n-1}{n}}} = \int \frac{k_0}{\beta} \times \exp \left[-\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_o} \right) \right] dT \quad (20)$$

$$[- \ln(1-\alpha)]^{\frac{1}{n}} = \frac{k_0 \exp \left(\frac{E_a}{RT_o} \right)}{\beta} \int \exp \left(-\frac{E_a}{RT} \right) dT \quad (21)$$

$$[- \ln(1-\alpha)]^{\frac{1}{n}} = \frac{k_0 \exp \left(\frac{E_a}{RT_o} \right)}{\beta} \left[T \exp \left(-\frac{E_a}{RT} \right) + \frac{E_a}{R} Ei \left(-\frac{E_a}{RT} \right) \right] \quad (22)$$

where $Ei \left(-\frac{E_a}{RT} \right)$ is the exponential integral of $-\frac{E_a}{RT}$.

We estimated the model parameters considering 95% confidence interval, coefficient of determination (R^2), estimated variance, and standard error, which are eventually generated by the afore-said *Mathematica* software. Convergence was accepted when the objective function changed less than the specified tolerance of 10^{-8} . For the sake of brevity and sufficiency, we list only R^2 for each of the estimated kinetic parameters. Now we address the model performance as follows.

Figure 9 compares the Avrami-Erofeev nonisothermal model-predicted crystallization profiles with the corresponding DSC-determined ones, selectively for Homopolymer B at different cooling rates. The match between model and experiment, in each case, is excellent. The same remark applies to Homopolymer A, Copolymer A, and Copolymer B. However, to avoid repetition, we excluded the corresponding crystallization profile plots. The premier finding, in this context, is the following. A single value of n represented the whole crystallization regime, including primary as well as secondary crystallizations. This indicates that the nucleation density, for a given cooling rate, did not change with crystallization temperature. This result is physically significant, and connotes that the mechanism of nucleation and crystal growth used in the development of Equation 10 holds, irrespective of the cooling rates, all throughout the crystallization process. This evidences how the present model overcame the drawbacks and limitations of the existing nonisothermal crystallization models. Therefore, the assumption of change in crystallization mechanism, as reported in the literature,^{94–97} is unnecessary. Table 4 shows that the model-predicted values of n_d differed between 2 and 3, depending on the cooling rates. This means that the resulting crystal dimension varied between cylindrical and spherical, that is, two and three dimensional alignments of the polymer backbone lamellae. Further, n showed to have an integral part and a fractional part. Therefore, according to Equation 17, the nucleation process mostly turned out to be intermediate between instantaneous (athermal/heterogeneous) and sporadic (thermal/homogeneous) ($0.05 \leq n_n \leq 0.80$) under the various experimental cooling rates. The variation in the backbone structure of the as-synthesized polyethylenes did not alter this intermediate nucleation phenomenon. See Table 4. Figure 6 partially complements the above finding. Figure 9 also evidences that a single E_a fits the

well-known isokinetic Avrami-Erofeev crystallization mechanism all throughout the crystallization process (primary plus secondary crystallization). Therefore, E_a is essentially constant of relative crystallinity α and crystallization time or temperature. Now we compare this finding with what has been published in the literature. Supaphol et al. modeled that the crystallization activation energy is a function of the relative crystallinity. Depending on the polymer type, it either monotonically increases, or it first increases and then it decreases as the relative crystallinity increases.⁹⁸ This functional behavior was attributed to the dependence of nucleation energy barrier on temperature. Such a justification ignores isokinetic concept, crystal growth as well as primary and secondary crystallizations. Hence, their model prediction and argument are insufficient and unacceptable.

Figure 10 shows the effect of cooling rates on the model-predicted apparent activation energy $E_a = E_{grow} - E_{nucl}$ for all the as-synthesized polyethylenes. This is a major motif of this study. In each case, E_a did not practically vary with the experimental cooling rates. This result differs from what Sahay and Krishnan have reported on the influence of cooling rate on activation energy.⁹⁹ To fit the DSC data, these authors assumed that the effective activation energy E_{ea} is composed of cooling rate-independent activation energy E_0 and cooling rate-dependent activation energy E_l , and these are related as follows: $E_{ea} = E_0 + E_l \ln(A\beta)$, where A is an arbitrary constant. Unfortunately, this argument has no mechanistic, kinetic, and thermodynamic basis. This is a purely data-fitting approach. Hence, the above definition of crystallization activation energy cannot be accepted. Our model, as stated above, duly considers isokinetic concept, crystal growth as well as primary and

secondary crystallizations; and mathematically shows that the activation energy does not depend on cooling rate.

Based on the overall findings of Figures 9 and 10, this study ratifies the invariance of activation energy articulated by Galwey and co-thinkers,^{100,101} and does not support the concept of variable/instantaneous *activation energy*^{94,98,99,102–104} which is practiced in analyzing nonisothermal crystallization kinetic data. This conclusion originates from the appropriate application of isokinetic concept and the current nonisothermal Avrami-Erofeev crystallization model, and the calculation algorithm that we developed. This is how we addressed in this study the subject of mathematical artefact that exists in the literature.

Effect of copolymer inter- and intra-chain inhomogeneity on E_a and bulk crystallinity X_c

The heating and cooling rate of $\beta = 10^\circ\text{C}/\text{min}$ is mostly used in the literature. Therefore, in this section, we address crystallization kinetics with reference to this particular value of β .

We can rate the model-predicted apparent crystallization activation energy as follows: $E_a \text{ Homopolymer A}, X_c \text{ Homopolymer A} > E_a \text{ Copolymer A}, X_c \text{ Copolymer A}$; and $E_a \text{ Homopolymer B}, X_c \text{ Homopolymer B} > E_a \text{ Copolymer B}, X_c \text{ Copolymer B}$. See Tables 1 and 4. This means that E_a and X_c of each homopolymer are greater than those of the corresponding copolymer. The similar order of variation of the weight average lamellar thickness $L_{wav DSC GT}$ supports this finding. $E_a \text{ Copolymer A}, X_c \text{ Copolymer A} > E_a \text{ Copolymer B}, X_c \text{ Copolymer B}$; $\langle r_{ERC} \rangle_{\text{Copolymer A}} < \langle r_{ERC} \rangle_{\text{Copolymer B}}$. Hence, the copolymer E_a and X_c inversely related to the level of backbone blockiness. Recall the earlier argument of steric hindrance

exerted by the *i*-butyl side chains and prevention of the whole of the regular ethylene sequences from incorporation into the crystallization lamella. For a specific MAO anion type and mode of polymerization, higher activation energy was modeled to attain higher crystallinity. To the best of our knowledge, this has been hardly reported in the literature. In other words, slower crystallization improved chain folding, which increased crystallinity. This finding is important from the viewpoint of processing the polymer to fabricate the end-products.

The above results show how the inter- and intra-chain inhomogeneity of the as-synthesized copolymers affected the resulting E_a and X_c . The inter- and intra-chain inhomogeneity is, in turn, associated with MAO anion structure, ion-pair gap, electronic effect, and coordination environment at $(^n\text{BuCp})_2\text{ZrCl}_2$ metal center (supported and unsupported).

Conclusions

Metallocenes, activated by methylaluminoxane (MAO) cocatalyst, are a significant innovation in polyolefin catalysts. In this context, the variation in the design of MAO anions, which is much easier and less costly than synthesizing new metallocenes, widens the scope for developing industrial catalyst. Additionally, ethylene–4-methyl-1-pentene (E–4M1P) copolymers have a lot of applications in power, control, optical, telephone, and signal cables; and their melting and crystallization behaviors are important processing parameters. This is why we undertook the present research that investigated the effects of MAO anion design on the homopolymer and E–4M1P copolymer backbone structure, melt behavior, and crystallization. We particularly studied how a silane, supported on silica as well as unsupported, could significantly revise the E–4M1P elementary copolymerization reactions and the associated

inter- and intra-chain backbone structure, including molecular weight distribution. We experimented this theme by conducting E-4M1P copolymerization using (i) MAO anion A (unsupported $[\text{MAOCl}_2]^-$) premixed with dehydroxylated silica, Me_2SiCl_2 , and $(^n\text{BuCp})_2\text{ZrCl}_2$; and (ii) the bulky MAO anion B ($\text{Si-O-Me}_2\text{Si-}[\text{MAOCl}_2]^-$) supported with $(^n\text{BuCp})_2\text{ZrCl}_2$ on Me_2SiCl_2 -functionalized silica. MAO anions A and B refer to *pseudo*-homogeneous polymerization and slurry-heterogeneous polymerization (without separate feeding of MAO), respectively. The salient findings of this study are summarized below.

- Two distinct E-4M1P copolymers—Copolymer A and Copolymer B—that correspond to MAO anion A and anion B, respectively, were synthesized. Copolymer A turned out to be a catalyst-mediated *in-situ* reactor blend of fairly ethylene-rich backbones and crystallizable E-4M1P backbones, devoid of E-4M1P soluble fraction. On the other hand, Copolymer B comprised only crystallizable E-4M1P backbones and E-4M1P soluble fraction (0.0018), without any significant level of ethylene-rich backbones, and it showed very low crystallinity and density. *Crystaf*, ^{13}C NMR, and DSC complemented this finding.
- Unsupported Me_2SiCl_2 acted as a co-chain transfer agent with 4M1P in the *pseudo*-homogeneous polymerization. Hence, they significantly decreased the weight average molecular weight of the corresponding homopolymers and shifted the copolymer molecular weight distribution (MWD) toward the left more than the corresponding homopolymer MWD, generating a fair amount of low molecular weight backbones. The slurry-heterogeneous polymerization, unlike the *pseudo*-homogeneous polymerization, showed relatively comparable homo- and

copolymerization MWDs and polydispersity indices. Therefore, the supported Me_2SiCl_2 , unlike the unsupported analogue, significantly suppressed the silanolytic as well as 4M1P-mediated chain transfer reactions. However, the ethylene homopolymerization chain transfer reactions appeared to be active.

- The % crystallinity X_c well correlated to weight average lamellar thickness $L_{\text{wav DSC GT}}$. The comonomer-induced structural/enchainment defects and the eventual partial disruption of the crystal package of the polyethylene chains, including the critical crystallite stability, were successfully modeled using Flory and Gibbs-Thompson equations. The modeling results added new insight to why crystallinity and density decrease in a typical ethylene- α -olefin copolymer with the incorporation of the α -olefin comonomer.
- For all the as-synthesized polyethylenes, despite having inter- and intra-chain backbone differences, the apparent crystallization activation energy E_a , predicted by the new Avrami-Erofeev nonisothermal crystallization model, did not practically vary with the cooling rates, relative crystallinity α , and crystallization time or temperature. This ratifies the invariance of activation energy articulated by Galwey and co-thinkers,^{100,101} and does not support the concept of variable/instantaneous *activation energy*^{94,98,99,102–104} which is practiced in analyzing nonisothermal kinetic data. The nucleation process, intermediate between instantaneous and sporadic, generated crystal dimensions that varied between cylindrical and spherical.

- For a defined MAO anion, higher E_a was predicted as a pre-requisite to attaining higher crystallinity. This means that slower crystallization increased crystallinity by improving chain folding.

This study especially underscores the in-situ synthesis of branched polyethylene from ethylene alone using particularly one metallocene-MAO ion pair *via* a *pseudo*-tandem oligomerization-cum-copolymerization process. This is an unprecedented finding. It also shows how a compound, that functionalizes silica as well as terminates the growing chain, can synthesize ethylene- α -olefin copolymers with novel structural backbones (branched to highly branched). Hence, it unfolds niches for prospective future research and areas of new applications for ethylene- α -olefin copolymers. The present approach to the problem can also be applied to investigate (from the perspective of this report) ethylene- α -olefin copolymerization, performed using MAO-activated non-metallocene precatalysts.

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Tables follow this page.

Table 1. Catalyst productivity and summary of as-synthesized polyethylene properties

Catalyst productivity and polyethylene properties	MAO anion A [MAOCl ₂] [−] and Me ₂ SiCl ₂ (both unsupported) <i>Pseudo-homogeneous polymerization</i> ¹		Bulky MAO anion B Si–O–SiMe ₂ –[MAOCl ₂] [−] (supported on Me ₂ SiCl ₂ -functionalized silica) <i>Slurry-heterogeneous polymerization</i> ¹	
	Ethylene homopolymer A	E–4M1P copolymer A	Ethylene homopolymer B	E–4M1P copolymer B ²
Catalyst productivity (g PE/g cat hr)	78.18	103.64 ²	54.55	88.18 ²
Weight average molecular weight M_w ³ (g/mol)	339,487	262,112	223,370	221,411
ΔM_w (%)	0.00	22.80	0.00	≈ 1.00
Polydispersity index (PDI)	1.63	3.50	1.54	1.82
Peak melting point ³ T_{pm} (°C)	132.62	118.93	126.91	106.80
Peak crystallization point ³ T_{pc} (°C)	116.97	105.96	111.10	87.70
Crystallinity ³ X_c (%)	59.64	48.41	44.87	34.85
Polymer material density ³ ρ_{polym} (g/cm ³)	0.937	0.920	0.915	0.890
Amorphous volume fraction ϕ_a	0.4433	0.5564	0.5914	0.6798
Weight average lamellar thickness ³ $L_{wav DSC GT}$ (nm)	20.49	9.77	8.86	6.44
Most probable lamellar thickness ³ $L_{MPDSC GT}$ (nm)	21.13	10.91	10.30	7.28
Variance $\sigma_{lamellar thickness}$ (nm)	7.98	3.99	2.67	2.17
Weight average lamellar thickness $L_{wav DSC SSA}$ (nm)	Does not apply.	10.89	9.73	7.30
Variance $\sigma_{lamellar SSA}$ (nm)	Does not apply.	2.40	2.32	2.05
Crystaf soluble fractions	0.0000	0.0000	0.0002	0.0018
$T_{\sigma Crystaf}$ (°C)	Does not apply.	8.15	8.10	5.16

$L_{wav DSC-GT} = 1.0317 \times L_{MP DSC GT} - 1.4082; R^2 = 0.9978.$

¹Both modes of polymerization prevented reactor fouling and thermal runaway, and they are likely to offer approximately comparable hydrodynamics and macro-mixing.

²Copolymerizations A and B show positive *comonomer effect*.

³Properties that decreased because of 4M1P incorporation.

Table 2. Comparison of microstructural parameters of the as-synthesized copolymers as a function of MAO anion types

Copolymer microstructural properties	MAO anion A [MAOCl ₂] ⁻ and Me ₂ SiCl ₂ (both unsupported) <i>Pseudo</i> -homogeneous polymerization	Bulky MAO anion B Si-O-SiMe ₂ -[MAOCl ₂] ⁻ (supported on Me ₂ SiCl ₂ -functionalized silica) Slurry-heterogeneous polymerization
	E-4M1P copolymer A	E-4M1P copolymer B
[EEE]	0.942	0.927
[EEC]	0.028	0.023
[CEC]	0.001	0.014
[ECE]	0.018	0.026
[ECC]	0.000	0.000
[CCC]	0.012	0.011
Average [E] mole fraction	0.971	0.963
Average [4M1P] mole fraction	0.029	0.037
Ethylene reactivity ratio r_E	63.72	36.60
Comonomer reactivity ratio r_C	0.24	1.14
Average reactivity ratio product experimental $\langle r_E r_C \rangle^{\S}$	15.21	41.72
Terminal model 1 st order Markov reactivity ratio product $r_E r_C^{\S}$	15.19	41.88
Ethylene perpetuation probability p	0.9778	0.9795
Copolymer type (based on $\langle r_E r_C \rangle$ values)	Less blocky than Copolymer B	Blockier than Copolymer A
Average ethylene sequence length $n_{E\text{ av NMR}}$	37	52
$n_{E\text{ MPNMR Flory}}$ (most probable number of ethylene units)	36	51
$n_{E\text{ MPDSC GT}}$ (most probable number of ethylene units)	43	29
$n_{E\text{ wav DSC GT}}$ (number of ethylene units)	38	25
$n_{E\text{ wav SSA DSC}}$ (number of ethylene units)	43	28

^{\S}Estimated by applying the relationships listed in References 52 and 53. $\langle r_E r_C \rangle \approx r_E r_C$ confirms terminal model statistical copolymerization mechanism.

E = Ethylene; C = 4M1P. $n_{E\text{ MPNMR Flory}}$ and $n_{E\text{ MPDSC GT}}$ were determined from Figures 3 and 4, respectively. $r_E = k_{EE}/k_{EC}$, and $r_C = k_{CC}/k_{CE}$, where k_{EE} and k_{CC} are ethylene and comonomer terminal model homo-propagation rate constants. k_{EC} and k_{CE} are the cross-propagation rate constants.

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Table 3. Effect of ethylene sequence distribution on perpetuation probability and critical crystallite stability of the as-synthesized copolymers

As-synthesized polyethylene parametric and crystallite properties	MAO anion A [MAOCl ₂] [−] and Me ₂ SiCl ₂ (both unsupported) <i>Pseudo-homogeneous</i> polymerization			Bulky MAO anion B Si–O–SiMe ₂ –[MAOCl ₂] [−] (supported on Me ₂ SiCl ₂ -functionalized silica) <i>Slurry-heterogeneous</i> polymerization		
	Ethylene Homopolymer A	Reference random Copolymer A	Blocky Copolymer A	Ethylene Homopolymer B	Reference random copolymer B	Blocky Copolymer B
Average ethylene mole fraction X_E	1.00	0.971	0.971	1.00	0.963	0.963
Ethylene perpetuation probability p	1.0000	0.9710	0.9778	1.0000	0.9630	0.9795
Level of undercooling θ (at 25 °C)	0.9615	0.9615	0.9615	0.9615	0.9615	0.9615
Crystal surface free energy effect $D \times 10^4$ (at 25 °C)	3.3883	3.3883	3.3883	3.3883	3.3883	3.3883
Critical crystallite stability n^* at 25 °C (number of C ₂ H ₄ units)	~9	~15	~16	~9	~15	~16

Table 4. Summary of model-predicted crystallization kinetic parameters

DSC cooling rates (°C/min)	Parameters of crystallization kinetics	MAO anion A [MAOCl ₂] [−] and Me ₂ SiCl ₂ (both unsupported) <i>Pseudo</i> -homogeneous polymerization		Bulky MAO anion B Si–O–SiMe ₂ –[MAOCl ₂] [−] (supported on Me ₂ SiCl ₂ -functionalized silica) Slurry-heterogeneous polymerization	
		Ethylene homopolymer A	E–4M1P copolymer A	Ethylene homopolymer B	E–4M1P copolymer B
10.0	<i>n</i>	2.65	3.45	3.12	2.20
	<i>k₀</i> (min ^{−1})	0.196 ± 0.010	0.269 ± 0.019	0.262 ± 0.008	0.538 ± 0.030
	<i>E_a</i> (kJ/mol)	51.16 ± 4.76	40.75 ± 4.25	48.10 ± 2.32	30.97 ± 1.53
	<i>R</i> ²	0.966	0.961	0.994	0.989
12.5	<i>n</i>	2.30	2.50	2.72	2.20
	<i>k₀</i> (min ^{−1})	0.240 ± 0.010	0.337 ± 0.027	0.347 ± 0.007	0.670 ± 0.038
	<i>E_a</i> (kJ/mol)	51.39 ± 3.45	40.26 ± 3.73	48.10 ± 1.77	30.51 ± 1.46
	<i>R</i> ²	0.968	0.961	0.995	0.988
15.0	<i>n</i>	3.42	2.80	2.23	2.40
	<i>k₀</i> (min ^{−1})	0.316 ± 0.012	0.530 ± 0.044	0.408 ± 0.011	0.806 ± 0.045
	<i>E_a</i> (kJ/mol)	51.12 ± 3.88	40.17 ± 3.87	48.17 ± 3.14	30.97 ± 1.47
	<i>R</i> ²	0.982	0.960	0.980	0.987
17.5	<i>n</i>	2.78	2.80	3.30	2.20
	<i>k₀</i> (min ^{−1})	0.382 ± 0.018	0.623 ± 0.051	0.427 ± 0.012	0.973 ± 0.054
	<i>E_a</i> (kJ/mol)	51.01 ± 4.36	40.00 ± 3.78	48.15 ± 2.20	30.18 ± 1.36
	<i>R</i> ²	0.968	0.962	0.994	0.990
20.0	<i>n</i>	3.40	3.05	2.65	2.20
	<i>k₀</i> (min ^{−1})	0.445 ± 0.019	0.731 ± 0.047	0.574 ± 0.012	1.158 ± 0.062
	<i>E_a</i> (kJ/mol)	51.23 ± 4.26	40.23 ± 3.20	48.07 ± 2.49	30.62 ± 1.30
	<i>R</i> ²	0.977	0.973	0.988	0.991

AICHE-15-17317.R1

**(ⁿBuCp)₂ZrCl₂-catalyzed Ethylene-4M1P Copolymerization:
Copolymer Backbone Structure, Melt Behavior, and Crystallization**

Figure 1. Comparison of inter-chain composition distributions of the as-synthesized polymers, measured using *Crystaf*. MAO anion A $\Rightarrow$ *Pseudo*-homogeneous polymerization; MAO anion B $\Rightarrow$ Slurry-heterogeneous polymerization.

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**(ⁿBuCp)₂ZrCl₂-catalyzed Ethylene-4M1P Copolymerization:
Copolymer Backbone Structure, Melt Behavior, and Crystallization**

Figure 2. Effect of MAO anions and polymerization modes on the molecular weight distributions of the as-synthesized homo- and E-4M1P copolymers. MAO anion A $\Rightarrow$ *Pseudo*-homogeneous polymerization; MAO anion B $\Rightarrow$ Slurry-heterogeneous polymerization.

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**(ⁿBuCp)₂ZrCl₂-catalyzed Ethylene-4M1P Copolymerization:
Copolymer Backbone Structure, Melt Behavior, and Crystallization**

Figure 3. Flory intra-chain ethylene sequence length distributions of the as-synthesized copolymers. MAO anion A $\Rightarrow$ *Pseudo-homogeneous*; MAO anion B $\Rightarrow$ *Slurry-heterogeneous* polymerization. $r_1 = r_E$ and $r_2 = r_{4M1P}$.

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**(ⁿBuCp)₂ZrCl₂-catalyzed Ethylene-4M1P Copolymerization:
Copolymer Backbone Structure, Melt Behavior, and Crystallization**

Figure 4. Effects of MAO anion types on the lamellar thickness distributions of the as-synthesized homo- and E-4M1P copolymers. MAO A $\Rightarrow$ *Pseudo-homogeneous*; MAO B $\Rightarrow$ *Slurry-heterogeneous* polymerization. The overlapping LTDs of Copolymer A and Homopolymer B matches what is noted in the corresponding *Crystaf* plots (Figure 1).

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**(ⁿBuCp)₂ZrCl₂-catalyzed Ethylene-4M1P Copolymerization:
Copolymer Backbone Structure, Melt Behavior, and Crystallization**

Figure 5. Variation of weight average lamellar thickness $L_{wav DSC GT}$ as a function of amorphous volume fraction ϕ_a . MAO anion A $\Rightarrow$ *Pseudo*-homogeneous; MAO anion B $\Rightarrow$ Slurry-heterogeneous polymerization.

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**(ⁿBuCp)₂ZrCl₂-catalyzed Ethylene-4M1P Copolymerization:
Copolymer Backbone Structure, Melt Behavior, and Crystallization**

Figure 6. Variation of % crystallinity as a function of weight average lamellar thickness $L_{wav DSC GT}$. MAO anion A $\Rightarrow$ *Pseudo-homogeneous*; MAO anion B $\Rightarrow$ *Slurry-heterogeneous* polymerization.

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(ⁿBuCp)₂ZrCl₂-catalyzed Ethylene-4M1P Copolymerization:
Copolymer Backbone Structure, Melt Behavior, and Crystallization

Figure 7. Comparison of successive self-nucleation and annealing (SSA) thermal fractionation of the as-synthesized E-4M1P copolymers. MAO anion A $\Rightarrow$ *Pseudo-homogeneous*; MAO anion B $\Rightarrow$ *Slurry-heterogeneous* polymerization.

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**(ⁿBuCp)₂ZrCl₂-catalyzed Ethylene-4M1P Copolymerization:
Copolymer Backbone Structure, Melt Behavior, and Crystallization**

Figure 8. Peak SSA thermal fractionation temperature versus the corresponding mass fraction of the as-synthesized E-4M1P copolymers. MAO anion A $\Rightarrow$ *Pseudo-homogeneous*; MAO anion B $\Rightarrow$ *Slurry-heterogeneous* polymerization.

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**(ⁿBuCp)₂ZrCl₂-catalyzed Ethylene-4M1P Copolymerization:
Copolymer Backbone Structure, Melt Behavior, and Crystallization**

Figure 9. Comparison of the crystallization profiles predicted by the new Avrami-Erofeev nonisothermal model with the corresponding DSC-determined ones, selectively for Homopolymer B at different cooling rates.

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**(ⁿBuCp)₂ZrCl₂-catalyzed Ethylene-4M1P Copolymerization:
Copolymer Backbone Structure, Melt Behavior, and Crystallization**

Figure 10. Invariance of apparent crystallization activation energy E_a with the variation in cooling rates.

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**(ⁿBuCp)₂ZrCl₂-catalyzed Ethylene-4M1P Copolymerization:
Copolymer Backbone Structure, Melt Behavior, and Crystallization**

Scheme 1. Generation of active metallocenium cations and MAO anions in *pseudo*-homogeneous and slurry-heterogeneous polymerizations.

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**(ⁿBuCp)₂ZrCl₂-catalyzed Ethylene-4M1P Copolymerization:
Copolymer Backbone Structure, Melt Behavior, and Crystallization**

Scheme 2. An analogous *pseudo*-tandem trimerization of a single feed ethylene to 1-hexene, and its copolymerization with ethylene in the presence of $[(^n\text{BuCp})_2\text{ZrMe}]^+\text{Si-O-Me}_2\text{Si-}[\text{MAOCl}_2]^-$ (MAO anion B $\Rightarrow$ heterogeneous polymerization).

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**(ⁿBuCp)₂ZrCl₂-catalyzed Ethylene-4M1P Copolymerization:
Copolymer Backbone Structure, Melt Behavior, and Crystallization**

Scheme 3. 1, 2 primary versus 2, 1 secondary insertion of 4M1P into the Zr⁺-copolymer backbone bond of the growing polymer chain.

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**(ⁿBuCp)₂ZrCl₂-catalyzed Ethylene-4M1P Copolymerization:
Copolymer Backbone Structure, Melt Behavior, and Crystallization**

Scheme 4. Proposed catalytic cycle, synthesizing (ⁿBuCp)₂ZrCl₂-mediated silyl-capped polyethylenes in *pseudo*-homogeneous polymerization (MAO anion A).