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Metallocene-catalyzed ethylene– α -olefin isomeric copolymerization: A perspective from hydrodynamic boundary layer mass transfer and design of MAO anion

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ABSTRACT

This study reports a novel conceptual framework that can be easily experimented to evaluate the effects of hydrodynamic boundary layer mass transfer, methylaluminoxane (MAO) anion design, and comonomer steric hindrance on metallocene-catalyzed ethylene polymerization. This approach was illustrated by conducting homo- and isomeric copolymerization of ethylene with 1-hexene and 4-methyl-1-pentene in the presence of bis(*n*-butylcyclopentadienyl) zirconium dichloride ($^n\text{BuCp}$)₂ZrCl₂, using (i) MAO anion 1 (unsupported [MAOCl₂][−]) and *pseudo*-homogeneous reference polymerization, and (ii) MAO anion 2 (supported Si–O–[MAOCl₂][−]) and *in-situ* heterogeneous polymerization. The measured polymer morphology, catalyst productivity, molecular weight distribution, and inter-chain composition distribution were related to the locus of polymerization, *comonomer effect*, *in-situ* chain transfer process, and micromixing effect, respectively. The peak melting and crystallization temperatures and %crystallinity were mathematically correlated to the parameters of microstructural composition distributions, melt fractionation temperatures, and average lamellar thickness. These relations showed to be insightful. The comonomer-induced enchainment defects and the eventual partial disruption of the crystal lattice were successfully modeled using Flory and Gibbs–Thompson equations. The present methodology can also be applied to study ethylene– α -olefin copolymerization, performed using MAO-activated non-metallocene precatalysts.

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1. Introduction

Olefin polymerization catalysts can be broadly classified as conventional Ziegler–Natta (Z–N), metallocene, post-metallocene, and late transition metal. Out of these four classes, metallocenes are capable of undergoing remarkable structural variations through modifications and substitutions in the cyclopentadienyl π -ligand, the central transition metal, and the related σ -ligands. Consequently, they can regulate the comonomer-introduced branch distribution, inter- and intra-chain microstructures, and structural/enchainment defects of ethylene– α -olefin copolymers in a highly versatile fashion. Additionally, well-defined polyolefin microstructures that range from atactic to stereoregular and stereoblock poly(α -olefins) can as well be synthesized. From a fundamental scientific viewpoint, our

current knowledge, regarding the mechanism of olefin polymerization, and the precatalyst structure versus polymer backbone and property relation, therefore, exceeds what we knew before. In parallel, we observe that the yearly journal publications and review reports [1–8] keep on adding since early 1980 when metallocene serendipity was first published by Kamnisky and his research group. Because of the above advantages, aggressive research continues worldwide in metallocene-catalyzed olefin polymerization to make polyolefin a dynamic technology-driven industry.

Three types of polyolefin-producing industrial processes exist. These are solution, slurry, and gaseous fluid-bed. Out of these three, the latter two processes dominate the commercial production because of their competitive benefits [1–8]. Despite the advantages summarized above, metallocene-based industrial polyolefin processes are far less than the most-prevalent Z–N ones.

Ethylene–4-methyl-1-pentene (E-4M1P) copolymers have a lot of applications in power, control, optical, telephone, and signal cables. BP's Innovex® grades are selected examples of commercial E-4M1P

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Fig. 1. Isomeric structures of 1-hexene and 4-methyl-1-pentene.

copolymers. Structurally, 1-hexene and 4M1P are isomers and the latter, unlike the former, is a sterically hindered α -olefin (see Fig. 1). However, we note that the contributions to metallocene-catalyzed ethylene–1-hexene (E–1-H) copolymerization are far greater in the literature than those related to ethylene–4-methyl-1-pentene (E–4M1P) copolymerization. In E–4M1P copolymerization, the published metallocene research can be summarized 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) [9–15]. Awudza and Tait [16] show to be the only group that studied E–4M1P slurry copolymerization, using supported silica/MAO/Cp₂ZrCl₂ catalyst, where MAO and Cp₂ZrCl₂ stand for methyl aluminoxane and bis(cyclopentadienyl) zirconium dichloride, respectively. They primarily investigated *comonomer effect*.

Reactor fouling, thermal runaway, poor polymer morphology, etc. are several major problems of a typical metallocene-catalyzed solution olefin polymerization. None of the above studies addressed these problems; they were rather more basic than applied. Also, the synthesis of E–1-H versus E–4M1P copolymers was not compared from a common isomeric copolymerization viewpoint. Hence, process developmental applied and engineering research in metallocene-catalyzed E–4M1P copolymerization should be paid more attention. This is the motivation behind this study. However, we would like to remain focused. Therefore, we aim at developing a novel general conceptual framework that can be easily experimented to evaluate the effects of the following three factors—hydrodynamic boundary layer (HBL), MAO anion design, and comonomer steric hindrance—on metallocene-catalyzed ethylene polymerization, including catalyst productivity, polymerization mechanism, comonomer and segregation effects, copolymer composition distribution, polymer microstructure, and thermal behavior.

We shall apply, in this regard, the concepts of *pseudo*-homogeneous polymerization (developed in our laboratory) and *in-situ* heterogeneous polymerization. The *in-situ* polymerization was originally conceived and published in 2000 by Soares et al. [17,18]. Both approaches will be applied to overcome the above-listed problems and ensure approximately comparable hydrodynamics and macro-mixing (which are very important).

In *pseudo*-homogeneous polymerization, an equivalent amount of the dehydroxylated support, 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 are immediately fed into 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. Methyl aluminoxane (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 reference polymerization. Note that a typical solution polymerization excludes the support and uses miscible solvent(s) for the metallocene, cocatalyst, and polymerization. Therefore, this is a limiting case of *pseudo*-homogeneous polymerization. On the other hand, in *in-situ* heterogeneous polymerization, ethylene, comonomer (1-hexene or 4-M1P), and metallocene first diffuse through a microemulsion hydrodynamic boundary layer (a mass transport barrier) of thickness δ . Then they contact the cocatalyst-impregnated support which is the major locus of polymerization. Thus, the need for separately supporting metallocene before polymerization is eliminated. In the present context, the above hydrodynamic boundary layer (HBL) means a thin liquid layer that exists, due to the solid–liquid interactive forces, at the interface of the cocatalyst-impregnated support particles and the vigorously stirred microemulsion transport fluid [19] (see Fig. 2).

We shall use the following two differing anions, unsupported [MAOCl₂][−] and supported Si–O–[MAOCl₂][−], the synthesis of which has been illustrated through Scheme 1 that shows the major relevant reactions [6,20]. Note that the variation in the design of novel co-catalyst anions, which is much easier and less costly than synthesizing new metallocenes, widens the scope of industrial process development.

To the best of our knowledge, the subject we propose to pursue has not been investigated before. Hence, we study this, which will

Fig. 2. In-situ heterogeneous polymerization and events taking place therein.

Scheme 1. Illustration of generation of MAO anions and active metallocenium cations in *pseudo*-homogeneous and *in-situ* heterogeneous polymerizations. $(\text{}^n\text{BuCp})_2\text{ZrCl}_2$, bis(*n*-butyl cyclopentadienyl) zirconium dichloride, is an *aspecific* C_{2v} -symmetric metallocene; this is very stable and commercially widely available.

hopefully add new insight to metallocene-catalyzed olefin polymerization and broaden our comprehension.

2. Experimental

2.1. Materials

Silica PQ 3030 having surface area of 322 m²/g, an average pore volume of 3.00 cm³/g, and a pore size of 374 Å was used as the cocatalyst support.

$(\text{}^n\text{BuCp})_2\text{ZrCl}_2$ 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), 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. United Petrochemicals, an affiliate of Saudi Basic Industries Corporation (SABIC), gifted 1-hexene.

2.2. Synthesis of MAO-impregnated silica

The MAO-impregnated silica was synthesized as follows by doing all the manipulations under argon using standard Schlenk technique.

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.

Toluene was dried using 4A activated molecular sieve. The required amounts of dehydroxylated silica and the dried toluene were slurried in a specially designed Schlenk flask. The calculated volume of MAO was added to this slurry drop by drop under argon using constant stirring at room temperature. Then this was heated for several hours for complete impregnation. The resulting product was dried under vacuum. The dry free-flowing MAO-impregnated silica was saved in a glove box.

2.3. 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 triisobutylaluminum (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 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

1-hexene or 4M1P was added. The resulting mixture was stirred at 50 rpm for 10 min. For the homopolymerization, no 1-hexene or 4M1P was used.

The *in-situ* heterogeneous polymerization was conducted as follows. An estimated amount of MAO-supported silica was slurried in 50 mL of *n*-hexane. The whole volume was siphoned into the reactor under mild argon flow. On the other hand, a solution of $(\text{}^n\text{BuCp})_2\text{ZrCl}_2$ in toluene, that corresponded to an Al:Zr molar ratio of about 50, was added to the reactor. Ethylene was passed through oxygen- and moisture-removing columns. Then it was fed into the reactor at a constant flow rate of 5000 Nml/min. The polymerization temperature and stirrer speed were set at 50 °C and 400 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 reference polymerization, the above amounts of silica, MAO, and $(\text{}^n\text{BuCp})_2\text{ZrCl}_2$ were first instantaneously pre-contacted in dried toluene. Note that toluene is a common solvent for MAO and $(\text{}^n\text{BuCp})_2\text{ZrCl}_2$. Then the resulting mixture, ethylene, and the experimental α -olefin comonomer were immediately introduced to the reactor. The rest of the above procedures were repeated.

After conducting the polymerization trials as described above, the reactor was opened; the resulting polyethylene was dried under ambient conditions 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 *in-situ* heterogeneous), one homo- and two copolymers were prepared.

2.4. Polymer particulate surface morphology

The experimental polyethylene samples were first coated with a layer of carbon to increase the surface conductivity. These coated samples were characterized using a scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectrometer (EDS). The particulate morphology was probed by operating the electron microscope in the backscattered electron imaging (BEI) mode.

2.5. 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.

Table 1

Catalyst productivity and summary of as-synthesized polyethylene properties.

Catalyst productivity and polyethylene properties	MAO anion 1: unsupported [MAOCl ₂] [−] Pseudo-homogeneous polymerization			MAO anion 2: silica-supported bulkier Si–O–[MAOCl ₂] [−] In-situ heterogeneous polymerization		
	Ethylene homopolymer	E–1-hexene copolymer	E–4M1P copolymer	Ethylene homopolymer	E–1-hexene copolymer	E–4M1P copolymer
Catalyst productivity (g PE/g cat hr)	60.00	116.36	110.91	46.36	67.00	61.50
M_w (g/mol)	329,664	291,092	181,811	318,574	229,051	255,864
ΔM_w (%)	0.00	11.70	44.85	0.00	28.10	19.68
Polydispersity index (PDI) [§]	1.43	2.42	2.61	1.58	2.51	2.22
Peak melting point T_{pm} (°C)	133.93	114.97	118.01	134.08	114.08	120.14
Peak crystallization point T_{pc} (°C)	116.76	100.25	104.06	117.36	100.66	106.82
DSC crystallinity X_c (%)	58.29	35.87	44.53	65.70	41.92	43.44
WAXRD crystallinity [†] X_c (%)	55.45	34.38	42.52	62.41	40.07	41.49
ΔT_{pm} (°C)	0.00	18.96	15.92	0.00	20.00	13.67
ΔT_{pc} (°C)	0.00	16.51	12.7	0.00	16.70	10.54
ΔX_c (%)	0.00	22.42	18.76	0.00	23.78	22.26
Polymer material density ρ_{polym} (g/cm ³)	0.935	0.902	0.914	0.947	0.900	0.913
Weight average lamellar thickness $L_{wav DSC GT}$ (nm)	20.53	7.90	9.45	20.72	8.04	9.96
Most probable lamellar thickness $L_{MPDSC GT}$ (nm)	21.13	9.27	10.64	21.47	9.07	11.60
Variance $\sigma_{lamellar thickness}$ (nm)	7.93	2.48	3.03	4.44	2.56	3.02
Weight average lamellar thickness $L_{wav SSA DSC}$ (nm)	Does not apply.	7.91	9.55	Does not apply.	7.93	10.64
Variance $\sigma_{lamellar SSA}$ (nm)	Does not apply.	2.00	2.84	Does not apply.	2.22	3.11
Crystaf soluble fractions	Does not apply.	0.0004	0.0005	Does not apply.	0.0014	0.0000
$T_{\sigma Crystaf}$ (°C)	Does not apply.	9.56	7.43	Does not apply.	11.51	6.72

PE = Ethylene homo- and copolymer.

 $L_{wav SSA DSC} = 1.2866 \times L_{wav DSC GT} - 2.3631$; $R^2 = 0.9703$. $L_{wav DSC GT} = 0.9584 \times L_{MPDSC GT} + 1.663$; $R^2 = 0.9976$.[§] PDI reports the deviation of the molecular weight distribution (MWD) from a situation where all the as-synthesized chains are of equal length, that is, PDI = 1. As the MWD broadens, the PDI exceeds 1. PDI does not represent the breadth of MWD.[†] Determined applying the correlation $X_{c WAXRD} = 0.9396 \times X_{c DSC} + 0.6779$; $R^2 = 0.9866$; WAXRD = wide angle X-ray diffraction. This correlation was developed using the Table 1 data of Reference [21]. The results are comparable. However, $X_{c WAXRD}$, being free of recrystallization effect, is a little lower than $X_{c DSC}$. In DSC, recrystallization effect is usually unavoidable.

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 [22]. Table 1 reports the measured average molecular weights and the polydispersity indices.

2.6. 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 [23,24]. 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 [25]: $X_c = (1/\rho_{polym} - 1/\rho_a)/(1/\rho_c - 1/\rho_a)$; 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. The %crystallinity measured using DSC was also estimated applying the correlation $X_{c WAXRD} = 0.9396 \times X_{c DSC} + 0.6779$; $R^2 = 0.9866$; WAXRD = wide angle X-ray diffraction. This correlation was developed using the Table 1 data of Reference [21]. The results are comparable. Table 1 reports the above thermal properties and densities 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 [26–32]. Seven annealing steps (160, 125, 119, 114, 111, 107, and 103 °C) were applied. Details are available in Reference [32].

2.7. 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 [33–35]. 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 to 35 °C. The qualitative differential composition distribution ($\frac{dw}{dT}$ versus T) was obtained by numerical differentiation of the integral analogue.

2.8. Copolymer microstructure and Flory ethylene sequence length distribution

The microstructural parameters, including average ethylene, 1-hexene, and 4M1P mole% in the synthesized copolymers, were determined using ¹³C NMR spectroscopy. For this purpose, 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 [24]. 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.

Table 2

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

Copolymer microstructural properties	MAO anion 1: unsupported [MAOCl ₂] [−] Pseudo-homogeneous polymerization		MAO anion 2: silica-supported bulkier Si–O–[MAOCl ₂] [−] In-situ heterogeneous polymerization	
	E–1-hexene copolymer	E–4M1P copolymer	E–1-hexene copolymer	E–4M1P copolymer
[EEE]	0.853	0.917	0.826	0.896
[EEC]	0.046	0.043	0.058	0.071
[CEC]	0.000	0.000	0.000	0.000
[ECE]	0.025	0.039	0.032	0.031
[ECC]	0.076	0.000	0.085	0.000
[CCC]	0.000	0.001	0.000	0.002
Average ethylene (major component) mole fraction [E]	0.899	0.960	0.884	0.967
Average comonomer (minor component) mole fraction [C]	0.101	0.040	0.116	0.033
Ethylene reactivity ratio r_E	21.78	37.26	20.6	35.62
Comonomer reactivity ratio r_C	0.39	0.02	0.32	0.05
Average reactivity ratio product $\langle r_E r_C \rangle^{\S}$	8.41	0.59	6.64	1.64
Terminal model 1 st order Markov reactivity ratio product $r_E r_C^{\S}$	8.03	0.58	6.29	1.65
Copolymer type (based on $\langle r_E r_C \rangle$ values)	Potentially block	Slightly alternating to random	Potentially block	Less blocky
r_E/r_C	55.85	1,863.00	63.38	712.40
Average ethylene sequence length $n_{E\text{ NMR}}$	14	25	12	31
$n_{E\text{ MPNMR Flory}}$ (number of ethylene units)	13	38	10	24
$n_{E\text{ MPDSC GT}}$ (number of ethylene units)	36	42	36	46
$n_{E\text{ WAV DSC GT}}$ (number of ethylene units)	31	37	32	39
$n_{E\text{ WAV SSA DSC}}$ (number of ethylene units)	31	38	31	42

E = Ethylene; C = 1-hexene or 4M1P (as appropriate). $n_{E\text{ MPNMR Flory}}$ and $n_{E\text{ MPDSC GT}}$ were determined from Figs. 7 and 12, 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.

$n_{E\text{ NMR}} = 2.1885 \times n_{E\text{ WAV DSC GT}} - 55.634$; $R^2 = 0.9994$.

[§] Estimated by applying the relationships listed in References [37, 38]. $\langle r_E r_C \rangle \approx r_E r_C$ confirms terminal model statistical copolymerization mechanism.

The E–1-H average copolymer compositions and microstructural parameters were calculated following the well-known publications of Hsieh and Randall [36], and Seger and Maciel [37]. According to these references, first the mole fractions of the copolymer triad sequences were calculated by using the reported peak assignment procedures (involving the associated collective peak assignment regions) and the Seger–Maciel algorithm. The concentration of a given triad being proportional to the algebraic expression of the concerned peak areas, this algorithm does not require signal calibration. Seger and Maciel have highlighted the advantages of this approach. Next, the monad and diad mole fractions, and the copolymer microstructural parameters of our interest were calculated using the relations reported in References [37, 38]. The E–4M1P average copolymer compositions and the corresponding microstructural parameters were calculated following the procedure published by Kimura et al. [39]. 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 side chains), that is, the equilibrium crystal length was calculated using the Flory equation [40,41]. According to this, the normalized weight fraction W_n of the sequence of n ethylene units is related to the ethylene perpetuation probability p through the following expression:

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

For a statistical copolymer with very long chains, p is related to experimental reactivity ratio product $\langle r_E r_C \rangle$ and ethylene mole fraction X_E as follows [41]:

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

$$p = X_M = X_E \quad \langle r_E r_C \rangle = 1 \quad (3)$$

where X_M is the mole fraction of the monomer.

3. Results and discussion

3.1. Reactor operability and as-synthesized polyethylene morphology

In this section, we discuss the influence of polymerization mode on polyethylene morphology. No reactor fouling and thermal runaway were observed during pseudo-homogeneous and in-situ heterogeneous polymerizations. Fig. 3 shows the SEM-determined morphology of the resulting polyethylenes. The pseudo-homogeneous reference polymerization produced a sort of powdery material, practically consisting of clumped miniature particles, because the reaction primarily occurred in the microemulsion bulk polymerization phase, mainly comprising *n*-hexane. On the other hand, the in-situ heterogeneous polymerization synthesized free-flowing fairly spherical particles, which may be elucidated as follows. Here, apparently a polymer film formed instantaneously around the catalyst particles (due to polymerization) by the active centers created by the contact of (ⁿBuCp)₂ZrCl₂ (an *aspecific* C_{2v}-symmetric metallocene) with the MAO-impregnated silica. This film coated the catalyst constituents with a surrounding shell and prevented leaching. Accordingly, the polymer grew on the fragmenting MAO-impregnated silica particles, not in the polymerization diluent, which generated the spherical morphology. This explanation follows the work of Smit et al. [42,43].

3.2. Polymerization activity versus steric hindrance and boundary layer mass transfer effect

Here, we revisit *comonomer effect* (irreversible increase of catalyst activity) from the perspective of (i) steric hindrance due to comonomer molecular branching and MAO anion bulkiness, and (ii) hydrodynamic boundary layer mass transfer effect, illustrated by Fig. 2.

Fig. 4 illustrates how the polymerization modes and the MAO anion- and comonomer types affect the resulting polymerization activity. The pseudo-homogeneous polymerization showed higher homopolymerization catalyst productivity than the in-situ

Fig. 3. SEM-determined morphology of the as-synthesized copolymers. To avoid repetition, homopolymer morphology has been excluded.

Fig. 4. Influence of cocatalyst anion types and isomeric copolymerization on catalyst productivity and comonomer effect. MAO anion 1 $\Rightarrow$ *Pseudo*-homogeneous polymerization; MAO anion 2 $\Rightarrow$ *In-situ* heterogeneous polymerization.

heterogeneous polymerization. The occurrence of polymerization in the bulk microemulsion phase, devoid of hydrodynamic mass transfer effect, in *pseudo*-homogeneous polymerization supports this finding. Also, for each MAO anion, the copolymerization catalyst productivity was greater than the corresponding homopolymerization catalyst productivity. Hence, both 1-hexene and 4M1P α -olefin comonomers separately introduced positive *comonomer effect*. However, MAO anion 1 (*pseudo*-homogeneous polymerization) and 1-hexene showed larger *comonomer effect* than MAO anion 2 (*in-situ* heterogeneous polymerization) and 4M1P. We shall discuss the influence of this *comonomer effect* on copolymer intra-chain compositional heterogeneity in Section 3.5. The above findings can be attributed to the following:

- The steric hindrance to comonomer insertion by the branched 4M1P and the bulkier supported MAO anion 2 ($\text{Si-O-}[\text{MAOCl}_2]^-$); and
- The diffusional mass transfer effect introduced by the hydrodynamic boundary layer δ .

The above factors variedly influenced the following chemically intrinsic phenomena: (i) the zirconocenium–MAO anion separation [20,44–48] (in ethylene homopolymerization) and (ii) the activation of the dormant/sleeping Zr^+-H catalytic sites [20,49–57] by 1-hexene and 4M1P (in ethylene copolymerization). Hence, we observe varying homopolymerization catalyst productivities and *comonomer effects*, respectively. Note that the closer is the ion-pair separation, the higher is the energy barrier associated with each polymerization step; hence, the less is the catalyst productivity [20,44–48].

3.3. Polymer molecular weight and chain transfer effect

We evaluate in this section the comonomer-induced chain transfer effect, measured by molecular weight distribution and its average. The following result is common between MAO anion 1 (*pseudo*-homogeneous polymerization) and anion 2 (*in-situ* heterogeneous polymerization). Both 1-hexene and 4M1P significantly decreased the weight average molecular weights of the corresponding homopolymers (see Table 1). Also, in each case, the copolymer molecular weight distributions shifted toward the left, generating low molecular weight backbones (see Fig. 5). Hence, 1-hexene and 4M1P, in addition to insertion into the growing copolymer backbone, also acted as *in-situ* chain transfer agents. In *pseudo*-homogeneous polymerization, 4M1P acted stronger than 1-hexene as a chain transfer agent while in *in-situ* heterogeneous polymerization, the order reversed. This phenomenon, being an integral part of the copolymerization mechanism, occurred independent of MAO anion type and the mode of copolymerization (without and with hydrodynamic boundary layer-mediated mass transfer effect). However, these factors

Fig. 5. Effect of cocatalyst anions and polymerization modes on the molecular weight distributions of the as-synthesized homo- and copolymers. MAO anion 1 $\Rightarrow$ Pseudo-homogeneous polymerization; MAO anion 2 $\Rightarrow$ In-situ heterogeneous polymerization.

Fig. 6. Comparison of intermolecular composition distributions of the as-synthesized copolymers, measured using Crystaf. MAO anion 1 $\Rightarrow$ Pseudo-homogeneous polymerization; MAO anion 2 $\Rightarrow$ In-situ heterogeneous polymerization.

particularly affected the level of chain transfer effect. The chain transfer is ascribed to occur as per the following three routes:

- **Route A:** Termination with ethylene as the last inserted unit, β -hydrogen transfer to Zr^{+} and/or to ethylene or the comonomer (1-hexene or 4M1P) generates vinyl terminus ($CH_2=CHR$).
- **Route B:** Termination with ethylene as the last inserted unit, 2, 1 misinsertion of the comonomer, followed by β -hydrogen elimination to the Zr^{+} active sites generates *trans*-vinylene terminus ($R_1CH=CHR_2$; $R_1 \neq R_2$).
- **Route C:** Termination with ethylene as the last inserted unit, 1, 2 insertion of the comonomer generates vinylidene terminus ($CH_2=CR_1R_2$; $R_1 \neq R_2$) (through β -hydrogen elimination to Zr^{+} active sites).

The above mechanisms are schematically detailed elsewhere in the literature [25].

3.4. 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 isomeric copolymerization inter-chain composition distribution, measured by Crystaf. Note that it is copolymer composition distribution that is particularly sensitive to micromixing/segregation effects [58–60].

Fig. 6 shows that MAO anion 1 (pseudo-homogeneous polymerization) and MAO anion 2 (in-situ heterogeneous polymerization), in

the presence of $(^nBuCp)_2ZrCl_2$, synthesized highly broad composition distribution E-1-H and E-4M1P copolymers. Also, see the root mean square crystallization temperature $T_{\sigma Crystaf}$ values in Table 1. The MAO anion 1 and anion 2 E-4M1P copolymers, during Crystaf cooling, successively crystallized as predominantly ethylene-rich linear ordered backbones (at around 78 °C), with sparse comonomer incorporation, to crystallizable E-4M1P backbones having negligible amounts of amorphous/rubbery E-4M1P soluble fractions (0–0.0005). On the other hand, the corresponding E-1-H copolymers did not show ethylene-rich linear ordered backbones. They only demonstrated crystallizable E-1-H backbones with varying amounts of amorphous/rubbery E-1-H soluble fractions (0.0004–0.0014). The absence of ethylene-rich backbones reflects the influence of restricted 4M1P incorporation due to steric hindrance imparted by this α -olefin comonomer. The observed common composition distribution broadness demonstrates the presence of strong micromixing/segregation effect [58–60]. This phenomenon can be ascribed to the three-dimensional MAO cage structures that feature the following [61–68]:

- Each MAO structure comprises n different MAO $[-(AlOMe)_n-]$ repeat units; and
- The above MAO structures have preferably one type of defined strong active Lewis acid catalyst site that can be attributed to the $-AlO_2Me-$ environment [67]. Accordingly, different active site ion-pairs $[Zr]^{+}[MAO]_n^{-}$ are likely to prevail in the experimental zirconocene catalysts. This subject—metallocene active center distribution—has been particularly detailed in some of our recent publications [20,24].

3.5. Copolymer intra-chain microstructure and copolymerization mechanism

Here, we discuss the effects of the modes of copolymerization, and cocatalyst anion- and comonomer types on the resulting copolymer intra-chain microstructures and the related copolymerization mechanisms. The copolymer microstructure, in this context, will be described in terms of the following:

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

The triad analysis shows that [HEH], [HHH], [CEC], and [ECC], where C is 4M1P comonomer, in the related copolymers, are zero. The

Fig. 7. Flory intra-chain comonomer composition distributions, that is, distributions of ethylene sequence/block (equilibrium crystal) length between the pendant side chains (branches) of the as-synthesized copolymers. MAO anion 1 $\Rightarrow$ Pseudo-homogeneous; MAO anion 2 $\Rightarrow$ In-situ heterogeneous polymerization.

literature supports this finding [36,69–72]. The remaining triad mole fractions of the as-synthesized copolymers differ among themselves (see Table 2).

Now we discuss the average copolymer compositions in E–1-H and E–4M1P copolymers, and correlate them to the corresponding monomer and comonomer reactivity ratios. The E–1-H copolymers showed comparable average ethylene and 1-hexene mole fractions, irrespective of anion types. Similar observation holds for E–4M1P copolymers, as well as ethylene reactivity ratio r_E and comonomer reactivity ratio r_C . These results complement the findings of Fig. 6 *Crystaf* curves.

^{13}C NMR-determined average reactivity ratio product $\langle r_E r_C \rangle$, in each case, fairly matched the corresponding 1st order Markov reactivity ratio product $r_E r_C$. Therefore, the terminal model statistical copolymerization mechanism prevailed despite variation in (i) the mode of copolymerization, and (ii) anion- and comonomer types. In other words, the hydrodynamic boundary layer-mediated mass transfer and the variance in the design of the MAO anion (characterized with different electronic and steric effects due to $^n\text{BuCpZrCl}_2$) and coordination environments, did not affect the copolymerization mechanism. However, what about the comonomer insertion process and its spatial positioning along the copolymer backbone? We address this concern as follows.

In the literature [38,73], based on experimental data, ethylene– α -olefin copolymers have been classified as follows: (i) random ($\langle r_E r_{\alpha\text{-olefin}} \rangle = 1$); (ii) slightly alternating to random ($\langle r_E r_{\alpha\text{-olefin}} \rangle = 0.2\text{--}1.0$); (iii) highly alternating ($\langle r_E r_{\alpha\text{-olefin}} \rangle = 0.005\text{--}0.01$); and (iv) blocky character ($\langle r_E r_{\alpha\text{-olefin}} \rangle \gg 1.0$), where r is the reactivity ratio. Accordingly, MAO anion 1 (pseudo-homogeneous polymerization) was prone to produce potentially block E–1-H, and alternating to random E–4M1P copolymers. On the other hand, MAO anion 2 (in-situ heterogeneous polymerization) was apt to synthesize potentially block E–1-H and E–4M1P copolymers. This shows the tendency to generate homosequences of ethylene and α -olefin comonomer (1-H or 4M1P) in the polymer backbone (see Table 2). These results demonstrate the combined role played by mass transfer effect (due to hydrodynamic boundary layer δ), and MAO anion- and comonomer types on the mode of insertion of the comonomer and its spatial positioning along the copolymer backbone.

For each MAO anion, we note the following:

- $r_E \gg r_C$;
- $r_{1\text{-H}} \gg r_{4\text{M1P}}$; and
- $n_{E\text{ NMR}|E\text{--}4\text{M1P copolymer}} > n_{E\text{ NMR}|E\text{--}1\text{-H copolymer}}$.

Therefore, $R_E \gg R_{1\text{-H}} \gg R_{4\text{M1P}}$, where R is the corresponding homopolymerization rate, argues why 4M1P inserted less than 1-hexene in the copolymer backbone. This may be attributed to more steric hindrance imparted by the branched 4M1P comonomer and the increase in r_E/r_C values. The above finding also aligns with showing less comonomer effect by 4M1P than 1-hexene, irrespective of MAO anion type (see Fig. 4).

Fig. 7 compares the Flory intra-chain comonomer composition distributions of the as-synthesized copolymers. It shows that the intra-chain comonomer composition distribution broadened as the copolymer crystallinity and the density increased. Therefore, the Flory equation is shown to model the eventual partial disruption of the crystal package of the polyethylene chains due to comonomer incorporation. This may be explained as follows. The lower density copolymers incorporated more 1-hexene or 4M1P units in the polymer backbone. As a result, the *n*-butyl or *i*-butyl side chains (short branches) were more crowded along the copolymer backbone. This creates a shorter ethylene sequence/block length between the side branches, making the distribution narrower. See Table 2 $n_{E\text{ NMR}}$ values, which support the above explanation.

3.6. Thermal behavior of the as-synthesized polyethylenes

In this section, we discuss the copolymer thermal behaviors in terms of peak melting and crystallization temperatures (T_{pm} and T_{pc}), %crystallinity (X_c), SSA-induced fractionation temperatures (using multiple alternate melting and cooling with intervening annealing), and lamellar thickness distributions (LTDs) and their averages; and compare them with the corresponding homopolymer properties. We observe the following.

In all the copolymers, the incorporation of 1-hexene or 4M1P, with reference to the corresponding homopolymers, depressed the T_{pm} , T_{pc} , and X_c . The depression of these properties, due to 1-hexene, showed to be more than that due to 4M1P (see Table 1).

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

- Inter-chain copolymer composition distribution (see Fig. 5), and average ethylene composition $[E]$;
- Intra-chain copolymer composition distribution, represented by various triad sequences, Flory distribution of ethylene sequence/block (equilibrium crystal) length between the

Fig. 8. Variation of %crystallinity X_c as a function of average ethylene mole fraction $[E]$ of the as-synthesized polyethylenes. MAO anion 1 $\Rightarrow$ Pseudo-homogeneous polymerization; MAO anion 2 $\Rightarrow$ In-situ heterogeneous polymerization.

Fig. 9. Variation of ΔT_{pm} and ΔT_{pc} as a function of average ethylene mole fraction $[E]$ of the as-synthesized polyethylenes. MAO anion 1 $\Rightarrow$ Pseudo-homogeneous polymerization; MAO anion 2 $\Rightarrow$ In-situ heterogeneous polymerization.

comonomer side chains; most probable ethylene sequence $n_{E\text{ MPNMR Flory}}$; and average ethylene sequence $n_{E\text{ NMR}}$; and
 iii. Average and most probable lamellar thicknesses ($L_{\text{wav DSC GT}}$, $L_{\text{MPDSC GT}}$, $L_{\text{wav DSC SSA}}$, and $L_{\text{nav DSC SSA}}$), which are affected by inter- as well as intra-chain copolymer composition distributions.

Now we quantitatively evaluate the effects of inter- and/or intra-chain copolymer composition distributions on X_c , ΔT_{pm} , and ΔT_{pc} by correlating these thermal properties to $[E]$, $n_{E\text{ NMR}}$, $n_{E\text{ MPNMR Flory}}$, $L_{\text{wav DSC GT}}$, $L_{\text{MPDSC GT}}$, and $L_{\text{wav DSC SSA}}$ (as appropriate).

Fig. 8 illustrates how the inter-chain copolymer compositional differences, characterized by average ethylene mole fraction $[E]$, influenced the %crystallinity X_c . The following concave-up 2nd order polynomial, $X_c (\%) = 4041.0[E]^2 - 7432.7[E] + 3452.7$, related X_c to $[E]$. On the other hand, concave-down 2nd order polynomials connected ΔT_{pm} and ΔT_{pc} to $[E]$ (see Fig. 9). These relations sustain irrespective of variation in comonomer and MAO anion types, and the modes of ethylene polymerization (pseudo-homogeneous versus in-situ heterogeneous). X_c increased whereas ΔT_{pm} and ΔT_{pc} decreased with the increase in $[E]$; hence, the variational relationship turned out to be inverse and opposite.

Fig. 10, unlike Fig. 9, demonstrates how the %crystallinity X_c varied as a function of average ethylene sequence length $n_{E\text{ NMR}}$. X_c increased

linearly with increasing $n_{E\text{ NMR}}$, following the relation, $X_c = 0.4479 \times n_{E\text{ NMR}} + 25.514$; $R^2 = 0.9246$. The variation in comonomer and MAO anion types, and the modes of ethylene polymerization (pseudo-solution versus in-situ) did not affect this linear relation. This result indicates that the incorporation of 1-hexene or 4M1P shortened $n_{E\text{ NMR}}$; consequently, the chains, on an average, were more frequently interrupted from folding than the corresponding homopolymers. Accordingly, the intrinsic crystallizability of the resulting copolymer backbones dropped, and X_c decreased. ΔT_{pm} and ΔT_{pc} also showed to be linearly related to $n_{E\text{ NMR}}$ but with a decreasing variational trend; $\Delta T_{pm} = -0.3771n_{E\text{ NMR}} + 30.583$, $R^2 = 0.9927$; and $\Delta T_{pc} = -0.5733n_{E\text{ NMR}} + 34.441$, $R^2 = 0.9971$. Hence, the effect is opposite (see Fig. 11). In summary, we showed (through modeling) that the influence of inter- and intra-chain copolymer composition distributions on depressible polyethylene thermal properties— X_c , ΔT_{pm} , and ΔT_{pc} —are qualitatively similar but not the same. To the best of our knowledge, such a finding has not been so far published in the literature.

Fig. 12 mutually compares the Gibbs–Thompson (GT) lamellar thickness distributions of the as-synthesized polyethylenes. We calculated them applying Gibbs–Thompson (GT) equation, the related literature expressions [24,41,74–77], and the DSC data. We valued the most probable lamellar thickness $L_{\text{MPDSC GT}}$ from the peak of each

Fig. 10. Variation of %crystallinity X_c as a function of average ethylene sequence length n_{ENMR} of the as-synthesized polyethylenes. MAO anion 1 $\Rightarrow$ Pseudo-homogeneous polymerization; MAO anion 2 $\Rightarrow$ In-situ heterogeneous polymerization.

Fig. 11. Variation of ΔT_{pm} and ΔT_{pc} as a function of average ethylene sequence length n_{ENMR} of the as-synthesized polyethylenes. MAO anion 1 $\Rightarrow$ Pseudo-homogeneous polymerization; MAO anion 2 $\Rightarrow$ In-situ heterogeneous polymerization.

Fig. 12. Effects of hydrodynamic boundary layer δ and MAO anion types on the lamellar thickness distributions of the as-synthesized homo- and copolymers, calculated using Gibbs–Thompson equation and conventional DSC. MAO 1 $\Rightarrow$ Pseudo-homogeneous; MAO 2 $\Rightarrow$ In-situ heterogeneous polymerization.

Fig. 13. Variation of %crystallinity as a function of weight average lamellar thickness $L_{wavDSC\ GT}$, calculated using Gibbs–Thompson (GT) equation and conventional DSC. MAO anion 1 $\Rightarrow$ Pseudo-homogeneous; MAO anion 2 $\Rightarrow$ In-situ heterogeneous polymerization.

lamellar thickness distribution. In these calculations, the following best parametric values were used [74]: T_m^0 (equilibrium melting temperature of a perfect crystal) = 145.5 °C, ΔH_f^0 (heat of fusion per unit volume for the perfect crystal) = 290 Jcm⁻³, and σ_{ssfe} (crystallite specific surface free energy) = 90 mJm⁻². However, T_m^0 (equilibrium melting temperature of the copolymer) was found as reported in the literature [41,74–77]. $L_{MPDSC\ GT}$ 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 $L_{wavDSC\ GT}$ was estimated using the whole LTD. We summarize below the findings of Fig. 12 and Table 1.

With respect to MAO anion 1 (pseudo-homogeneous polymerization), $L_{wavDSC\ GT}$, $L_{MPDSC\ GT}$, $L_{wavDSC\ SSA}$, and $\sigma_{lamellar\ thickness}$ decreased in the following order: homopolymer > E–4M1P copolymer > E–1-hexene copolymer. The corresponding lamellar thickness distributions also translated toward left in the same order. The same variational trends persisted with MAO anion 2 (in-situ heterogeneous polymerization). Note that the ethylene homopolymer has neither inter- nor intra-chain composition distributions. On the other hand, the copolymers have such distributions which influenced the corresponding $L_{wavDSC\ GT}$, $L_{MPDSC\ GT}$, $L_{wavDSC\ SSA}$, and $\sigma_{lamellar\ thickness}$ values. Therefore, 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.

Fig. 13 shows that the %crystallinity X_c of the as-synthesized polyethylenes increased linearly as a function of $L_{wavDSC\ GT}$; X_c (%) = $1.7735 \times L_{wavDSC\ GT} + 25.428$; $R^2 = 0.9235$. Despite variation in comonomer and MAO anion types and the modes of polymerization (pseudo-homogeneous versus in-situ heterogeneous), this linear relation prevailed. This finding has important physical significance. This indicates that the homopolymers and the copolymers undergo similar chain folding behavior. Repulsive energy generated between ethylene sequences and the butyl branch (that exerts steric hindrance) increased. The incorporation of 4M1P and 1-hexene created the *iso*- and *n*-butyl branches, respectively. Consequently, they refrained from chain folding, and made the interlamellar amorphous phase. This means that the structural/enchainment defects due to 4M1P or 1-hexene were excluded from the pure polyethylene-phase crystal lattice. The [ECC] and [CCC] values (where C = H or 4M1P) of Table 2 as well as the relevant literature support this conclusion [41,78–82]. The 4M1P or 1-hexene homosequence was not long

enough to arrange in a crystal lattice. Note that the formation of such amorphous and crystalline phases influences the copolymer mechanical and various end-use properties. In parallel, Fig. 13 summarizes how Gibbs–Thompson (GT) equation successfully modeled the combined influence of comonomer-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 $L_{wavDSC\ GT}$ and $L_{MPDSC\ GT}$ are linearly related; $L_{wavDSC\ GT} = 0.9584 \times L_{MPDSC\ GT} + 1.663$; $R^2 = 0.9976$.

Now, we discuss the multiple alternate melting and cooling behavior (with intervening annealing) of the as-synthesized copolymers. They displayed similar successive self-nucleation and annealing (SSA) thermal fractionation melting peaks. For example, E–1-hexene and E–4M1P copolymers, synthesized by (ⁿBuCp)₂ZrCl₂ and MAO anion 1 (pseudo-homogeneous polymerization), showed the following five temperature peaks: 100, 106, 111, 115, and 118 °C. The difference in comonomer type, that is, E–4M1P did not affect this endothermic temperature series. We even notice the same comonomer-independent temperature series, augmented by 124 °C, for the above copolymers prepared by (ⁿBuCp)₂ZrCl₂ and MAO anion 2 (in-situ heterogeneous polymerization) (see Figs. 14 and 15). We calculated $n_{E\ wavDSC\ SSA}$ using these temperatures, Gibbs–Thompson (GT) equation, and the length of an ethylene repeat unit (0.254 nm). $n_{E\ wavDSC\ SSA}$ was found to correlate to $n_{E\ NMR}$ as follows: $n_{E\ wavDSC\ SSA} = 0.3554 \times n_{E\ NMR} + 28.040$; $R^2 = 0.9924$. We already established that $X_c = 0.4479 \times n_{E\ NMR} + 25.514$; $R^2 = 0.9246$. Hence, these copolymers have varying crystallizable lengths of PE sequences; however, their mass fractions differed (Fig. 15). Based on this finding and the exclusion of the butyl group from chain folding (Fig. 13), we can remark that the SSA trace of each copolymer also indicates the structural defects resulting from comonomer-introduced butyl branches. This was masked in *Crystaf* analysis (Fig. 6). However, SSA DSC showed it with much better resolution than *Crystaf*. The above correlations, to the best of our knowledge, are new and insightful.

Each SSA peak signifies a population of backbones that have the same side chain branch (SCB) content, crystallinity, and lamellar thickness. SCB is inversely connected to the latter two, which are directly related by X_c (%) = $1.7735 \times L_{wavDSC\ GT} + 25.428$; $R^2 = 0.9235$. Therefore, the branch content decreased, and the lamellar thickness increased with the increase in these peak melting temperatures. Note that in SSA fractionation, the polymer undergoes multiple alternate melting and crystallization processes (without physical separation of

Fig. 14. Comparison of successive self-nucleation and annealing (SSA) thermal fractionation of the as-synthesized E-1-hexene and E-4M1P copolymers. MAO 1 $\Rightarrow$ Pseudo-homogeneous; MAO 2 $\Rightarrow$ In-situ heterogeneous polymerization.

Fig. 15. Peak thermal fractionation temperature versus the corresponding mass fraction of the as-synthesized E-1-hexene and E-4M1P copolymers, determined by successive self-nucleation and annealing (SSA) technique. MAO 1 $\Rightarrow$ Pseudo-homogeneous; MAO 2 $\Rightarrow$ In-situ heterogeneous polymerization.

the chains) as the temperature decreases. Therefore, it is sensitive to linear and uninterrupted chain sequences; hence to both intra- and inter-chain defects [26–31]. The ^{13}C NMR results, reported earlier, complement this remark.

Fig. 15 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.

4. Conclusions

Metallocenes, being capable of undergoing remarkable structural variations, have several competitive advantages over the conventional Ziegler–Natta (Z–N) catalysts. Despite so, metallocene industrial polyolefin processes are far less than the most-prevalent Z–N ones. Therefore, it is important to investigate metallocene catalysis from an applied and engineering research viewpoint. The present study is a modest contribution toward this direction. It reports a

novel general conceptual framework that can be easily experimented to evaluate the effects of the following three factors—hydrodynamic boundary layer (HBL), MAO anion design, and comonomer steric hindrance—on metallocene-catalyzed ethylene polymerization. We illustrated this conceptual framework by conducting homo- and isomeric copolymerization of ethylene with 1-hexene and 4-methyl-1-pentene in the presence of $(^n\text{BuCp})_2\text{ZrCl}_2$, using (i) MAO anion 1 (unsupported $[\text{MAOCl}_2]^-$) and *pseudo*-homogeneous reference polymerization (developed in our laboratory), and (ii) the bulky MAO anion 2 (supported $\text{Si}-\text{O}-[\text{MAOCl}_2]^-$) and *in-situ* heterogeneous polymerization.

The above factors variedly affected the polymer morphology, catalyst productivity, molecular weight distribution, inter- and intra-chain composition distributions, and selected thermal properties, excluding the copolymerization and crystallization mechanisms. The polymer morphology, catalyst productivity, molecular weight distribution, and inter-chain composition distribution were eventually correlated to the locus of polymerization, *comonomer effect*, *in-situ* chain transfer process, and micromixing effect, respectively. The inter-chain composition distribution (copolymer microstructure) was characterized in terms of various triad sequences, Flory ethylene sequence distribution, most probable ethylene sequence $n_{E\text{MPNMR Flory}}$, and average ethylene sequence $n_{E\text{NMR}}$. The thermal properties were measured in terms of peak melting and crystallization temperatures (T_{pm} and T_{pc}), %crystallinity (X_c), melt fractionation temperatures (determined using successive self-nucleation and annealing (SSA) technique), and lamellar thickness distributions (LTDs) and their averages. They were mathematically correlated to the afore-said representative parameters of microstructural composition distributions. The resulting correlations showed to be perceptive. The comonomer-induced structural/enchainment defects and the eventual partial disruption of the crystal package of the polyethylene chains were successfully modeled using Flory and Gibbs–Thompson equations. The present approach to the problem generated several new and insightful findings, and it can also be applied to study ethylene– α -olefin copolymerization, performed using MAO-activated non-metallocene precatalysts.

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