

SYNTHESIS AND CHARACTERIZATION OF
ETHYLENE-ALPHA-OLEFIN METALLOCENE AND
POSTMETALLOCENE ELASTOMERS

BY

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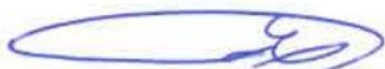
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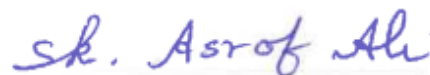
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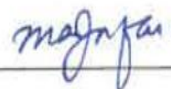
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Dedicated to:

My revered parents and family
who untiringly supported my professional career,
and
My beloved wife
who highly inspired and very strongly assisted all my academic pursuits.

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LIST OF ABBREVIATIONS

a :	Cohesion parameter
a_{mix} :	Cohesion parameter of the mixture
AAD:	Absolute average deviation
A^V :	$\frac{a_{mix}^V P}{(RT)^2}$
A^L :	$\frac{a_{mix}^L P}{(RT)^2}$
$\hat{A}, \hat{B}, \hat{C}$:	Antoine equation parameter
b:	Covolume
b_{mix} :	Covolume of the mixture
bp:	Boiling point
BHT:	2,6-Di-tert-butyl-4-methylphenol
B^V :	$\frac{b_{mix}^V P}{RT}$
B^L :	$\frac{b_{mix}^L P}{RT}$
CRYSTAF:	Crystallization analysis fractionation
CGC:	Constrained geometry catalysts
CCD:	Chemical composition distribution

<i>CI</i> :	Cluster index
<i>C</i> :	Tait equation constant
¹³ C NMR:	Carbon nuclear magnetic resonance
DSC:	Differential scanning calorimetry
DFT:	Density-functional theory
DMSO-d:	Deuterated dimethylsulfoxide
EoS:	Equation of state
<i>E</i> :	A temperature-dependent constant
E:	Ethylene
GPC:	Gel permeation chromatography
GD:	Gradient descent
GN:	Gauss-Newton
HDPE:	High-density polyethylene
¹ H NMR:	Proton nuclear magnetic resonance
<i>HC</i> :	Henry's constant
<i>HC_{E 1-hexene}</i> :	Ethylene–1-hexene Henry's constant
<i>HC_{E 1-octene}</i> :	Ethylene–1-octene Henry's constant

$HC_{E\text{ toluene}}$:	Ethylene–toluene Henry’s constant
H_{gL} :	Gas-single liquid Henry’s constant
H_{gL1-L2} :	Gas-binary liquid Henry’s constant
H_{gL1} :	Gas-liquid 1 Henry’s constant
H_{gL2} :	Gas-liquid 2 Henry’s constant
H_0 :	Reference Henry’s constant corresponding to $\frac{1}{T} = 0$
IR:	Infrared
l_{ij} :	Binary interaction parameter
$I_{E\ 1-hexene}$:	Interaction between ethylene and 1–hexene
$I_{E\ 1-octene}$:	Interaction between ethylene and 1–octene
$I_{E\ toluene}$:	Interaction between ethylene and toluene
K :	Partition coefficient
K_1 :	Partition coefficient of liquid L1 $\frac{P_{s1}}{P}$
K_2 :	Partition coefficient of liquid L2 $\frac{P_{s2}}{P}$
k_{ij} :	Propagation rate constant
k_{ij} :	Adjustable binary interaction parameter
KF:	Karl Fischer

LLDPE:	Linear low-density polyethylene
LDPE:	Low-density polyethylene
LMDPE:	Linear medium-density polyethylene
LMA:	Levenberg-Marquardt algorithm
$L_{1\text{ }NAV}$:	Average sequence length of monomer
$L_{2\text{ }NAV}$:	Average sequence lengths of comonomer
L1–L2:	Liquids 1 and 2, respectively
LA:	Lewis acid
mLLDPE:	Medium linear low-density polyethylene
MDPE:	Medium-density polyethylene
MAO:	Methylaluminoxane
MMAO:	Modified methyl aluminoxane
MoS:	Molecular sieve
MWD:	Molecular weight distribution
MW:	Molecular weight
MTCM:	Microkinetic terminal copolymerization model
MD :	Monomer dispersity

M_n :	Number-average molecular weight
M_w :	Weight-average molecular weight
M_1 :	Molar concentration of monomer 1
M_2 :	Molar concentration of monomer 2
MW_{M_1} :	Molecular weight of the gaseous monomer
MW_1 :	Molecular weight of liquid 1
MW_2 :	Molecular weight of liquid 2
Mol_{01} :	Mole of solvent used in a copolymerization trial at room temperature
Mol_{02} :	Mole of comonomer used in a copolymerization trial at room temperature
M_{01} :	Mole fraction of solvent used in a copolymerization trial at room temperature
M_{02} :	Mole fraction of comonomer used in a copolymerization trial at room temperature
Mol_1 :	Mole of solvent
Mol_2 :	Mole of comonomer
Mol_{M_1} :	Mole of the gaseous monomer
NMR:	Nuclear magnetic resonance
$n_{1\text{ NAV}}$:	Number-average monomer sequence
$n_{2\text{ NAV}}$:	Number-average comonomer sequence

$n_{1\text{ }WAV}$:	Weight-average monomer sequence
$n_{2\text{ }WAV}$:	Weight-average comonomer sequence
PE:	Polyethylene
PDI:	Polydispersity index
PR:	Peng-Robinson
P_{ij} :	Binary conditional probabilities
P :	System pressure
P_S :	Saturation vapor pressure
P_{smix} :	Saturation vapor pressure of the mixture
P_c :	Critical pressure
P_0 :	Atmospheric pressure
P_{Si} :	Temperature-dependent saturation vapor pressure of component i
P_{ci} :	Pure component critical pressure
R&D:	Research and Development
RI:	Refractive index
RN :	Run number
r_E :	Reactivity ratio of ethylene

r_H :	Reactivity ratio of 1-hexene
r_O :	Reactivity ratio of 1-octene
R:	Universal gas constant
r^2 :	Coefficient of determination
SS:	Single site
SSC:	Single site catalyst
SF:	Schulz-Flory
S_{M_1} :	Solubility of the gaseous monomer
$S_{E\ model}$:	Model-predicted solubility of ethylene
$S_{E\ 1-hexene}$:	Experimental solubility of ethylene in 1 –hexene
$S_{E\ 1-octene}$:	Experimental solubility of ethylene in 1 –octene
$S_{E\ toluene}$:	Experimental solubility of ethylene in toluene
TREF:	Temperature rising elution fractionation
TMA:	Trimethyl aluminum
TEA:	Triethyl aluminum
TTB:	Trityltetrakis(pentafluorophenyl)borate
TIBA:	Triisobutyl aluminum

TCB:	1,2,4-trichlorobenzene
T:	Temperature
T_g :	Glass transition temperature
T_m :	Melting point temperature
T_{mp} :	Peak melting temperature
T_{pc} :	Peak crystallization temperature
T_{g1} :	Glass transition temperature of polyethylene
T_{g2} :	Glass transition temperature of poly(alpha-olefin)
T_b :	Atmospheric boiling point
T_c :	Critical temperature
T^V :	Vapor phase temperature
T^L :	Liquid phase temperature
T_{nbp} :	Normal boiling point (a liquid has 1 atm vapor pressure)
T_{ci} :	Pure component critical temperature
ULLDPE:	Ultralinear low-density polyethylene
UHMWPE:	Ultrahigh molecular weight polyethylene
VLLDPE:	Very linear low-density polyethylene

VLDPE:	Very low-density polyethylene
VLE:	Vapor liquid equilibrium
$vdW1f$:	van der Waals single fluid
V :	Molar volume
V_1 :	Component 1 molar volume
V_2 :	Component 2 molar volume
V^E :	Excess molar volume
v_{01} :	Volume of solvent used in a copolymerization trial at room temperature
v_{02} :	Volume of comonomer used in a copolymerization trial at room temperature
V_{01} :	Molar volume of solvent used in a copolymerization trial at room temperature
V_{02} :	Molar volumes of comonomer used in a copolymerization at room temperature
$w_1(n)$:	Sequence distributions of monomer
$w_2(n)$:	Sequence distribution of comonomer
W_E :	Ethylene weight fraction
XPS:	X-ray photoelectron spectroscopy
X_c :	Crystallinity

X :	Thermodynamic model-predicted ratio of molar concentrations of monomer 1 and monomer 2 (comonomer)]
x_i :	Liquid phase mole fraction of component i
x_{M_1} :	Mole fraction solubility of the gaseous monomer
$\hat{x}_1, \hat{x}_2$:	Ethylene-free mole fractions of binary solvent components
$\hat{x}_{02}$:	Ethylene-free mole fractions of commoner components at room temperature
x_{10} :	Initial guess liquid phase mole fraction solubility of ethylene
y_i :	Vapor phase mole fraction of component i
y_{10} :	Initial guess vapor phase mole fraction solubility of ethylene
ZN:	Ziegler-Natta
$^{91}\text{Zr NMR}$:	Zirconium nuclear magnetic resonance
Z :	Compressibility factor
Z_{model}^L :	Model-predicted liquid phase compressibility factor
Z^V :	Vapor phase compressibility factor
Z^L :	Liquid phase compressibility factor
Z_{1-2}^L :	Ternary system— M_1 , solvent, and comonomer—compressibility factor
$Z_{M_1-1}^L$:	Individual equilibrium compressibility factors of the gaseous monomer M_1 in the solvent

$Z_{M_1-2}^L$:	Individual equilibrium compressibility factor of the gaseous monomer M_1 in comonomer
ΔH_L :	Gas-liquid solvation enthalpy
$\gamma_1 \gamma_2$:	Activity coefficients of binary solvent components
ρ :	Persistence ratio
ρ :	Density
χ :	Departure from randomness
ω_i :	Pure component Pitzer acentric factor

ABSTRACT

Full Name: [Yahya Alaauddeen Rawas]

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Major Field: [Chemistry]

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Saudi Arabia is the 2nd largest global polyolefin (PO) producer (16.25 mmpta). Here, SABIC's catalytic polyethylenes account for 7.30 mmpta (~45%). The conventional semicrystalline PO applications are maturing. Research, therefore, continues worldwide to make amorphous PO elastomers using the emerging metallocene and postmetallocene precatalysts. World elastomer production has been predicted to rise to 7.38 mmpta. In this context, ethylene- α -olefin elastomers show versatile applications. They are, therefore, capturing the market. One of the major applications of such elastomers is to improve the low impact resistance of stiff and brittle thermoplastics such as isotactic polypropylene (iPP) and random PP (a copolymer of propylene and a small amount of ethylene or α -olefin) via blending them with these elastomers.

The overall objective of this research is, therefore, to (i) catalytically synthesize ethylene-1-hexene and ethylene-1-octene elastomers, (ii) characterize them, (iii) model the related process thermodynamics, and (iv) add novel, new, and insightful contributions to the related catalyst field and polymer science and engineering.

This study addresses making value-added elastomers using locally available ethylene, 1-hexene, and 1-octene. Hence, it aligns with strategic olefin valorization research, Kingdom's Sustained Development and Growth (SDG), and Vision 2030.

A solution copolymerization process synthesized ethylene-1-hexene and ethylene-1-octene elastomers using a preactivated mixture of a Spaleck metallocene and a Dow CGC post-metallocene with methylaluminoxane (MAO), and tritylborate plus triisobutyl aluminum (TTB + TIBA) cocatalysts at 4 bar(g) and 40 °–70 °C. The precatalyst-cocatalyst active site behavior was studied using ¹H NMR spectroscopy. The as-synthesized elastomers were characterized using gel

permeation chromatography (GPC), Crystaf, differential scanning calorimetry (DSC), and ^{13}C NMR spectroscopy. The process thermodynamics and catalyst active site residential environment were investigated by modeling ethylene solubility in the solvent-comonomer binary liquid mixture and the liquid phase compressibility factor. The predicted ethylene solubilities well matched the experimental values at laboratory to industrial temperatures and pressures.

This research studied the influence of the Spaleck metallocene and Dow CGC post-metallocene precatalyst structures, the cocatalysts listed above, and temperature on the catalyst activation, macroscopic and microscopic deactivation, average comonomer incorporation, elastomer average molecular weight, polydispersity index, microstructural parameters, solution precipitation behavior, and elastomer thermal properties. Both precatalysts productivity differed but they incorporated greater than 20 mol% comonomer and made E-1-hexene and E-1-octene industrial level MW ($> 10^5$ g/mol) elastomers having glass transition temperatures (T_g s) of $-64.0\text{ }^\circ\text{C}$ and $-69.0\text{ }^\circ\text{C}$, respectively.

The novel, new, and insightful contributions of this study include (i) thermodynamic modeling of catalyst active residential environment and monomer reactivity ratios, (ii) separation of physical phenomena from chemical ion-pair phenomena and precatalyst-cocatalyst microscopic deactivation (using the present new catalyst active site environment parameter concept), and (iii) better depiction of polymerization mixture ensemble, (iv) appropriate explanation for MW-temperature decreasing relation and MWD broadening, (v) introduction of polyalkyl pseudo-single site (SS) catalyst active center, (vi) correction of misapplying fringed micelle crystallization model to elastomer morphology progression, and (vii) elucidation of origin of elastomer copolymer backbone amorphous phase.

The above contributions will help develop better catalysts, copolymerization process, and elastomers. This study concludes by listing recommendations for future work.

ملخص الرسالة

الاسم الكامل: يحيى علاء الدين رواصل

عنوان الرسالة: تفاعل الإيثيلين مع الأوليفينات الأحادية لتكوين اللدائن المرنة باستخدام محفزات الميتالوسين وما بعد الميتالوسين وتحليلها.

التخصص: كيمياء

تاريخ الدرجة العلمية: مايو - 2024

تعد المملكة العربية السعودية ثاني أكبر منتج عالميًا للبولي أوليفينات، إذ يقدر إنتاجها بحوالي 16.25 مليون طن متري سنويًا. وتمثل مادة البولي إيثيلين التي تنتجها سابقًا باستخدام الحفازات حوالي 7.30 مليون طن متري سنويًا وهي تمثل تقريبًا 45% من الناتج الإجمالي. وبما أن تطبيقات البولي أوليفينات شبه البلورية التقليدية في حالة نمو، فإن الأبحاث تستمر في جميع أنحاء العالم لتصنيع المطاط الصناعي غير المتبلور من البولي أوليفينات باستخدام حفازات الميتالوسين وما بعد الميتالوسين. من المتوقع أن يرتفع الإنتاج العالمي للمطاط الصناعي إلى 7.38 مليون طن متري سنويًا، وفي هذا السياق، تظهر لدائن الإيثيلين-ألفا-أولفين تطبيقات واستخدامات متعددة وتسيطر على السوق. أحد التطبيقات الرئيسية لهذه اللدائن هو تحسين مقاومة الصدمات المنخفضة لللدائن الحرارية والقاسية والهشة مثل البولي بروبيلين الأيزوتاكتيك (iPP) والبولي بروبيلين العشوائي (بوليمر مشترك من البروبيلين وكمية صغيرة من الإيثيلين أو ألفا-أولفين) عن طريق مزجها مع هذه اللدائن.

إن الهدف العام لهذا البحث هو: (i) التوليف التحفيزي للإيثيلين-1-هيكسين والإيثيلين-1-أوكتين، و(ii) تحليلها، و(iii) نمذجة الديناميكا الحرارية للعملية ذات الصلة، و(iv) إضافة مساهمات جديدة ومفيدة في مجال الحفازات ذات الصلة وعلوم وهندسة البوليمرات.

تتناول هذه الدراسة صناعة اللدائن ذات القيمة المضافة باستخدام الإيثيلين المتوفر محليًا، و1-هيكسين، و1-أوكتين. لذلك، فإن هذا البحث يتماشى مع البحوث الاستراتيجية لتثمين الأوليفين، والتطوير والتنمية المستدامة في المملكة العربية السعودية، ورؤية 2030.

لقد تم تصنيع لدائن إيثيلين-1-هيكسين، وإيثيلين-1-أوكتين من خلال عملية بلمرة مشتركة محلوليها باستخدام خليط منشط مسبقًا من ميتالوسين سباليك (Spaleck) وما بعد الميتالوسين Dow CGC مع الحفازات المساعدة من ميثيل ألومينوكسان (MAO)

، وتريتيل بورات بالإضافة إلى ثلاثي إيزوبيوتيل ألومنيوم (TTB + TIBA) في تفاعل عند ضغط 4 بار جرام من الإيثيلين و دراجة حرارة بين 40 الى 70 درجة مئوية. تمت دراسة سلوك الموقع النشط في الحفاز المسبق باستخدام تحليل طيف الرنين المغناطيسي النووي للهيدروجين ($^1\text{H NMR}$). وتم تشخيص وتحليل اللدائن المصنعة باستخدام كروماتوجرافيا تخلل الهلام (GPC)، و (Crystaf)، والمسح الحراري التفاضلي (DSC)، وتحليل طيف الرنين المغناطيسي النووي للكربون.

تمت دراسة الديناميكا الحرارية للعملية وبيئة الموقع النشط في الحفاز من خلال نمذجة قابلية ذوبان الإيثيلين في خليط السائل الثنائي من المذيب والمونومير المشترك وعامل انضغاط الطور السائل. وكان هنالك توافق جيد بين ذاتية الإيثيلين المتوقعة من النتائج التجريبية في المختبر ودرجات الحرارة والضغط الصناعية.

في هذا البحث تمت دراسة تأثير هياكل ميتالوسين سباليك (Spaleck) وحفازات Dow CGC ما بعد الميتالوسين المسبقة، والحفازات المساعدة المذكورة أعلاه، ودرجة الحرارة على تنشيط المحفز، والتعطيل المرئي والمجهري، ومتوسط دمج المونومير المشترك، ومتوسط الوزن الجزيئي، ومؤشر تعدد التشتت للوزن الجزيئي، والمؤشرات المجهريّة، وسلوك ترسيب المحلول، والخصائص الحرارية للمطاط الصناعي. اختلفت انتاجية كلا من الحفازين المسبقين، لكنهما دمجا أكثر من 20% (نسبة مولية) من المونومير المشترك وأنتجا لدائن إيثيلين-1-هيكسين وإيثيلين-1-أوكتين لها وزن جزيئي بالمستوى الصناعي (10^5 جرام/مول) وذات درجات حرارة انتقال زجاجي (T_g) تبلغ سالب 64.0 درجة مئوية وسالب 69.0 درجة مئوية، على التوالي.

تشمل المساهمات الجديدة والثاقبة لهذه الدراسة: (i) النمذجة الديناميكية الحرارية للبيئة السكنية النشطة للحفاز ونسب تفاعل المونومير، و(ii) فصل الظواهر الفيزيائية عن ظواهر زوج الأيونات الكيميائية والتعطيل المجهرى للحفاز المشترك-الحفاز المساعد (باستخدام مفهوم مؤشر بيئة الموقع النشط للحفاز الجديد)، و(iii) تصوير أفضل لمجموعة خليط البلمرة، و(iv) تفسير مناسب لعلاقة انخفاض الوزن الجزيئي للمادة بدرجات الحرارة وتوسع مؤشر تعدد تشتت الوزن الجزيئي، و(v) تقديم مصطلح المركز المحفز النشط للموقع الفردي-الزائف متعدد الألكيل (SS)، و(vi) تصحيح سوء تطبيق نموذج تبلور مورفولوجيا المطاط الصناعي، و(7) توضيح أصل الطور غير المتبلور في العمود الفقري للبوليمر المشترك المطاطي.

سوف تساعد هذه المساهمات المذكورة أعلاه في تطوير حفازات أفضل، وعملية بلمرة مشتركة أفضل، ولدائن أفضل. وتختتم هذه الدراسة بإدراج توصيات للعمل المستقبلي.

CHAPTER 1

INTRODUCTION

This thesis titled *Synthesis and Characterization of Metallocene and Post-metallocene Ethylene–Alpha-olefin Elastomers* originates from my MS research work at the Department of Chemistry and Interdisciplinary Research Center for Refining & Advanced Chemicals (IRCRCAC), Research Institute, King Fahd University of Petroleum & Minerals (KFUPM). The background of selecting the above research theme and thesis committee is summarized in Appendix A.

I work as a scientist at SABIC Technology Center at KAUST (STC-K) for more than six years in the polyolefin (PO) department. SABIC is the second largest polyolefin producer in the world where catalyst makes the heart of polyolefin synthesis, manufacture, process, and diverse applications. Catalyst research, among other activities, meets the growing market needs. SABIC, therefore, wants me to grow as a future leader in this catalyst area. Accordingly, I was awarded a full scholarship and my manager, Mark Vlaar, and Sensei Nicolaas Friederichs (Research Fellow)—both from SABIC Technology Center at Geleen (STC-G), The Netherlands—strongly recommended me to work with Prof. Muhammad Atiqullah (Ex-Senior Research Engineer, IRCRCAC). Prof. Atiqullah, during his over 35-year research and teaching career at KFUPM Research Institute, established a world-class PO catalyst research program and laboratories at IRCRCAC and completed a series of strategic metallocene and post-metallocene projects for SABIC. These projects produced patents and notable journal publications. Additionally, note that STC-G is one of Europe's largest polymer research centers.

1.1 Growth of petrochemical-polymer industries in Saudi Arabia and their impact

Saudi Basic Industries Corporation (SABIC)—the nation's 1st petrochemical-polymer company—was established in 1976. By 2020, the number increased from 1 to 32 and by 2025, this will further rise to 37. Almost all of them produce polymers. Note that without producing polymers, these companies cannot remain competitive and profitable in the international market. They will collapse.

Appendix B [1] shows that Saudi Arabia is the 4th largest global polymer producer (22 mmtpa), and at present makes 30 different polymer types. In polyolefin production, the country currently holds the 2nd largest international (16.25 mmtpa) ranking. This huge Saudi polymer production accounts for 1/3rd of the national chemical sales revenue (70 billion SAR/yr). Here, SABIC's total catalytic polyethylenes account for 7.30 mmtpa (~45%). The over 30 petrochemical-polymer companies also impact the country's internal economy as follows (Appendix B) [1]:

- They have established over 20 polymer compound and masterbatch industries and more than 1,300 polymer processors/converters and plastic industries.
- The establishment and growth of 6 non-polymer industrial sectors (which include automotive, building and construction, electrical and electronics, agriculture, packaging, and materials transport) further reflect the industrial impact of Saudi polymers on the national economy.

1.2 Classification of Polyethylenes

Polyethylenes (PEs) can be classified in several ways. But in context of the present work, the following two concepts are important. One is polymer morphology progression, and the other is

transformation of thermoplastic to elastomeric behavior via increasing comonomer incorporation during synthesis. Both concepts are eventually related to material density as well as crystallinity. Hence, density- and crystallinity-based polyethylene classification approaches are adopted in this study. Table 1 classifies polyethylenes based on various ethylene and alpha-olefins and lists the different commercial polyethylene types [2]. Density and crystallinity are directly related.

Table 1.1: Density-based polyethylene classification [2].

Full name	Acronym	Density (g/mL)	Comonomer	Catalyst/initiator
Low-density polyethylene	LDPE	0.915–0.925	None	Organic peroxides
Linear low-density polyethylene	LLDPE	0.919–0.925	α -olefins	ZN, supported Cr, SSC
Medium-density polyethylene	MDPE	0.926–0.940	α -olefins	ZN, supported Cr
Linear medium-density polyethylene	LMDPE			
High-density polyethylene	HDPE	> 0.941	None to very minor α -olefins	ZN, supported Cr
Ultrahigh mol wt polyethylene	UHMWPE	~ 0.940	None	ZN
Very low-density polyethylene	VLDPE ZN	0.885–0.915	α -olefins	ZN
	VLDPE SSC	0.855–0.885	α -olefins	SSC

ZN = Ziegler-Natta; SSC = Single site catalyst; Cr = Chromium; α -olefins = 1-butene, 1-hexene, and 1-octene.

PE chains are made of several thousand ethylene monomer units. The chains develop via addition chain growth mechanism. The addition of an alpha-olefin comonomer affects the PE crystallinity and morphology. Under this situation, morphology transition from crystalline to amorphous occurs, which is illustrated by Figure 1.1. Polyethylenes, therefore, can be classified into (i) highly crystalline to semicrystalline polymers as well as (ii) amorphous (extremely low to zero crystallinity) copolymers. Figure 1.2 depicts the corresponding branching types in polyethylenes. Whether a PE melts like a regular solid, or goes through a phase transition among a glassy, thermoplastic, and viscoelastic liquid is directly connected to its degree of crystallinity. Amorphous polymers do not melt abruptly when heated. Instead, they show glassy, rubbery,

gummy, and viscoelastic liquid behavior with increasing temperature. Consequently, an ideal amorphous polymer does not exhibit a melting point; instead, it demonstrates a glass transition temperature T_g . The glass transition temperature of a particular polymer may be reported as a single temperature, however this value represents a temperature range.

Amorphous polyolefins are more flexible and translucent than crystalline polymers because they lack the ordered structure that makes them rigid. Market- and industry-driven applications of crystalline polyethylenes are approaching saturation. This work, therefore, focuses on amorphous elastomeric polyethylenes that have a lot of scope for generating scientifically interesting novel knowledge as well as creating new applications.

1.3 Applications of Ethylene–Alpha-Olefin Elastomers

Ethylene–alpha-olefin elastomers are applied in automotive, building and construction, footwear, appliances, house wares, medical and hygiene, wire and cable, sport/leisure/toys, packaging, etc. [3, 4]. They expand the applications of commodity thermoplastics, particularly polyethylene and polypropylene, as well as specialty polyolefins. Polyolefin blends and composites occupy a large part of them. One is recommended to review the recent paper published by Zanchin and Leone [2020] that well addresses the growing ethylene–alpha-olefin elastomers. This paper is one of those that celebrates “one 100 years of polymer science” [5]. Commercial elastomers have molecular weights of approximately 150,000–450,000 Dalton and polydispersity index 2.5–5.0 [5].

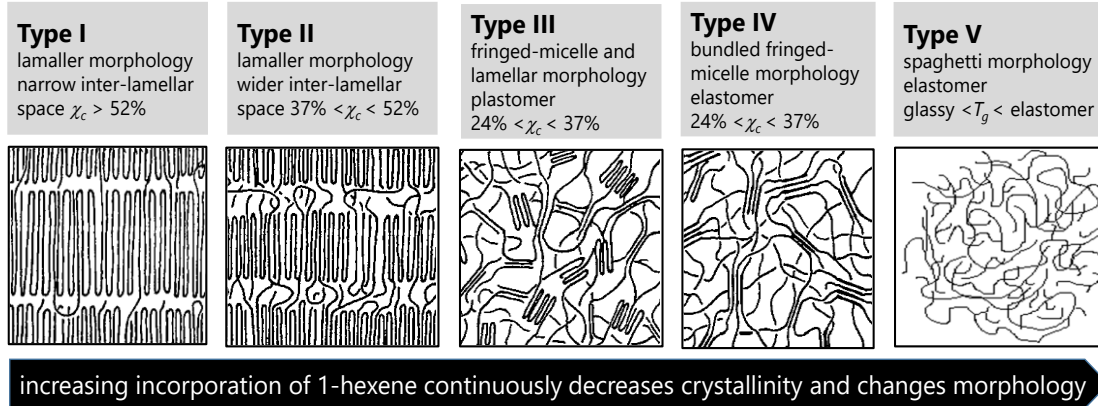


Figure 1.1: Copolymer morphology progression in a thermoplastic elastomer due to increasing comonomer incorporation [6].

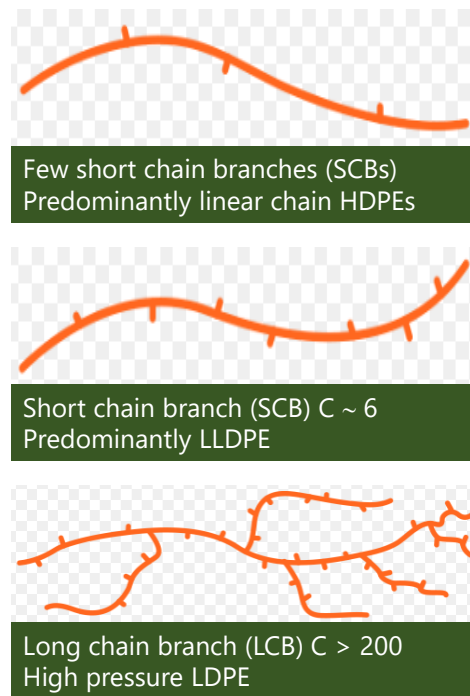


Figure 1.2: Types of branching in polyethylenes [7].

Ethylene–alpha-olefin elastomers, because of the common presence of C–H bond in the backbone, hold strong promise to improve the impact resistance of brittle polypropylene (PP) without using costly compatibilizers. Note that PP brittleness limits its wide application. The global elastomer production has been recently predicted to rise to 7.38 mmpta [4]. This, therefore, underscores the industrial drive for this MS thesis research theme.

CHAPTER 2

LITERATURE REVIEW AND RESEARCH OBJECTIVES

The literature review of this MS thesis research is designed as follows:

- Ethylene–alpha-olefin elastomer synthesis precatalysts and cocatalysts, and
- Catalytic research niche in ethylene–alpha-olefin elastomer synthesis.

2.1 Ethylene-Alpha-Olefin Elastomer Synthesis Precatalysts and Cocatalysts

The literature reports the synthesis of ethylene–alpha-olefin elastomers using metallocenes as well as post-metallocenes. The present review is restricted to only metallocene and CGC post-metallocene precatalysts. Other post-metallocenes such as tridentate titanium [8, 9] and tetradentate zirconium [10, 11], late transition metal precatalysts [12], and Nomura (cyclopentadienyl)(aryloxy)titanium metalorganic ones [13] are excluded.

2.1.1 Ethylene–Alpha-Olefin Elastomer Synthesis using Metallocene Precatalysts

Metallocenes have been widely used to copolymerize ethylene with alpha-olefins, particularly 1-hexene. In this regard, one can consult the personal account of Atiqullah [2022] and the references therein for acquiring a comprehensive knowledge about metallocenes and their applications [1]. However, this research work particularly concerns the synthesis and characterization of ethylene–alpha-olefin copolymers with higher alpha-olefin incorporation (> 15 mol %). A comprehensive literature review, therefore, identifies the application of the following three metallocene families in this context:

- C_s symmetric zirconocenes– $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2$ and $\text{Ph}_2\text{C}(\text{Cp})(2,7^t\text{Bu}_2\text{Flu})\text{ZrCl}_2$,
- C_2 symmetric Spaleck zirconocenes, and

- Nonsymmetric constrained geometry catalysts (CGCs) (special half metallocenes).

The above metallocenes, especially copolymerizing ethylene and 1-hexene with high comonomer affinity, are discussed below.

Yano et al. [1999] copolymerized ethylene with 1-hexene using the following two *Cs* symmetric zirconocenes— $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2$ and $\text{Ph}_2\text{C}(\text{Cp})(2,7^t\text{Bu}_2\text{Flu})\text{ZrCl}_2$ [14]. Figure 2.1 shows their structures. The objective was to evaluate the effect of the bulky 5 tertiary butyl (^tBu) substitution at the 2,7 position of the fluorenyl ligand, particularly on comonomer incorporation, and the resulting copolymer microstructure, MW, and thermal properties. Two different reactor operating conditions were used: lower temperature (40 °C) and pressure [4 bar(g)], and higher temperature (170 °C) and pressure [20 bar(g)].

First, the E-1-hexene copolymerization at the above lower temperature and pressure is addressed (see Table 2.1). The resulting copolymer MW, MWD, and thermal properties (such as peak melting temperature T_{mp} and crystallization temperature T_{pc}) were not reported.

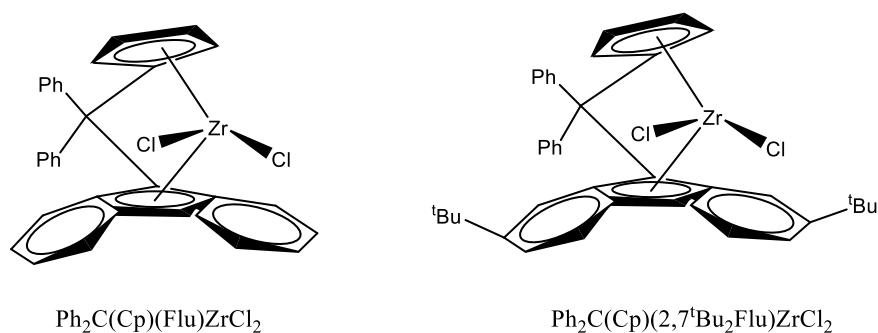


Figure 2.1: Structure of $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2$ and $\text{Ph}_2\text{C}(\text{Cp})(2,7^t\text{Bu}_2\text{Flu})\text{ZrCl}_2$.

Table 2.1: Effect of 2,7 ^tBu substitution at the fluorenyl ligand on E–1-hexene copolymer microstructure at lower temperature and pressure [14].

Metallocenes	[EE] (mol %)	[EH] (mol %)	[HH] (mol %)	[E] (mol %)	[H] (mol %)	r_E	r_H	$r_E r_H$
Ph ₂ C(Cp)(Flu)ZrCl ₂	34.7	59.5	5.8	64.45	35.55	4.6	0.049	0.23
Ph ₂ C(Cp)(2,7 ^t Bu ₂ Flu)ZrCl ₂	36.2	59.7	4.1	66.05	33.95	4.8	0.035	0.17

[EE], [EH], and [HH] are mol % of dyad sequences. [E] and [H] are mol % of ethylene and 1-hexene, respectively, incorporated into the copolymer backbone. r_E and r_H are the reactivity ratios of ethylene and 1-hexene, respectively. $r_E r_H$ is the reactivity ratio product.

Copolymerization conditions: ethylene pressure = 4 bar(g), temperature = 40 °C, time = 10 min, toluene = 2,000 mL, and 1-hexene = 500 mL. Catalyst system: metallocene/Me₂PhNH•B(C₆F₅)₄/i-Bu₃Al = 1:2:250.

The results in Table 2.1 summarize the following:

- i. Both precatalysts incorporated 1-hexene in a comparable fashion (33.95–35.55 mol %).

This value is much higher than that incorporated by other metallocenes such as Et(Ind)₂ZrCl₂ (3.80 mol %) [15] and supported (ⁿBuCp)₂ZrCl₂ (1.80–3.80 mol %) [16].

- ii. The average reactivity ratio product $r_E r_H$, in each case, is much less than 1. Therefore, each precatalyst synthesized alternating E–1-hexene copolymer. This is a consequence of the above very high incorporation of 1-hexene (33.95–35.55 mol %).

- iii. The bulky tertiary butyl (^tBu) substitution at the 2,7 position of the fluorenyl (C₁₃H₉) ligand did not appreciably resist the incorporation of 1-hexene. See the comparable r_H values (with and without ^tBu substitution).

Table 2.2 reports copolymerization results at the higher temperature and pressure. The 2,7 ^tBu substitution at the fluorenyl ligand appreciably increased M_w with mildly decreasing the activity. Hence, it enhances the potential to make high M_w polyolefins without substantially decreasing the catalyst activity. The bulky fluorenyl ligand, with increased steric due to ^tBu substitution, suppresses the major chain-terminating β -H elimination reaction; this increases the M_w [17]. However, this precatalyst structural variation did not affect the peak melting temperature T_{mp} . No results on 1-hexene incorporation and copolymer microstructure were reported.

Table 2.2: Effect of 2,7 ^tBu substitution at the fluorenyl ligand on E-1-hexene copolymer properties at higher temperature and pressure [14].

Metallocene type	Activity× 10 ⁻³ kg polym/(mol Zr)	$M_w \times 10^{-4}$ Dalton*	M_w/M_n	T_{mp} (°C)
Ph ₂ C(Cp)(Flu)ZrCl ₂ ^ψ	148	6.6	2.0	120
Ph ₂ C(Cp)(2,7 ^t Bu ₂ Flu)ZrCl ₂ ^ψ	144	8.6	1.7	120

Copolymerization conditions: ethylene pressure = 20 bar(g), temperature = 170 °C, time = 20 min, C₉–C₁₂ hydrocarbon solvent = 600 mL, and 1-hexene = 20 mL. Catalyst system: metallocene/Me₂PhNH•B(C₆F₅)₄/iBu₃Al = 1:2:250. Metallocene amount = 0.25 μmol. *Polystyrene-based. ^ψSuitable for use at high temperature and pressure. M_w = weight-average molecular weight; M_n = number-average molecular weight; M_w/M_n = polydispersity index; T_{mp} = peak melting temperature.

Choo and Waymouth [2002] also copolymerized ethylene with 1-hexene using Ph₂C(Cp)(Flu)ZrCl₂ under the following polymerization conditions: [1-hexene] = 0.38–1.21 M, [Zr] = 7.5–9.4 μM, toluene = 53 mL, MAO (methyl aluminoxane) = 120 mg, temperature = 20 °C, ethylene = 0.54 bar(g), and time = 10 min. Incorporation of 1-hexene was reported to be 57–72 mol % [18]. This short communication particularly investigated a dual-site alternating mechanism for ethylene–α-olefin copolymerization. It does not report MW and MWD, T_{mp} , T_{pc} , reactivity ratios, and microstructural parameters such as ethylene and 1-hexene average sequence lengths and their distributions.

Przybyla et al. [1999] evaluated the E-1-hexene copolymerization performance of the following silica-supported Spaleck catalyst–SiO₂–MAO/Me₂Si(2-Me-4-Ph-Ind)₂ZrCl₂ [19]. This means that the dehydroxylated silica was first passivated by loading MAO. Next, Me₂Si(2-Me-4-Ph-Ind)₂ZrCl₂ was impregnated on SiO₂–MAO [20]. Figure 2.2 shows the structure of the C₂ symmetric Me₂Si(2-Me-4-Ph-Ind)₂ZrCl₂.

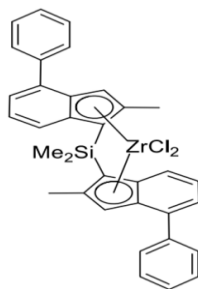


Figure 2.2: Structure of Spaleck $\text{Me}_2\text{Si}[2\text{-Me-4-Ph-Ind}]_2\text{ZrCl}_2$ precatalyst.

The copolymerization was conducted under the following polymerization conditions: solvent = toluene, $[\text{Zr}] = 4 \times 10^{-5}$ mol/L, $[\text{MAO}] = 10^{-2}$ mol/L, $[\text{TIBA}] = 1.7 \times 10^{-2}$ mol/L, ethylene = 2 bar(g). No MAO (methyl aluminoxane) cocatalyst was separately fed during polymerization. Reactor 1-hexene concentrations were varied from 66.84–93.43 mol %. This made E–1-hexene copolymers having 43.05–69.36 mol % of 1-hexene. The following microstructural properties were determined: $r_E = 4.34\text{--}6.49$; $r_H = 0.24\text{--}0.28$; and $r_{EH} = 1.13\text{--}1.82$. The r_{EH} values indicate the formation of random to minor blocky copolymer backbone. Copolymer composition and sequence length distributions were not reported. The most interesting finding is summarized below.

The resulting copolymers showed simultaneous presence of melting points T_{mp} s (121.05–122.21 °C) and glass transition temperatures T_g s (–53.63 to –49.70 °C). This shows coexistence of crystalline and amorphous phases, and a procedure to make them, using a single catalyst and reactor. The T_{mp} and weight-average molecular weight M_w of the polyethylene homopolymer was found to be 127.47 °C and 4.30×10^5 Dalton, respectively. The average 1-hexene sequence length varied from 1.5 to 4.3. Accordingly, the E–1-hexene copolymer M_w s dropped from 2.30×10^5 to 1.68×10^5 Dalton. This supports that 1-hexene acted as a strong chain transfer agent.

The preceding results were explained as follows using filter effect, coined by Przybyla et al. [1999] [19]. When the copolymerization starts, ethylene and 1-hexene access all the active centers on the heterogeneous catalyst surface. Consequently, a copolymer envelope forms around the catalyst particle. This copolymer envelope works as a filter. The smaller ethylene molecule diffuses through this filter and polymerizes inside the intra-catalyst active centers. On the other hand, the larger 1-hexene molecule penetrates the copolymer layer much slower and hardly reaches the inner active centers. As a result, ethylene and 1-hexene essentially copolymerize on the supported catalyst surface while ethylene polymerizes inside the catalyst particle.

The above *filter effect* explanation is subject to criticism. It supports the synthesis of two crystalline phase-E-1-hexene copolymer and PE homopolymer and contradicts the practical coexistence of a crystalline phase and an amorphous phase that exhibit T_{mp} and T_g , respectively. Also, to assume the formation of an amorphous E-1-hexene copolymer envelope, as done by Przybyla et al. [1999], is a wrong consideration. A Crystaf (crystallization analysis fractionation) characterization, which the authors did not do, could better elucidate such findings [19].

Spaleck's zirconocene original π -ligands can undergo so many positional substitutions. Therefore, Ehm et al. [2020] studied how such substitutions affect 1-hexene incorporation affinity into ethylene-1-hexene copolymer backbone [21]. This research theme is important for particularly making elastomers that will balance increasing 1-hexene incorporation with high MW. They evaluated comonomer affinity in terms of reactivity ratio of 1-hexene r_H and that of ethylene r_E which were calculated using ^{13}C NMR-determined triad sequences. They considered 40 silicon-bridged C_2 symmetric *ansa*-zirconocenes (listed in Appendix C) which used a high-throughput copolymerization approach. The copolymerization was conducted at 60 °C; hence, industrial level high temperature was not considered. The major finding of this research is the following. Spaleck

zirconocenes that do not influence the *open quadrant* show marginal substituent effects even though the substitution occurs at 2-, 4-, 5-, 6- or 7- positions. Unfortunately, no 1-hexene incorporation value was reported.

Nomura and Imanishi [2001] copolymerized ethylene with 1-hexene using various nonbridged (cyclopentadienyl)(aryloxy)titanium(IV) precatalysts, and compared their performance with that of Dow CGC [(Me₂Si)(Cp*)(^tBu amido)]TiCl₂, the reference half-metallocene precatalyst [13]. Figure 2.3 shows selective examples. Table 2.3 summarizes the comparative E-1-hexene copolymerization results.

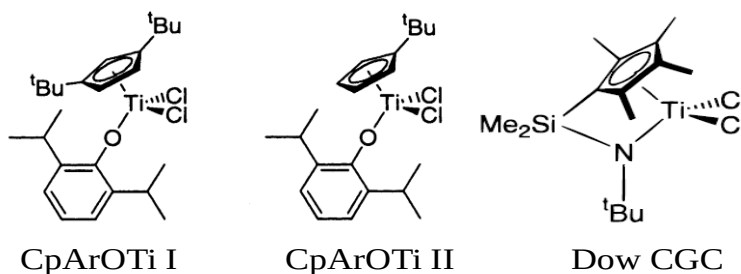


Figure 2.3: Structures of selected nonbridged (cyclopentadienyl)(aryloxy)titanium(IV) precatalysts [13].

Table 2.3 results conclude the following:

- i. CpArOTi I, CpArOTi II, and Dow CGC synthesize E-1-hexene copolymers (having greater than 20 mol % 1-hexene) at Al:Ti molar ratios that vary from 5,000–9,000. Such very high values of Al:Ti molar ratios will hesitantly favor the development of an industrial polymerization process. The industrial Al:Ti molar ratios are preferably from 100–200.

- ii. CpArOTi II showed much less activity and M_w than Dow CGC (the reference precatalyst). However, the incorporation of 1-hexene (23.7–33.9 mol %) and polydispersity index (1.60–2.30) were found to be comparable.

Table 2.3: Nonbridged (cyclopentadienyl)(aryloxy)titanium(IV) precatalyst-mediated E–1-hexene copolymerization results [13].

Precatalyst (μmol)	Al:Ti molar ratio	Ethylene bar(g)	1-hexene (M)	Time (min)	Activity $\times 10^{-3}$	1-hexene (mol %)	$M_w \times 10^{-4}$ Dalton*	M_w/M_n	r_E	r_H	$r_E r_H$
0.30 ^ψ	9,000	5	0.73	6	11.30	27.0	19.7	1.82	3.19	0.15	0.48
0.45 ^ψ	6,500	7	1.45	8	6.85	33.9	12.4	1.78	3.23	0.14	0.45
0.60 ^χ	5,000	5	0.73	8	6.41	32.0	11.4	1.99	2.46	0.18	0.45
0.60 ^χ	3,300	7	0.73	6	14.20	26.9	12.7	1.60	2.35	0.18	0.41
0.60 ^φ	5,000	5	0.73	6	9.49	30.0	74.5	2.05	3.42	0.29	0.99
0.60 ^φ	5,000	7	0.73	4	14.6	23.7	119.0	2.30	6.69	0.14	0.96

^ψCpArOTi I, ^χCpArOTi II, ^φDow CGC, and *Polystyrene based. Temperature = 40 °C. Cocatalyst = Dried MAO. Activity = kg polym/(mol Ti h). Toluene–1-hexene mixture = 55 mL. M_w = weight-average molecular weight; M_n = number-average molecular weight; M_w/M_n = polydispersity index. r_E and r_H are the reactivity ratios of ethylene and 1-hexene, respectively. $r_E r_H$ is the average reactivity ratio product.

- iii. All the above Nomura and Dow CGC precatalysts made narrow polydispersity E–1-hexene copolymers having $M_w > 1 \times 10^5$ Dalton. This value is commercially important for achieving good mechanical properties of the end-products.
- iv. The $r_E r_H$ values report distinct effect of precatalyst structure on the resulting E–1-hexene copolymer microstructure. Both CpArOTi I and CpArOTi II formed alternating copolymer whereas Dow CGC synthesized random one. This backbone difference was attributed to the variation in bond angle and the flexible internal rotation of cyclopentadienyl and aryloxy groups. Note that in CpArOTi I and CpArOTi II, the Cp–Ti–O bond angle is about 120.5° whereas in Dow CGC the Cp–Ti–N bond angle is 107.6° [13].

The previous work of Nomura and Imanishi [2001] on Dow CGC ethylene–1-hexene copolymerization is restricted to 40 °C [13]. But in making ethylene–alpha-olefin elastomer, the following three factors are important: temperature, alpha-olefin incorporation level, and MW. These factorial effects are addressed below.

High temperature operation is needed for better process control, productivity, and solubility of the elastomer product in the solvent used. But it, in parallel, decreases the MW which requires to be high for achieving improved mechanical properties. Increased alpha-olefin incorporation level imparts elastomer properties to the copolymer backbone. Klosin et al. [2001; 2015], therefore, investigated the influence of (i) alkoxy and amino substitutions at 2- and 3-position of the indenyl π -ligand of the experimental CGC and (ii) high temperature such as 140 °C on ethylene–1-octene copolymerization [22, 23].

Figure 2.4 shows the subject substituted CGCs. The amino-substituted CGC demonstrated results having industrial significance. It offered both high catalytic activity and MW. But 1-octene incorporation value was not published.

2.1.2 Single Site Cocatalysts, Precatalyst Active Species, and Catalyst Dormancy and Deactivation

This section categorically reviews cocatalysts used for activating the single site precatalysts, the genesis of the precatalyst active species, and the catalyst dormancy and deactivation phenomena.

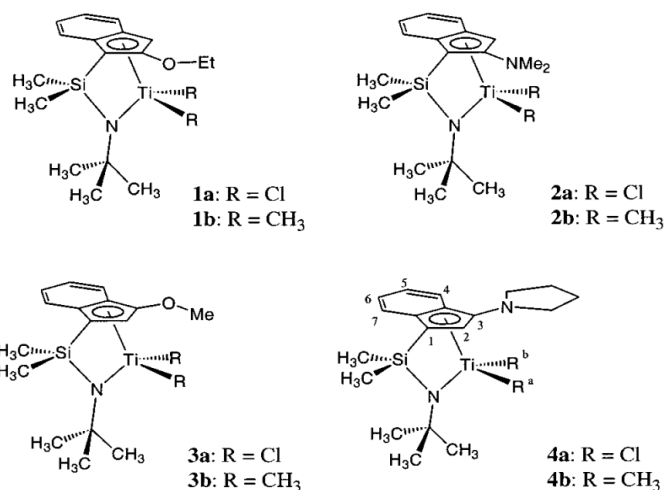


Figure 2.4: Alkoxy and amino substitutions at 2- and 3-position of indenyl π -ligand CGCs [22, 23].

2.1.2.A Single Site Cocatalysts

Single site cocatalysts can be broadly divided into methylaluminoxanes (MAOs) and perfluoroarylboranes and borate salts. MAOs can be further classified into toluene-soluble regular MAO and *n*-hexane-soluble modified methyl aluminoxanes (MMAOs). Controlled/partial hydrolysis prepares regular MAO—called Kaminsky-Sinn cocatalyst—by reacting TMA with water. It comprises $[-\text{Al}(\text{Me})-\text{O}]_n$ repeat units where $n \approx 5-20$ represents the molecular size distribution. Academia and industry are still conducting research to elucidate MAO exact backbone composition and structure. It is inferred that all the Al sites do not have equal Lewis acid strength. Only a certain fraction of them has exceptional Lewis acidity that generates the transition metal active catalyst center [24]. But this subject is still not clearly understood. Figure 2.5 shows the following proposed MAO structures [25]:

- i. One dimensional linear chains (1),
- ii. Cyclic rings that contain three-coordinate Al centers (2),

- iii. Two-dimensional lattice structures (3), and
- iv. Three dimensional clusters/cages (4 and 5).

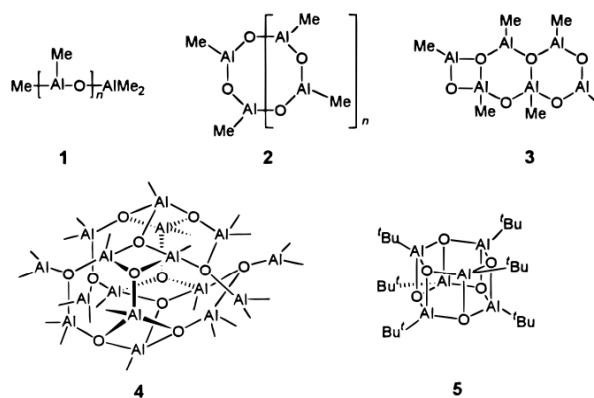


Figure 2.5: Proposed MAO structures.

Structure 4, proposed by Sinn [1995], originates from structural similarities with *tert*-butylaluminummoxanes which form cage structure 5 [26]. Such structures can be isolated and characterized using X-ray crystallography [27]. The basic formula $[\text{Al}_4\text{O}_3(\text{CH}_3)_6]_4$ represents structure 4. It has a $\text{CH}_3:\text{Al}$ ratio of ~ 1.5 . This value agrees with the general MAO formula $[\text{AlO}_{0.75-0.80}(\text{CH}_3)_{1.4-1.5}]_n$, found by Albemarle researchers using ^1H NMR [28]. Multinuclear NMR measurements also support MAO cage structure. Structure 4 aluminum centers, excluding the peripheral (surface) ones, are mostly tetracoordinated which dominate in solution. Three-coordinate Al sites also prevail.

What has been stated above upholds that regular MAO has primarily cage structure that features the following. Multiple equilibria exist in solution. Residual TMA, irrespective of the synthetic route, is an integral component of MAO. Two types of TMAs—free and associated—are present in typical MAO solutions. See Figure 2.6 below [25].

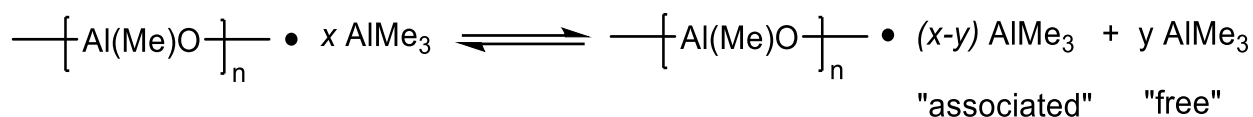


Figure 2.6: Existence of associated and free TMAs in MAO.

Evaporation can hardly reduce the CH₃:Al ratio below ~1.5 because the associated TMA is only chemically removable. Owing to unresolved structural features, it is a common practice to represent MAO as simplified [–Al(CH₃)–O–]_n linear chain or cyclic ring structures having three-coordinate Al centers though the cage structure is more supported via DFT calculation, NMR studies, and X-ray crystallography.

Regular MAOs have several disadvantages. They have low solubility in aliphatic solvents (which are environmentally less hazardous) and poor storage and transportation stability due to gelling tendency. Both limit their practical utility.

To overcome the above disadvantages, Akzo-Nobel produced MMAOs by co-oligomerizing TMA with triisobutylaluminum or *n*-trioctylaluminum in the presence of water. In MMAOs, *iso*-butyl or *n*-octyl longer alkyl groups, therefore, replace preferably a minor percentage of the outer surface methyl groups of the MAO cage/cluster structure ([MMAO 3A: (CH₃)_{0.7}(*i*-C₄H₉)_{0.3}AlO]_n, [MMAO 12: (CH₃)_{0.95}(*n*-C₈H₁₇)_{0.05}AlO]_n) [29, 30, 31]. This enhances cocatalyst solubility in aliphatic solvents and storage stability. They can be produced at lower cost while providing good polymerization efficiency. But the presence of free TMA, triisobutylaluminum or *n*-trioctylaluminum persists, which usually decreases catalyst activity and polymer molecular weight. To solve the MAO synthesis residual TMA problem, Akzo-Nobel next introduced PMAO–IP which is substantially free of TMA. Using nonhydrolytic thermal and/or catalytic route achieves this. PMAO–IP is prepared in two steps. The first step involves reaction between an oxygen-containing reagent and TMA that forms a PMAO–IP precursor specie. The

second step thermally converts the precursor species to pure methylaluminoxane. PMAO-IP contains less free TMA and shows higher catalytic activity [25].

MAO entered the olefin polymerization field in 1980. It unprecedentedly influenced the related catalysis subject. It has expanded the understanding of metallocene-mediated olefin polymerization, especially the mechanism kinetics, and versatility of applications. Hence, MAO-cocatalyzed metallocene is considered as the next revolution in olefin polymerization organometallic catalyst, following the seminal mid-1950 contributions of Nobel laureates Prof. Karl Ziegler and Prof. Giulio Natta [1]. This development originates from the enormous versatility embedded in the precatalyst structure and synthesis work. In this context, one can list the following three areas—the transition metal incorporation, the ancillary coordinating π -ligands, and the bridge that connects the π -ligand sandwich. The π -ligand expansion and substitution herein tremendously multiply the synthesis of so many different metallocenes, as well as post-metallocenes. This has enabled the organometallic and polymer chemists to elucidate the mechanism of olefin polymerization in a much more comprehensive fashion. Consequently, today we better understand catalyst active center generation, precatalyst deactivation, monomer/comonomer coordination and insertion, and chain initiation, propagation, and termination (chain transfer).

The above successes of MAO and MMAO, in promoting high-activity metallocene-mediated olefin polymerization, are noteworthy. However, a critical disadvantage is the following. High MAO:precatalyst ratios (200:1–10,000:1) are usually needed to achieve acceptable polymerization activity and relatively stable kinetic profiles. This incurs high cocatalyst cost and unacceptable polymer ash content (Al_2O_3). Poor polymer morphology in slurry and gas phase polymerizations is another concern. Finally, the poorly understood and complicated MAO structure as well as the exceedingly high MAO amount, required in the precatalyst activation

process, prevent the active catalytic species from full characterization. The overall activation process and the nature of the active species are, therefore, not well understood. The requirement of high MAO:precatalyst ratios is not yet convincingly explained. Consequently, new alternative cocatalysts, which can provide equivalent or even greater catalytic activity and allow isolation and characterization of the active species, require to be developed. This will lead to a better fundamental understanding of cationic transition metal-mediated coordination polymerization.

To overcome all the MAO and MMAO disadvantages listed above, perfluoroarylboranes and borate salts next join the cocatalyst family. $B(C_6F_5)_3$ and TTB are typical practical examples of perfluoroarylborane and borate salt, respectively. TTB consists of (i) Ph_3C^+ trityl cation (a strong alkide, and a H-abstracting and an oxidizing agent) and (ii) noncoordinating/weakly coordinating $B(C_6F_5)_4^-$ borate anion. Note that these compounds, unlike MAO and MMAO, have the following advantages:

- They have precisely defined structures.
- The precatalyst:cocatalyst (without using an additional alkylaluminum compound) molar ratio can be stoichiometric to a little excess.
- They, unlike MAO and MMAO, do not exist in solution in multiple equilibria.
- They do not gel and lose product quality consistency during transportation and storage.

$[B(C_6F_5)_4]$ -based cocatalysts are effective for olefin polymerization. But they have the following disadvantages. They show poor solubility in hydrocarbons and especially weak thermal stability. The ability of $[B(C_6F_5)_4]^-$ mediated cationic complexes to crystallize shortens catalytic lifetime and prevents adequate characterization [25].

Note that for Cl₂-containing precatalysts, perfluoroarylboranes and borate salts (called primary cocatalysts), effectively function only in the presence of excess alkylaluminum compounds (called secondary cocatalysts). The next section elaborates on the underlying chemistry and scheme.

Research continues to chemically remove the residual TMA and TIBA via a non-aluminum aryl Lewis acid, such as tris(pentafluorophenyl)borane B(C₆F₅)₃, that plays the following dual roles. It rapidly reacts with TMA and TIBA, and the anionic (C₆F₅)₃ may partially transfer to the MAO/MMAO backbone. The objective is to improve the commercial MAO/MMAO performance. Accordingly, in a hydrocarbon solution, the residual TMA (present in MAO) and TMA and TIBA (present in MMAO) undergo facile ligand exchange with B(C₆F₅)₃ to form mixtures of aluminum-containing Lewis acids, having the formula $[(-AlR-O-)(-Al(C_6F_5)-O)]-[(C_6F_5)_xAl_2R_{6-x}]$; R = Me and ⁱBu [32]. Here, as stated above, apart from B/Al (in TMA and TIBA) ligand exchange, some of the C₆F₅ groups are postulated to transmit to the MAO/MMAO backbone [32, 33]. This binary mixture shows to be an efficient cocatalyst in mixed alkanes for copolymerizing ethylene with 1-octene at 130 °C in the presence of [(tetramethylcyclopentadienyl)dimethylsilyl-N-tert-butylamido]titanium-1,3-pentadiene]. The above activator composition utilizes the rapid reaction between R₃Al and B(C₆F₅)₃ and alkyl/aryl redistribution to chemically remove the MMAO/MAO R₃Al residues [25]. This illustrates how to modify the MAO/MMAO architecture for making a cocatalyst more reactive than the commercial ones.

MAO, MMAO, TMA, TIBA, B(C₆F₅)₃, and TTB are all Lewis acids of varying strengths. This common Lewis acidity is the key to generating the active single site catalytic species L_nM⁺R(olefin). The following section elaborates this part. Note that understanding the genesis of

active catalytic species clearly is a prerequisite to comprehending the catalyst deactivation phenomena properly which is addressed in Section 2.1.2.3.

2.1.2.B Generation of Active Single Site Precatalyst Species

We can divide single site polyolefin precatalysts into dialkyl and dichloride organometallic complexes. In both cases, the coordinatively unsaturated alkyl transition metal cation is the active catalytic species. We illustrate its genesis below with reference to the following most common cocatalysts—MAO, TTB, and TIBA.

For the dialkyl precatalyst, MAO generates the active catalytic species via only a single alkyl abstraction. On the other hand, for the dichloride, first a chloride/alkyl ligand exchange by MAO alkyl ligand occurs; then subsequent alkyl/halide abstraction activates the metal halide precatalyst. See Figure 2.7. Based on XPS and ^{13}C NMR studies as well as ^{91}Zr and ^{13}C NMR investigations, it is concluded that this abstraction process is attained only by some of the Al centers in MAO [24, 25]. Additionally, MAO scavenges (through coordination complexation) adventitious polar impurities, particularly from solvent, liquid monomer, and comonomer.

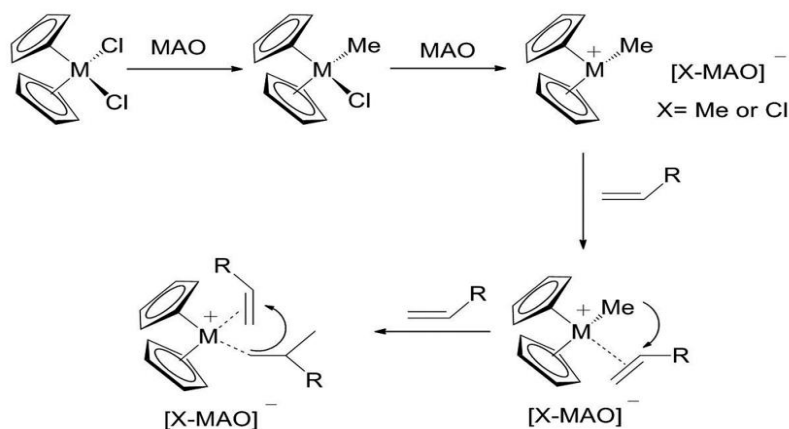


Figure 2.7: The role played by MAO in generating the active metallocenium cation in homogeneous olefin polymerization.

For the dialkyl precatalyst, TTB, like MAO, generates the active catalytic species L_nM^+R (coordinatively unsaturated alkyl transition metal cation) via a single alkyl (R) abstraction without using a secondary alkylaluminum cocatalyst [25]. More precisely speaking, the active catalyst center is $L_nM^+R(\text{olefin})$ that includes the inserted olefin. See Figure 2.8. Molar borate salt:alkylated precatalyst transition metal (M) ratio, unlike that in MAO cocatalyst, varies from 1 to 2.

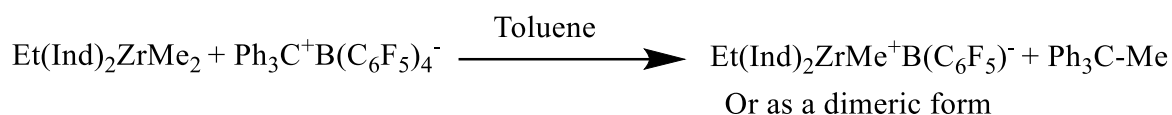


Figure 2.8: Generation of catalyst active cationic species via reaction of TTB with a dialkyl precatalyst.

A dialkyl transition precatalyst is more unstable than the dichloride analogue and is also cumbersome to synthesize. Hence, commercial precatalysts are mostly dichloride. The challenge, therefore, involves developing appropriate borate cocatalyst systems for the dichloride precatalyst. Here, the precatalyst is usually alkylated, in the presence of the primary borate cocatalyst, using a large excess of the alkylaluminum secondary cocatalyst. A part of this excess alkylaluminum scavenges (through coordination complexation) adventitious polar impurities, particularly from solvent, liquid monomer, and comonomer. The interactions among the precatalyst, primary and secondary cocatalysts and the related chemistry compose a complex topic. Two works—one by Chien et al [1993] and the other by Zaccaria et al. [2021] are particularly worthwhile to review in this context [34, 35, 36].

Chien et al. [1993] showed that a zirconocene dichloride, a trialkyl aluminum, and $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$, added following the order stated, polymerized ethylene and propylene with high activity [34, 35]. They perceived that the overall activation process consists of (i) initial in-situ

alkylation of zirconocene dichloride by alkylaluminum and (ii) subsequent oxidative cleavage of the resulting Zr–R bond by Ph_3C^+ because $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ is a strong oxidizing agent. See Figure 2.9 below. Note that the above alkylation argument due to R_3Al is weak.

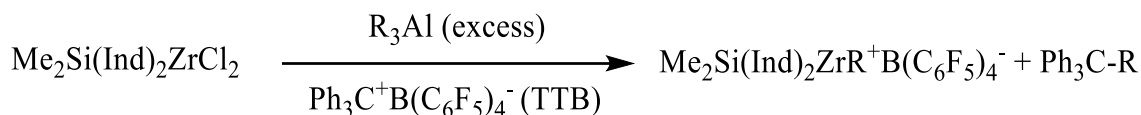


Figure 2.9: Generation of catalyst active cationic species via reaction of R_3Al and TTB with a dichloride precatalyst [34].

According to Zaccaria et al. [2021], the following subjects based on comprehensive NMR studies, are important to understand [36]:

- i. The order of addition of the precatalyst, and primary and secondary cocatalysts. Different orders of addition can lead to different results. See below.
- ii. Generation of the *in-situ* transient Cl-abstracting Al-cation $[\text{Al}^i\text{Bu}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ balanced by the borate anion (Figure 2.10) and subsequent alkylation of Cl via ligand exchange (Figure 2.11), *in the presence of the precatalyst*, using excess TIBA. The above ion-pair complex shows itself to be the real cocatalyst [36, 37]. This protocol includes precatalyst + TIBA + TTB or precatalyst + TTB + TIBA. Both are practically the same because (dichloride precatalyst + TIBA) or (dichloride precatalyst + TTB)—the first binary addition—is non-reactive, and only (TTB + TIBA or *vice versa*) are highly reactive. According to Beck and Brintzinger [1998], the exchange of both Cl ligands by the R analogue of R_3Al may also happen, particularly in the presence of excess TIBA [38]. Notwithstanding, the explanation of Zaccaria et al. [2021] holds equally in this context.

Protecting $[\text{Al}^i\text{Bu}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ —the most critical species—from degradation is indispensable. What follows elaborates this point [36].

- iii. The premixture of TIBA + TTB, contacting the precatalyst, will be ineffective to generate the active catalytic species. In this case, TIBA (in much greater excess) reacts with TTB that involves hydride abstraction and isobutene elimination and produces $[\text{Al}^i\text{Bu}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ which degrades into B^iBu_3 , $\text{B}^i\text{Bu}_2(\text{C}_6\text{F}_5)$, and $\text{B}^i\text{Bu}(\text{C}_6\text{F}_5)_2$ [39]. See Figure 2.12.

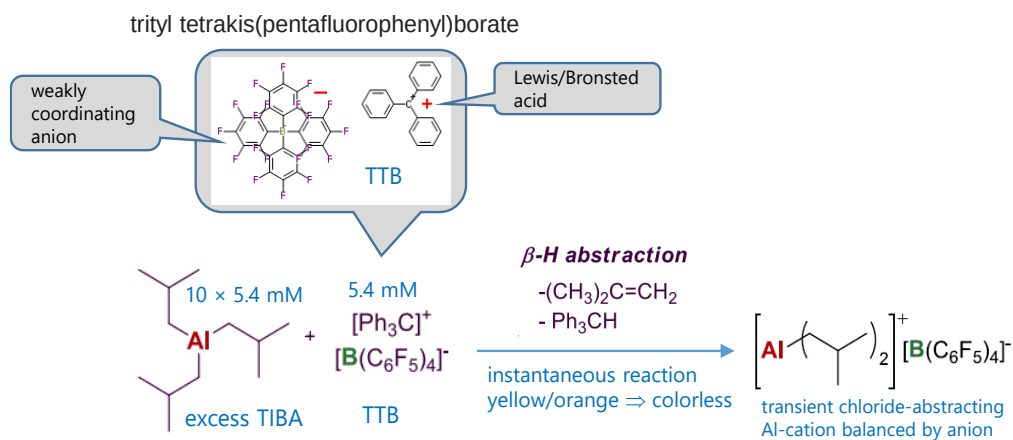


Figure 2.10: Generation of the transient Cl-abstracting Al-cation balanced by the borate anion using excess TIBA [36].

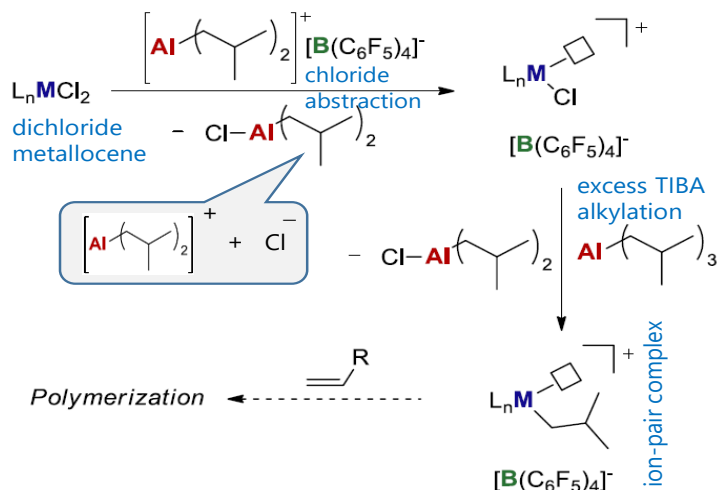


Figure 2.11: Activation of dichloride precatalysts by borate salt/TIBA cocatalysts, involving Cl-abstraction by transient $[Al^iBu_2]^+[B(C_6F_5)_4]^-$ and subsequent alkylation, both by excess TIBA [36].

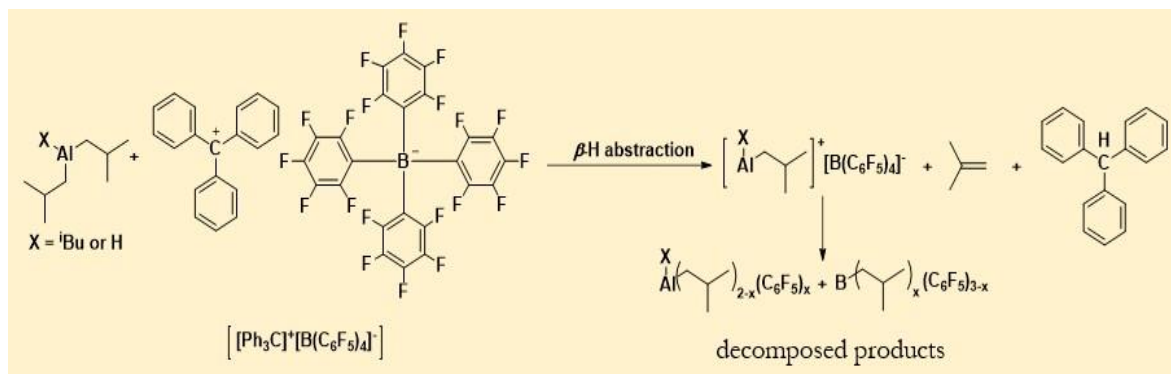


Figure 2.12: Degradation of TTB by TIBA [39].

Note that the explanation put forward by Zaccaria et al. [2021] [36] is much stronger than that reported by Chien et al. [1993] [34, 35].

The above approach avoids using zirconocene dialkyl precatalysts. However, the proposed large excess of trialkylaluminum is disadvantageous. A part of the excess trialkylaluminum can serve as a scavenger. But it can also cause catalyst deactivation. For example, TMA has been found to react with $Ph_3C^+B(C_6F_5)_4^-$ to form several exchange products [39] as well as deactivate the active metallocenium cation via forming heterodinuclear complexes [40, 41]. The next section,

therefore, critically reviews the precatalyst deactivation subject. The activity of this system (a zirconocene dichloride, a trialkyl aluminum, and $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$), unlike the MAO-activated analogue, is quite sensitive to the polymerization temperature [34, 35, 42, 43, 44, 45].

2.1.2.C Single Site Catalyst Dormancy and Deactivation

Catalyst dormancy as well deactivation may simultaneously prevail. Dormancy is reversible; here, the catalyst active center reactivity is apparently ineffective. But deactivation, the catalyst active center being dead, is usually irreversible. Therefore, polymerization cannot take place. However, depending on the polymerization conditions, catalyst steric, electronic, and surrounding residential environments, the catalyst activity can be revived in either case. The knowledge of catalyst dormancy and deactivation is necessary to:

- i. Conduct successful and reproducible polymerization trials,
- ii. Evaluate catalyst performance and stability,
- iii. Elucidate polymerization mechanism and kinetics, and
- iv. Develop high-performance polymerization processes.

The catalyst can be dormant as well as deactivate because of (i) trapping the catalyst active center and (ii) forming mononuclear and heterodinuclear complexes. We review them as follows.

Trapping of the catalyst active center

Me–H transfer reaction, producing methane, deactivates MAO-activated catalytic systems [25, 46, 47, 13]. This condensation reaction between the active methyl metallocenium cation and MAO

forms catalytically inactive and sterically hindered $\text{Zr-CH}_2\text{-Al}$ or $\text{Zr-CH}_2\text{-Zr}$ species. The steric hindrance originates from MAO bulky cage structure. See Figure 2.13.

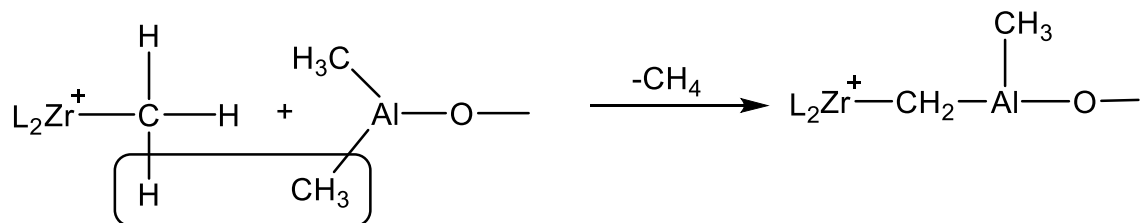


Figure 2.13: Deactivation of MAO-activated catalytic systems via Me-H transfer reaction.

Metallocene structure, temperature, Al:Zr ratio, and concentration affect the rate of the above deactivating condensation reaction. MAO, in Me-H transfer reaction, produces methane much faster than the less Lewis acidic TMA. ^1H NMR shows that excess MAO can reactivate the inactive $\text{Zr-CH}_2\text{-Al}$ species, forming $\text{L}_2\text{Zr}(\text{CH}_3)^+$ and $\text{Al-CH}_2\text{-Al}$ structures, as shown by Figure 2.14 [25, 46, 47]:

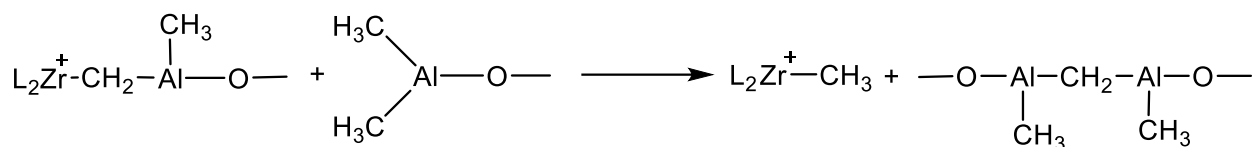


Figure 2.14: Reactivation of the inactive $\text{Zr-CH}_2\text{-Al}$ species by excess MAO.

Coordination of the MAO counteranion oxygen, having a lone pair of electrons, to the metallocenium cation is another form of trapping the catalyst active center [25, 41, 48]. See Figure 2.15.

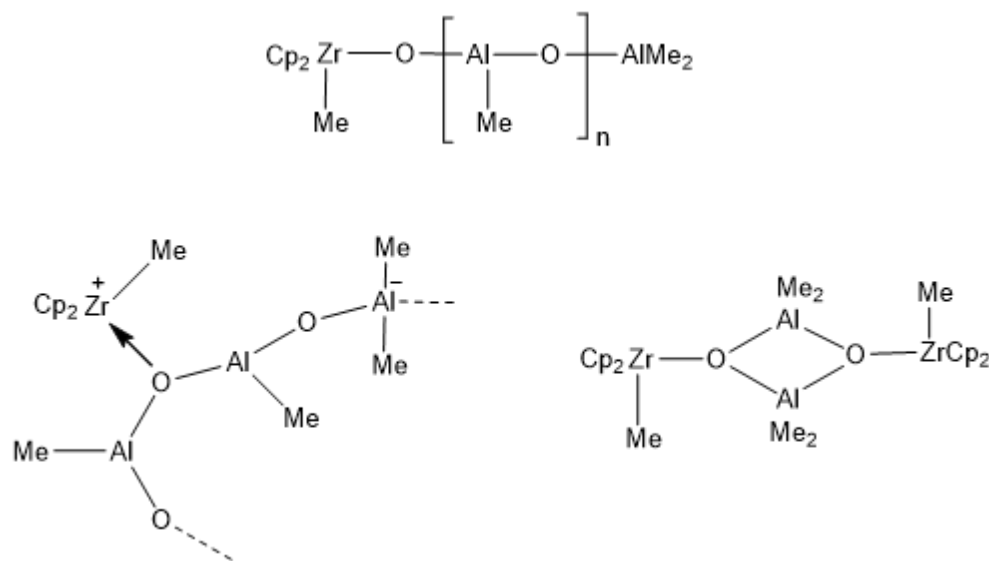


Figure 2.15: Deactivation of the catalyst active center via coordination of the MAO counteranion oxygen.

Above structures represent various forms of adducts between $[\text{Cp}_2\text{ZrMe}]^+$ and $[\text{Al}_2\text{O}_2\text{Me}_4]_2^-$. They do not have any readily accessible coordination sites. They are, therefore, not catalytically active for olefin polymerization. However, excess MAO may reactivate them [25, 48, 49, 13].

Forming of inactive mononuclear and heterodinuclear adduct complexes

Dialkyl sterically hindered $\text{Cp}^*_2\text{ZrMe}_2$ zirconocene, in the presence of TMA or TTB and excess TMA, form Me-bridged Zr^+ -Al heterodinuclear complexes (adducts) [40, 41, 50]. See Figure 2.16. Similar product forms by $\text{Cp}_2\text{HfMe}_2/\text{TTB}/\text{TEA}$ [41]. These adducts are coordinatively saturated. The cation-bound TMA, therefore, does not insert olefins and excess TMA consequently inhibits or lowers catalytic activity. This metallocenium cation-alkyl aluminum adduct formation concept can explain catalyst deactivation for dichloride metallocene, TTB primary cocatalyst and excess TMA/TIBA secondary cocatalyst. See Section 2.2.2.2.

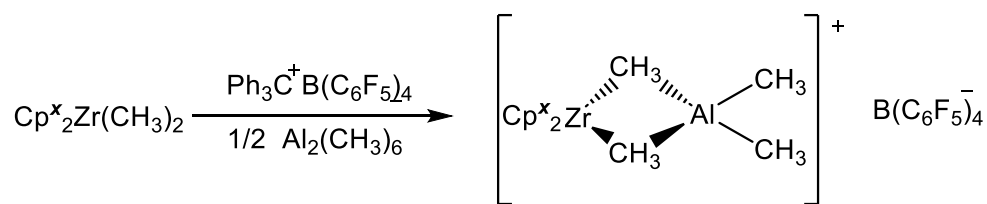


Figure 2.16: Formation of inactive Zr-Al heterodinuclear adduct [39, 41].

On the other hand, $\text{Cp}_2\text{ZrMe}_2/\text{MAO}$, forms the following Me-bridged adducts— $[\text{Cp}_2\text{ZrMe}(\mu\text{-Me})\text{Cp}_2\text{ZrMe}]^+[\text{Me-MAO}]^-$ (symmetric Zr-Zr homodinuclear dimer), $[\text{Cp}_2\text{ZrMe}_2\text{AlMe}_2]^+[\text{Me-MAO}]^-$ (Zr-Al heterodinuclear), and $\text{Cp}_2(\text{Me})\text{Zr}^+ \leftarrow \text{Me}^- \text{-Al}(\text{MAO})$ (unsymmetric Zr-Al heterodinuclear *pseudo-Zwitterion*) [51, 52]. See Figure 2.17. $[\text{Cp}_2\text{ZrMe}(\mu\text{-Me})\text{Cp}_2\text{ZrMe}]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$, $[\text{Cp}_2\text{HfMe}(\mu\text{-Me})\text{Cp}_2\text{HfMe}]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ and $[\text{Me}_2\text{SiInd}_2\text{ZrMe}(\mu\text{-Me})\text{Me}_2\text{SiInd}_2\text{ZrMe}]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ (symmetric Zr-Zr homodinuclear) adducts have also been reported to form by $\text{Cp}_2\text{ZrMe}_2/\text{B}(\text{C}_6\text{F}_5)_3$ [52], $\text{Cp}_2\text{HfMe}_2/\text{TTB}$ [53, 54], and $\text{Me}_2\text{SiInd}_2\text{ZrMe}_2/\text{TTB}$ [41], respectively. $\text{Cp}_2\text{TiX}_2/\text{MAO}$ ($\text{X} = \text{Me}$ or Cl) also produces the same series of adducts [55]. In contrast, $[(\text{Me}_4\text{C}_5)\text{SiMe}_2\text{N}^t\text{Bu}]\text{TiX}_2/\text{MAO}$ (CGC/MAO, $\text{X} = \text{Me}$ or Cl) shows $[(\text{Me}_4\text{C}_5)\text{SiMe}_2\text{N}^t\text{Bu}](\text{Me})\text{Ti}^+ \leftarrow \text{Me}^- \text{-Al}(\text{MAO})$ (unsymmetric Ti-Al heterodinuclear *pseudo-Zwitterion*) adduct [55]. See Figure 2.17. Al:Zr ratios regulate their relative formation amount [51, 55]. However, the situation differs with respect to activating the dialkyl $\text{Me}_2\text{C}(\text{Cp})\text{IndZrMe}_2$ using $\text{B}(\text{C}_6\text{F}_5)_3$ (a relatively strong organo-Lewis acid). Here, inactive mononuclear Zr-HB (Zr-borohydride) species such as $\text{Me}_2\text{C}(\text{Cp})\text{IndZrMe}(\mu\text{-H})\text{B}(\text{C}_6\text{F}_5)_3$ is formed [56, 57]. With $\text{Cp}_2\text{ZrMe}_2/\text{B}(\text{C}_6\text{F}_5)_3$, however, only the active $[\text{Cp}_2\text{ZrMe}]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ has been reported to form [52].

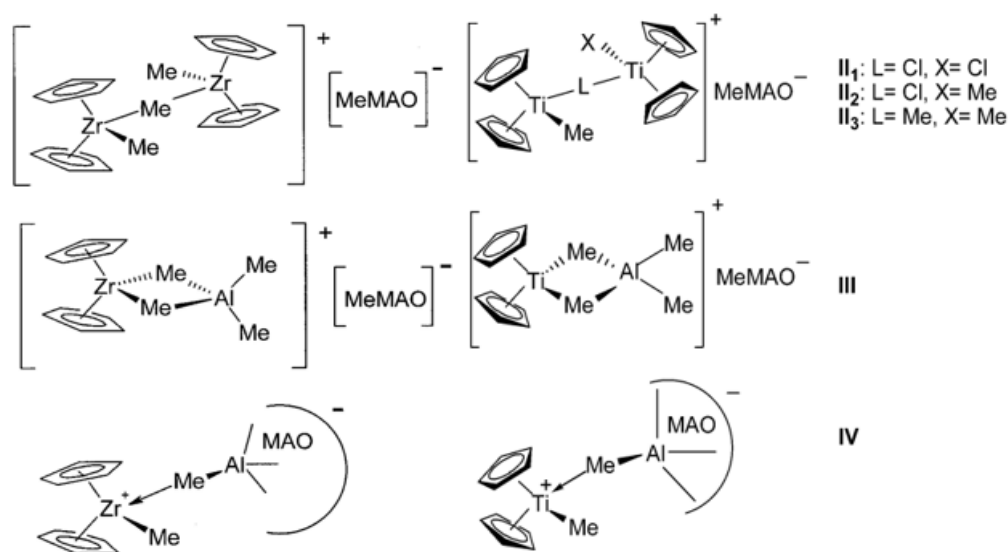


Figure 2.17: Structures of selected inactive symmetric M-M homodinuclear, M-Al heterodinuclear, and unsymmetric M-Al heterodinuclear pseudo-Zwitterion adducts (M = Zr or Ti) [51, 52, 55].

The free TMA (a very poor Me abstractor) in MAO also forms the above Me-bridged heterodinuclear Zr⁺-Al adducts which reduce catalytic activity [50, 58, 59, 60]. See Figure 2.18. This is why removing the free TMA via evaporation or reaction with a sterically hindered phenol increases the catalytic activity [61]. If TIBA/TTB is the source of generating the cation, then a H-bridged heterodinuclear Hf⁺-Al adduct forms that is *surprisingly active*. See the figure below [58, 59]. But TIBA/MAO forms R-bridged heterodinuclear Zr⁺-Al adducts with zirconocenes. These results show transition metal effect on adduct formation involving the active cation. bulky monomer effect 2,4,4-trimethyl-1-pentene.

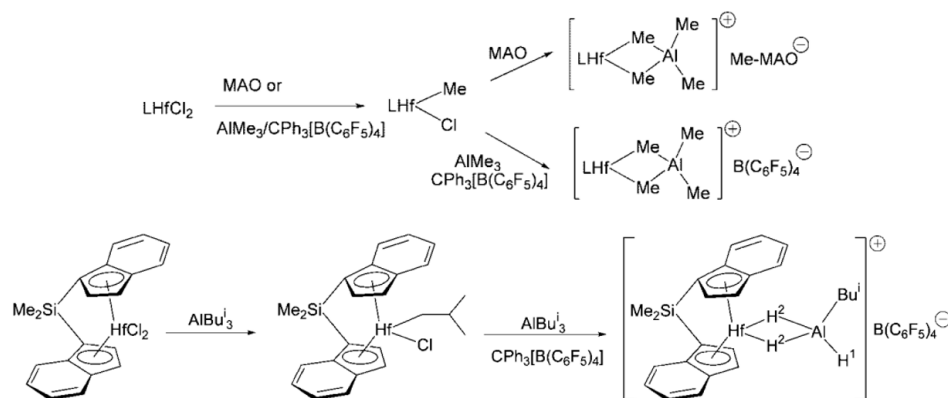


Figure 2.18: Formation of a surprisingly active H-bridged heterodinuclear Hf^+ -Al adduct [58, 59].

Now we review dialkyl and dichloride precatalyst deactivation, particularly in the presence of TTB primary and TIBA secondary precatalysts. This review is especially important for the present thesis research theme. Here, the adduct formation depends on Al:Zr molar ratios. For example, at $\text{Al:Zr} < 10$, $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2/\text{TIBA}/\text{TTB}$ forms the symmetric homodinuclear $[\text{Me}_2\text{Si}(\text{Ind})_2\text{Zr}(\mu\text{-Cl})_2\text{ZrMe}_2\text{Si}(\text{Ind})_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]_2^-$ (IV) adduct (ion-pair). On the other hand, at $\text{Al:Zr} \geq 20$, it forms the heterodinuclear $\text{Me}_2\text{Si}(\text{Ind})_2\text{Zr}(\mu\text{-H})(\mu\text{-Bu})\text{Al}^i\text{Bu}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (V) adduct [62]. See Figure 2.19.

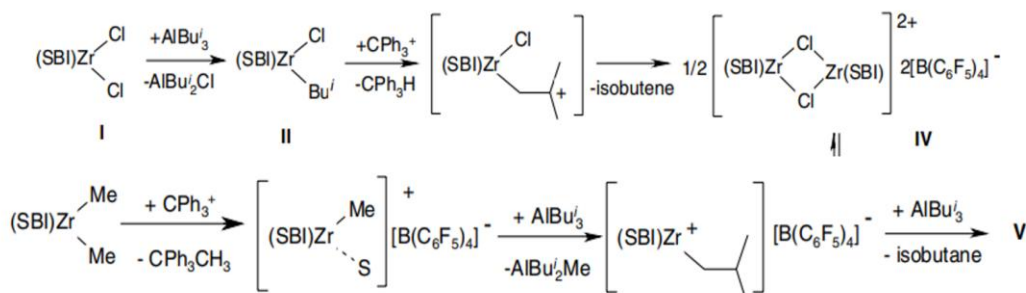


Figure 2.19: Formation of homo- and heterodinuclear adducts/ion-pairs [62].

The formation of a deactivating R-bridged heterodinuclear Zr^+ -Al adduct is primarily a reaction between the Zr^+ metallocenium cation and an R_3Al where $\text{R} = \text{Me}, \text{Me}_2^i\text{Bu}, \text{Me}^i\text{Bu}_2$, etc.

(gradual replacement of Me with bulkier ⁱBu). This can, therefore, happen with alkyl and dichloride metallocenes and post-metallocenes activated by all the cocatalysts (MAO, MMAO, MAO-IP, boranes, and borates, as well as a mixture of primary borate and excess secondary R₃Al cocatalysts) discussed in Section 2.1.2.2. The adduct stability depends on R type [63]. Above are general comments with reference to metallocene and post-metallocene deactivation. However, exceptions may happen when the catalytic cation experiences transition metal and bulky comonomer effects [58, 59].

The above precatalyst deactivation review classifies the inactive species as (i) Cl-bridged symmetric homodinuclear [M–M]⁺ adducts, (ii) H-bridged and R-bridged heterodinuclear M⁺-Al adducts, (iii) unsymmetric Zr-Al heterodinuclear *pseudo-Zwitterion*, and (iv) *mononuclear* Zr-HB (Zr-borohydride) species. However, H-bridged heterodinuclear Hf⁺-Al adduct, being active, is an exception to this list. Several factors such as precatalyst and cocatalyst structures and types and their molar ratios, catalyst active center residential environment, polymerization system and conditions, etc. affect (i) the formation of the above adducts, and (ii) their concerted interaction with the active cationic metal center M⁺. Generalization of the adduct product types, their structures, and the concerned reactions is, however, difficult. This reversible-irreversible interaction is reflected qualitatively by the polymerization kinetic profile. Measuring the kinetic profile can, therefore, evaluate the microscopic catalyst deactivation during polymerization. These homo- and heterodinuclear ion-pairs are inactive because they do not insert olefins. But they later may convert into active species if they decompose into mononuclear active ion-pairs [58, 59, 63]. The related precatalyst deactivation mechanisms have been mostly reported using various NMR investigations. Such experiments have the following limitations:

- i. They ignore the effects of active catalyst center residential environment [demonstrated by gaseous monomer solubility (in comonomer and solvent), comonomer concentration, and particularly solvent coordination (involving arene complexation)] on the catalyst active center.
- ii. They do not consider macro- and micromixing and viscosity effects.
- iii. The hydrodynamics of mixing in a typical laboratory reactor significantly differs from that of a *quiescent* mini-NMR tube reactor. The same precatalyst deactivation mechanism, therefore, may not necessarily hold.

The above analysis suggests that precatalyst deactivation mechanisms be reevaluated using appropriate laboratory reactor experiments that can investigate (i) macroscopic and microscopic catalyst deactivation phenomena, and (ii) relative competition between propagation and termination rates. This is an important research niche.

2.2 Catalytic Research Niche in Ethylene–Alpha-Olefin Elastomer Synthesis

This section is the heart of this literature review. It first critically evaluates the work done, particularly in metallocene-aided synthesis of ethylene–alpha-olefin elastomer. Next, the new research direction is set.

2.2.1 Critical Evaluation of Metallocene-aided Synthesis of Ethylene–Alpha-Olefin Elastomer

Two subjects, which complement each other, are crucially important in the catalytic synthesis of ethylene–alpha-olefin elastomer. One relates to catalyst phenomena such as precatalyst and cocatalyst structural effect, activation, deactivation, and stability. The other concerns copolymerization phenomena, for example, monomer saturation and starvation, mechanism and

kinetics, monomer reactivity ratios, micromixing effects, etc. Note that both phenomena eventually influence copolymer properties such as MW, MWD, copolymer composition distribution (CCD), backbone defect, morphology, sequence length distribution and average, etc. which finally dictate product and application development as well as business and market. Figure 2.20 shows ethylene–alpha-olefin copolymer backbone structure as a function of alpha-olefin type. It helps visualize better the influence of catalyst and copolymerization phenomena on the resulting elastomer properties.

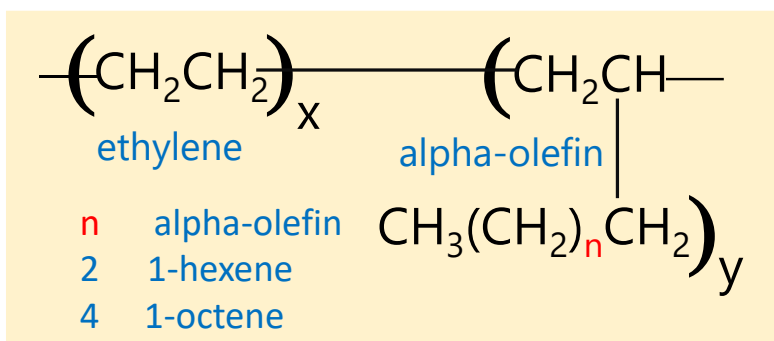


Figure 2.20: Ethylene–alpha-olefin copolymer backbone structure as a function of alpha-olefin type.

The metallocene work summarized in Section 2.1 shows the following. Precatalysts such as $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2$, $\text{Ph}_2\text{C}(\text{Cp})(2,7^t\text{Bu}_2\text{Flu})\text{ZrCl}_2$, supported $\text{Me}_2\text{Si}(2\text{-Me-4-Ph-Ind})_2\text{ZrCl}_2$ (developed by Spaleck et al., 1994) [20], and Dow CGC incorporate 1-hexene much higher than other metallocenes. However, the following constructive criticism holds:

- i. The reported precatalysts have not been evaluated using liquid phase catalyst active center residential environment framework under a unified footing and the same set of polymerization conditions. *Note that characterization of metallocenium active center, generated by methylaluminoxane (MAO) or borate cocatalyst using NMR and the*

- above new model-predicted catalyst active center residential environment framework, recently developed by Atiqullah et al. [2023] can direct to adding new insights to the catalytic synthesis of elastomers.*
- ii. *The synthesis of elastomeric copolymers has not been addressed from the activation as well as macroscopic and microscopic deactivation behavior of the catalyst systems involved.*
 - iii. The resulting copolymeric elastomers have not been coherently and comprehensively characterized in terms of the above catalyst and copolymerization phenomena as well as copolymer properties such as MW, MWD, copolymer composition distribution (CCD), average copolymer composition, and thermal property (T_g and T_m), backbone defect, morphology, sequence length distribution and average, etc. The published characterization profile shows itself to be partial and incomplete.
 - iv. Recent reports on Spaleck and CGC zirconocenes include introducing positional substitutions at the π -ligands. They also study alpha-olefin comonomer affinity, catalyst activity, and MW weight at high temperatures. Similar topical works on Cs symmetric (Cp)(Flu) *ansa*-zirconocenes do not appear in the literature.

2.2.2 New Research Direction

The new research direction, henceforth, recommends making technical advancement in the catalysis, copolymerization, and polymer science of making and characterizing ethylene-linear higher alpha-olefin elastomers, considering Sections 2.1.2.3 and 2.2.1 constructive criticism.

Note that Saudi Arabia's current alpha-olefin production is 150 kmtpa (by UNITED) which will increase to 550 kmtpa by 2025. It is appropriate to remark that diversification and

enhancement of non-oil revenue make a major objective Saudi Sustained Development and Growth (SDG) and Vision 2030. In this context, conversion of local feedstock, such as ethylene and alpha-olefins, into value-added products namely synthetic elastomers, can expand Saudi economy and employment. Hence, this is highly important and worthwhile.

2.3 Research Objectives

2.3.1 Overall Objective

Make modest scientific and technical advancement in the catalysis, copolymerization, and polymer science of making and characterizing ethylene-linear higher alpha olefin elastomers.

2.3.2 Particular Objectives

As per Sections 2.1.2 and 2.2 literature review, various worthwhile scientific subjects can be addressed. But considering the time frame and a typical Chemistry MS thesis requirement, the following objectives were particularly pursued under the *new liquid phase catalyst active center residential environment framework*:

- Correlate the liquid phase catalyst active center residential environment to NMR-elucidated transition metal catalyst active center, generated by methylaluminoxane (MAO) and the trityl borate cocatalyst.
- Evaluate the catalyst active center macroscopic as well as microscopic deactivation behavior.
- Evaluate the effects of precatalyst (Spaleck versus Dow CGC) and cocatalyst (MAO versus trityl borate) on ethylene-alpha olefin elastomeric copolymerization by conducting polymerization trials free of ethylene starvation and micromixing effects.
- Investigate the effects of ethylene pressure, copolymerization temperature, and comonomer steric hindrance on the as-synthesized elastomer unsaturation MW, MWD, copolymer composition distribution (CCD) and average composition, thermal property (T_g and T_m), backbone defect, morphology, microstructure parameters etc. by using relevant characterization techniques.

CHAPTER 3

MODELING OF COPOLYMERIZATION MICROKINETICS AND MICROSTRUCTURE, MONOMER SOLUBILITY, AND CATALYST ACTIVE SITE RESIDENTIAL ENVIRONMENT

Chapter 3 is divided into modeling copolymerization microkinetics and microstructure (Section 3.1), and monomer solubility and catalyst active site residential environment (Section 3.2). Copolymerization microkinetics knowledge develops better catalysts and advanced synthetic elastomers. This subject is also related to the (i) rational catalyst design and (ii) conservation of energy and environment. Such modeling approach correlates catalyst microscopic properties to its macroscopic performance, identifies the rate-limiting steps, and guides the rational catalyst design. On the other hand, monomer solubility connects Section 3.1 theme to Section 3.2 catalyst activation-deactivation and active site residential environment eventually through polymerization liquid phase mixture compressibility factor.

3.1 Modeling of Copolymerization Microkinetics and Copolymer Microstructure

This section is designed as follows. It first revisits the fundamentals of copolymerization microkinetics and copolymer microstructure, which are based on:

- Microkinetic terminal copolymerization model elementary propagation rate expressions (Figure 3.1),
- Relation among 1st order Markov statistical model binary conditional probabilities (P_{11} , P_{21} , P_{22} , and P_{12}), elementary propagation kinetic rate expressions, and reactivity ratios r_1 and r_2 , and
- Correlation between conditional probabilities and experimentally determined ¹³C NMR triad (via 1st order Markov model).

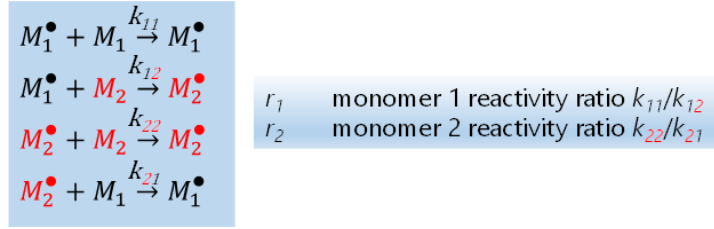


Figure 3.1: Terminal copolymerization model elementary propagation rate expressions.

Next it correlates the derivations resulting from the above considerations to the catalyst active site behavior, and copolymer microstructures and their mechanisms.

The relation among binary conditional probabilities, elementary kinetic expressions, and the reactivity ratios r_1 and r_2 can be written as [64]:

$$P_{11} = \frac{k_{11}M_1^\bullet M_1}{k_{11}M_1^\bullet M_1 + k_{12}M_1^\bullet M_2} = \frac{\left(\frac{k_{11}}{k_{12}}\right)\left(\frac{M_1}{M_2}\right)}{\left(\frac{k_{11}}{k_{12}}\right)\left(\frac{M_1}{M_2}\right) + 1} = \frac{r_1 X}{r_1 X + 1}; P_{22} = \frac{r_2}{r_2 + X} \quad (3.1)$$

where $X = \left(\frac{M_1}{M_2}\right) = \frac{x_{M_1}}{x_{M_2}}$. M_1 and M_2 represent molar concentrations of monomer 1 and monomer 2 (comonomer), respectively. k_{11} , k_{12} , k_{22} , and k_{21} are defined in Scheme 38.

Equation 3.2 expresses the binary conditional probabilities in terms of monad and diad mole fractions as follows [65, 66]:

$$P_{11} = \frac{M_1 M_1}{M_1}; P_{22} = \frac{M_2 M_2}{M_2}; P_{12} = \frac{M_1 M_2}{2M_1}; P_{21} = \frac{M_1 M_2}{2M_2} \quad (3.2)$$

where according to Markov model, $P_{12} = 1 - P_{22}$ and $P_{21} = 1 - P_{11}$ [64].

Equation 3.3 relates monad to diad mole fractions as expressed below [65]:

$$M_{11} = M_1 M_1 + \frac{M_1 M_2}{2}; M_{22} = M_2 M_2 + \frac{M_1 M_2}{2} \quad (3.3)$$

Using Equations 3.1 to 3.3, r_1 and r_2 can be finally written in terms of diad mole fractions, conditional probabilities, and triad mole fractions as [64, 67, 68, 69]:

$$r_1(X) = \left(\frac{2M_1M_1}{M_1M_2} \right) \frac{1}{X} = \left(\frac{P_{11}}{P_{21}} \right) \frac{1}{X} = \left(\frac{2M_1M_1M_1 + M_1M_1M_2}{2M_1M_2M_1 + M_1M_2M_2} \right) \frac{1}{X}; Xr_1(X) \neq f(X) \quad (3.4)$$

$$r_2(X) = \left(\frac{2M_2M_2}{M_1M_2} \right) X = \left(\frac{P_{22}}{P_{21}} \right) X = \left(\frac{2M_2M_2M_2 + M_2M_2M_1}{2M_1M_2M_1 + M_2M_2M_1} \right) X; \frac{r_2(X)}{X} \neq f(X) \quad (3.5)$$

where $M_1M_2M_2 = M_2M_2M_1$, $M_1M_1 = M_1M_1M_1 + \frac{1}{2}M_1M_1M_2$, and $M_1M_2 = M_1M_2M_2 + 2M_1M_2M_1$. Note that these necessary relations do not depend on polymerization mechanism or statistics [65]. Equations 3.4 and 3.5 show how $r_1(X)$ and $r_2(X)$ can be calculated using the experimentally determined ^{13}C NMR triad mole fractions and thermodynamic model-predicted X . Note that X can be calculated via modeling the solubility of gaseous monomer M_1 in the liquid mixture of M_2 and solvent [6]. Section 3.2 elaborates this modeling part.

Equation 3.6 calculates the average mole fractions of M_1 and M_2 , using the ^{13}C NMR triad mole fractions, as follows:

$$M_1 = M_1M_1M_1 + M_1M_1M_2 + M_2M_1M_2; M_2 = M_2M_2M_2 + M_1M_2M_2 + M_1M_2M_1 \quad (3.6)$$

The Markov model equals the Bernoulli's one when $\left(\frac{P_{21}}{P_{12}+P_{21}} \right) = \left(\frac{P_{11}}{P_{11}+P_{22}} \right)$ [65]. Under this condition, the triad mole fractions can be calculated using the Table 3.1 relations and compared with the corresponding ^{13}C NMR values.

Table 3.1: Triad-calculating Markov and Bernoulli model relations.

Markov model	Bernoulli model
$M_1M_1M_1 = P_{11}^2 \times \left(\frac{P_{21}}{P_{12} + P_{21}} \right)$ (T8M. a)	$M_1M_1M_1 = P_{11}^2 \times \left(\frac{P_{11}}{P_{11} + P_{22}} \right)$ (T8B. a)
$M_1M_1M_2 = 2P_{11}P_{12} \times \left(\frac{P_{21}}{P_{12} + P_{21}} \right)$ (T8M. b)	$M_1M_1M_2 = 2P_{11}P_{12} \times \left(\frac{P_{11}}{P_{11} + P_{22}} \right)$ (T8B. b)
$M_2M_1M_2 = P_{12}^2 \times \left(\frac{P_{21}}{P_{12} + P_{21}} \right)$ (T8M. c)	$M_2M_1M_2 = P_{12}^2 \times \left(\frac{P_{11}}{P_{11} + P_{22}} \right)$ (T8B. c)
$M_1M_2M_1 = 2P_{12}P_{21} \times \left(\frac{P_{21}}{P_{12} + P_{21}} \right)$ (T8M. d)	$M_1M_2M_1 = 2P_{12}P_{21} \times \left(\frac{P_{11}}{P_{11} + P_{22}} \right)$ (T8B. d)
$M_2M_2M_1 = 2P_{12}P_{22} \times \left(\frac{P_{21}}{P_{12} + P_{21}} \right)$ (T8M. e)	$M_2M_2M_1 = 2P_{12}P_{22} \times \left(\frac{P_{11}}{P_{11} + P_{22}} \right)$ (T8B. e)
$M_2M_2M_2 = P_{22}^2 \times \left(\frac{P_{21}}{P_{12} + P_{21}} \right)$ (T8M. f)	$M_2M_2M_2 = P_{22}^2 \times \left(\frac{P_{11}}{P_{11} + P_{22}} \right)$ (T8B. f)

The reactivity ratios $r_1(X)$ and $r_2(X)$, ^{13}C NMR triad mole fractions, and X calculate important copolymer microstructural parameters that help (i) develop improved catalysts and polymerization processes, and (ii) better elucidate copolymerization mechanisms and reaction kinetics, and copolymer morphology as well as properties. Table 3.2 summarizes these parameter expressions with physical significances.

Section 3.1 lists the following concluding remarks:

- Equations 3.4 and 3.5 become X -free when $X = 1$. This refers to the situation when the molar concentration or mole fraction of the gaseous monomer M_1 in the liquid mixture of monomer M_2 and solvent equals that of M_2 .
- Equations 3.4 and 3.5 also become X -independent when only conditional probabilities and 1st order Markov statistical model are considered in the derivation, and microkinetic terminal copolymerization model (MTCM) propagation rate expressions are excluded [66, 70]. This propagation rate-exclusive statistical approach is incorrect. The

catalyst behavior and performance and the comonomer effects on the copolymer microstructure, because of excluding the above microkinetics, cannot be evaluated.

- MTCM does not hold in the presence of viscosity build-up (that is, gel, micromixing, and diffusional effects).
- Triad mole fractions, calculated using Markov and Bernoulli models (Table 3.1), set limits of accuracy for the ^{13}C NMR triad mole fractions.
- Only the reactivity ratios r_1 and r_2 are functions of X . But all the microstructural parameters listed in Table 3.2 are X -free because $Xr_1(X)$ and $\frac{r_2(X)}{X}$ do not depend on X .
- Table 3.2 shows how the catalyst active site, Markov and Bernoulli models, and copolymer microstructures and their mechanisms are related.

Table 3.2: Copolymer microstructural parameters and their significances.

Parameters	Parameter expressions	Significances
▪ Run number	$RN = \frac{2}{2 + r_1(X)X + r_2(X)/X} \quad (\text{T9.1a})$ $rn = 100 \times \left(M_1M_2M_1 + \frac{1}{2}M_1M_2M_2 \right)$ $= 100 \times \left(M_2M_1M_2 + \frac{1}{2}M_1M_1M_2 \right) \quad (\text{T9.1b})$	Fraction of M_1 and M_2 sequences that occur in a copolymer chain, calculated neglecting end effects.^A Represents the average number of times the monomer switches from M_1 to M_2 (or M_2 to M_1, but not both) per 100 monomer units.^B
▪ Average M_1 and M_2 sequence lengths	$L_{1\text{NAV}} = \frac{M_2M_1M_2 + M_2M_1M_1 + M_1M_1M_1}{M_2M_1M_2 + \frac{1}{2}M_1M_1M_2} = 1 + r_1(X)X \quad (\text{T9.2a})$ $L_{2\text{NAV}} = \frac{M_1M_2M_1 + M_1M_2M_2 + M_2M_2M_2}{M_1M_2M_1 + \frac{1}{2}M_2M_2M_1} = 1 + r_2(X)/X \quad (\text{T9.2b})$	Average length of consecutive addition of M_1 or M_2 in a copolymer chain.^A Average number of monomers in an M_1-only or M_2-only monomer sequence.^B
▪ Persistence ratio	$\rho = 2 \times \frac{(M_1M_1M_1 + M_1M_1M_2 + M_2M_1M_2)}{M_1M_1M_2 + 2M_2M_1M_2} \times (M_1M_2M_1 + M_1M_2M_2 + M_2M_2M_2) \quad (\text{T9.3})$	1 Bernoullian statistics > 1 non-Bernoullian statistics^B
▪ Reactivity ratio product	$r_1r_2 = \left(\frac{2M_1M_1M_1 + M_1M_1M_2}{2M_1M_2M_1 + M_1M_2M_2} \right) \times \left(\frac{2M_2M_2M_2 + M_1M_2M_1}{2M_1M_2M_1 + M_2M_2M_1} \right) \quad (\text{T9.4})$	≈ 1 random < 1 alternating > 1 blocky^C. Practically, $r_1r_2 = 5.0$ is considered blockier [71].

Parameters	Parameter expressions	Significances
▪ Departure from randomness	$\chi = \frac{2 + r_1(X)X + r_2(X)/X}{1 + r_1(X)X + r_2(X)/X + r_1(X)r_2(X)} \quad (\text{T9.5})$	1 completely random > 1 alternating tendency 2 completely alternating < 1 blocky tendency 0 block copolymer ^A
▪ Average of reactivity ratio product	$\begin{aligned} < r_1 r_2 > \\ &= 4 \times \frac{\left(M_1 M_1 M_1 + \frac{1}{2} M_1 M_1 M_2\right) \left(M_2 M_2 M_2 + \frac{1}{2} M_1 M_2 M_2\right)}{(M_1 M_1 M_2 + 2 M_2 M_1 M_2)(M_1 M_2 M_2 + 2 M_1 M_2 M_1)} \end{aligned} \quad (\text{T9.6})$	1 Bernoullian or 1 st -order Markov statistics and single-site catalysis ≠ 1 non-Bernoullian statistics and multiple-site catalysis ^B
▪ Cluster index	$\begin{aligned} CI &= 10 \times \frac{(M_1 M_2 M_1 + M_1 M_2 M_2 + M_2 M_2 M_2) - M_1 M_2 M_1}{(M_1 M_2 M_1 + M_1 M_2 M_2 + M_2 M_2 M_2)^2} \\ &\times \frac{1}{(2 - [(M_1 M_2 M_1 + M_1 M_2 M_2 + M_2 M_2 M_2)])} \end{aligned} \quad (\text{T9.7})$	0 All M_2 units are separated by at least one M_1 unit $\Rightarrow$ no clustering of M_2 10 Bernoullian statistics > 10 non-Bernoullian statistics ^B
▪ Monomer dispersity	$\begin{aligned} MD &= 100 \times \frac{M_1 M_2 M_1 + \frac{1}{2} M_1 M_2 M_2}{M_2 M_2 M_2 + M_1 M_2 M_2 + M_1 M_2 M_1} \\ &= 100 \times \frac{M_2 M_1 M_2 + \frac{1}{2} M_2 M_1 M_1}{M_2 M_2 M_2 + M_1 M_2 M_2 + M_1 M_2 M_1} \end{aligned} \quad (\text{T9.8})$	100 All M_2 units are isolated as $M_1 M_2 M_1$ sequences $\Rightarrow$ no clustering of M_2 < 100 M_2 tends to sequence repeatedly or cluster ^D
▪ Sequence distributions	$w_1(n) = n \left(\frac{r_1(X)X}{1 + r_1(X)X} \right)^{n-1} \left(1 - \frac{r_1(X)X}{1 + r_1(X)X} \right)^2 \quad (\text{T9.9})$	Variation of weight fraction of same sequence length in a copolymer chain as a function of the corresponding sequence length n . ^A
▪ Sequence distributions	$w_2(n) = n \left(\frac{r_2(X)/X}{1 + r_2(X)/X} \right)^{n-1} \left(1 - \frac{r_2(X)/X}{1 + r_2(X)/X} \right)^2 \quad (\text{T9.10})$	
▪ Number and weight-average monomer and comonomer sequences	$n_{1 \text{ NAV}} = \frac{1}{\sum \left[\frac{w_1(n)}{n} \right]}; n_{2 \text{ NAV}} = \frac{1}{\sum \left[\frac{w_2(n)}{n} \right]} \quad (\text{T9.11})$ $n_{1 \text{ WAV}} = \sum [w_1(n)] \times n; n_{2 \text{ WAV}} = \sum [w_2(n)] \times n \quad (\text{T9.12})$	Number- and weight- averages of $w_1(n)$ and $w_2(n)$. ^E

^A[64]; ^B[65]; ^C[21]; ^D[70]; and ^E[72].

3.2 Modeling of Monomer Solubility and Catalyst Active Site Residential Environment

A solution copolymerization process makes elastomers using particularly alpha olefin-rich comonomer feeds, and metallocene and postmetallocene precatalysts in the presence of organoaluminum cocatalysts. Copolymerization trials are conducted at laboratory to industrial temperatures and pressures, and they need the solubility of the gaseous monomer M_i in the solvent-alpha olefin mixture for several technical reasons. Atiqullah et al. [2023], therefore, modeled

ethylene solubility in toluene–1-hexene and n-hexane–1-hexene mixtures under the above conditions [6]. Based on this work, this section is composed as follows:

- Derive constitutive model equations concerning the gas solubility in a single solvent using fugacity coefficient vapor-liquid equilibrium criterion, Peng-Robinson EoS and *vdW1f* mixing rule, and predict gas-single liquid solubility, and compare the results with available literature data.
- Develop temperature-dependent Arrhenius Henry's constant relations for (i) gas-single solvent system and (ii) the Shulgin's activity coefficient–Henry's constant formalism for binary liquid systems.
- Calculate gaseous monomer solubility in solvent-alpha olefin binary mixture using the above binary liquid system Henry's constant.
- Derive expressions for X [the ratio of molar concentrations of monomer 1 and monomer 2 (comonomer)] and the binary liquid phase compressibility factor (applying the model-predicted solubility).
- Correlate the above binary liquid phase compressibility factor to catalyst active site residential environment.

The constitutive model equations concerning the gas solubility in a single solvent, as per Atiqullah et al. [2023], can be written as follows:

$$(Z^V)^3 + r^V(Z^V)^2 + s^V Z^V + t^V = 0 \quad (3.7)$$

$$(Z^L)^3 + r^L(Z^L)^2 + s^L Z^L + t^L = 0 \quad (3.8)$$

where $r^V = -1 + B^V$; $s^V = A^V - 2B^V - 3(B^V)^2$; $t^V = -A^V B^V + (B^V)^2 + (B^V)^3$. Similar definitions hold for r^L , s^L , and t^L . Above equations represent dimensionless Peng-Robinson EoS in terms of Z^V (vapor phase) and Z^L (liquid phase) compressibility factors, respectively.

$$\begin{aligned}
& \frac{b_1}{b_{mix}^V} (Z^V - 1) - \ln(Z^V - B^V) \\
& - \frac{A^V}{2\sqrt{2}B^V} \left(\frac{2}{a_{mix}^V} [a_{12} + (a_1 - a_{12})y_1] - \frac{b_1}{b_{mix}^V} \right) \ln \left(\frac{Z^V + (1 + \sqrt{2})B^V}{Z^V + (1 - \sqrt{2})B^V} \right) \\
& + \ln y_1 - \frac{b_1}{b_{mix}^L} (Z^L - 1) + \ln(Z^L - B^L) + \frac{A^L}{2\sqrt{2}B^L} \left(\frac{2}{a_{mix}^L} [a_{12} + (a_1 - a_{12})x_1] - \frac{b_1}{b_{mix}^L} \right) \\
& \ln \left(\frac{Z^L + (1 + \sqrt{2})B^L}{Z^L + (1 - \sqrt{2})B^L} \right) - \ln x_1 = 0
\end{aligned} \tag{3.9}$$

$$\begin{aligned}
& \frac{b_2}{b_{mix}^V} (Z^V - 1) - \ln(Z^V - B^V) \\
& - \frac{A^V}{2\sqrt{2}B^V} \left(\frac{2}{a_{mix}^V} [a_2 + (a_{12} - a_2)y_1] - \frac{b_2}{b_{mix}^V} \right) \ln \left(\frac{Z^V + (1 + \sqrt{2})B^V}{Z^V + (1 - \sqrt{2})B^V} \right) + \ln(1 - y_1) \\
& - \frac{b_2}{b_{mix}^L} (Z^L - 1) + \ln(Z^L - B^L) + \frac{A^L}{2\sqrt{2}B^L} \left(\frac{2}{a_{mix}^L} [a_2 + (a_{12} - a_2)x_1] - \frac{b_2}{b_{mix}^L} \right) \\
& \ln \left(\frac{Z^L + (1 + \sqrt{2})B^L}{Z^L + (1 - \sqrt{2})B^L} \right) \ln(1 - x_1) = 0
\end{aligned} \tag{3.10}$$

In Equations 3.9 and 3.10, Z^V and Z^L are implicit functions of y and x , respectively. They should be, therefore, solved numerically. Note that $(Z^V - B^V)$ and $(Z^L - B^L)$ must be positive. All the terms in Equations 3.7 to 3.10 are elaborately defined in Atiqullah et al. [2024] [6].

For a regular binary liquid mixture, the resultant Henry's constant H_{gL1-L2} relates to the corresponding gas-single liquid Henry's constant H_{gL} via Shulgin-Ruckenstein formalism as follows [73]:

$$\ln H_{gL1-L2} = A - B \left[\frac{\ln V}{(V_2 - V_1)} + \frac{(\hat{x}_2 - \hat{x}_1 - 2)V_2 E \hat{x}_2}{(V_2 - V_1)^2} + \frac{2V_1 V_2 E \ln V}{(V_2 - V_1)^3} \right] - 2E \quad (3.11)$$

$$A = \frac{\ln V_1 \ln H_{gL2} - \ln V_2 \ln H_{gL1}}{\ln V_1 - \ln V_2} \quad (3.12)$$

$$B = \frac{(\ln H_{gL2} - \ln H_{gL1})(V_2 - V_1)^3}{(\ln V_1 - \ln V_2)[(V_2 - V_1)^2 + 2V_1 V_2 E]} \quad (3.13)$$

$$V = \hat{x}_1 V_1 + \hat{x}_2 V_2 + V^E; 1 = \text{solvent and } 2 = \text{comonomer} \quad (3.14)$$

$$\ln \gamma_1 = Ex_2; \ln \gamma_2 = Ex_1 \text{ (Margules equation)} \quad (3.15)$$

In Equation 3.15, γ_1 and γ_2 can be determined using experimental VLE data, or the following expression [74]:

$$\gamma_i = \left(\frac{y_i}{x_i} \right) \left(\frac{P}{P_s} \right) \quad (3.16)$$

where y_i (vapor) and x_i (liquid) are equilibrium compositions. They can be obtained using an appropriate EoS formalism such Equations 3.9 and 3.10. P_s and P are saturation and system pressures, respectively. For an ideal solution, γ_1 and $\gamma_2 = 1$, $E(T) = 0$, and $V^E = 0$. Therefore, Equations 3.11 and 3.14 respectively reduce to the following:

$$\ln H_{gL1-L2} = \frac{\ln H_{gL1}(\ln V - \ln V_2) + \ln H_{gL2}(\ln V_1 - \ln V)}{\ln V_1 - \ln V_2}; V = \hat{x}_1 V_1 + \hat{x}_2 V_2 \quad (3.17)$$

The application of Equation 3.15 involves two steps. First, determine H_{gL1} and H_{gL2} , at a given temperature by plotting experimental pressure as a function of gaseous monomer mole fraction in the subject solvent, or model it by using the EoS approach reported earlier. Use the linear part of

the plot to obtain H_{gL1} and H_{gL2} . Second, evaluate the temperature-dependent Henry's constant $H_{gL}(T)$ using Equation 3.18.

$$H_{gL}(T) = H_0 \exp\left(\frac{\Delta H_L}{RT}\right); HC = \lim_{x \rightarrow 0} \frac{P}{x} \quad (3.18)$$

The mole fraction solubility of the gaseous monomer x_{M_1} in L1–L2 binary liquid mixture (solvent plus comonomer) can be now calculated from the following expression:

$$x_{M_1} = \frac{P}{H_{gL1-L2}(P, T)} \quad (3.19)$$

Finally, the solubility of the gaseous monomer S_{M_1} in L1–L2 binary liquid mixture can be estimated as follows:

$$S_{M_1} = \frac{x_{M_1}}{(1 - x_{M_1})} \times \frac{MW_{M_1}}{(1 - \hat{x}_2)MW_1 + \hat{x}_2 MW_2} \quad (3.20)$$

Equation 3.20 applies to a single liquid for $\hat{x}_2 = 0$. With reference to the experimental copolymerization conditions, we can write the following:

$$Mol_{01} = \frac{v_{01}}{V_{01}}; Mol_{02} = \frac{v_{02}}{V_{02}}; \hat{x}_{02} = \frac{M_{02}}{M_{01} + M_{02}} \quad (3.21)$$

where Subscript 0 refers to room temperature values, and v_{01} and v_{02} indicate volumes of solvent and comonomer used in a copolymerization trial, respectively. V_{01} and V_{02} refer to the corresponding molar volumes. Use Tait equation to calculate the molar volumes [6].

Using Equation 3.19, we can derive the following:

$$x_{M_1} = \frac{Mol_{M_1}}{Mol_{M_1} + Mol_1 + Mol_2} \Rightarrow Mol_{M_1} = (Mol_1 + Mol_2) \left(\frac{x_{M_1}}{1 - x_{M_1}} \right) \quad (3.22)$$

Equations 3.21 and 3.22 can be combined to write X as follows:

$$\begin{aligned} X &= \frac{Mol_{M_1}}{Mol_2} = \left(1 + \frac{Mol_1}{Mol_2} \right) \left(\frac{x_{M_1}}{1 - x_{M_1}} \right) = \left(1 + \frac{1 - \hat{x}_2}{\hat{x}_2} \right) \left(\frac{x_{M_1}}{1 - x_{M_1}} \right) \\ &= \left(\frac{1}{\hat{x}_2} \right) \left(\frac{x_{M_1}}{1 - x_{M_1}} \right) \approx \left(\frac{1}{\hat{x}_{02}} \right) \left(\frac{x_{M_1}}{1 - x_{M_1}} \right) \end{aligned} \quad (3.23)$$

Equation 3.23 correlates the model-predicted gaseous monomer solubility mole fraction x_{M_1} to X [the ratio of molar concentrations of monomer 1 and monomer 2 (comonomer)]. It, therefore, calculates r_1 and r_2 using Equations 3.4 and 3.5, respectively.

The binary liquid phase, comprising solvent (1) and comonomer (2), compressibility factor Z_{1-2}^L is given by:

$$Z_{1-2}^L = (1 - \hat{x}_{02})Z_{M_1-1}^L + \hat{x}_{02}Z_{M_1-2}^L \quad (3.24)$$

where $Z_{M_1-1}^L$ and $Z_{M_1-2}^L$ represent the individual equilibrium compressibility factors of the gaseous monomer M_1 in the solvent and comonomer, respectively. $Z_{M_1-1}^L$ and $Z_{M_1-2}^L$ can be obtained from Equation 3.10. Equation 3.24, in fact, shows how the ternary system— M_1 , solvent, and comonomer—compressibility factor Z_{1-2}^L can be obtained from $Z_{M_1-1}^L$ and $Z_{M_1-2}^L$.

Z_{1-2}^L , $Z_{M_1-1}^L$ and $Z_{M_1-2}^L$ (the liquid phase compressibility factors) are fundamentally dimensionless thermodynamic parameters. They characterize a completely incompressible liquid to more compressible fluids for 0 and 1, respectively. They quantify the intra- and intermolecular compactness of the liquid phase dispersed molecules, consisting of gaseous monomer M_1 , solvent (1), and comonomer (2). The compactness decreases as the compressibility factor increases. Hence, *it conceptually represents the catalyst active center residential environment* [6]. The correlation between model-predicted S_{M_1} and Z_{1-2}^L creates a new and better approach to investigate catalyst as well as copolymerization phenomena, which particularly include catalyst activation and deactivation, and the reactivity ratios r_1 and r_2 . Note that both phenomena influence copolymer properties such as chain length, backbone defect, morphology, thermal properties, and microstructures (Table 3.2). For a given catalyst or a group of varying catalysts, they can be now studied using a common concept and footing.

CHAPTER 4

EXPERIMENTAL PROCEDURE

Chapter 4 is designed as follows:

- Materials,
- Washing and drying of glasswares,
- Activation of adsorbents and purification of solvents, monomers, and gases,
- Precatalyst-cocatalyst mixing routes,
- Synthesis of ethylene-alpha-olefin copolymer elastomers, and
- Evaluation of precatalyst-cocatalyst interaction and characterization of ethylene-alpha-olefin elastomer.

4.1 Materials

The project-related materials—monomer, comonomers, chemicals (), solvents, gases, and scavengers and scavenging columns—are listed in Table 4.1. Appendix D reports the structures of the proposed precatalysts, cocatalysts, and reactor impurities scavenger.

4.2 Washing and Drying of Glasswares

The experimental glasswares were washed first applying aqua regia (a mixture of nitric acid and hydrochloric acid, optimally in a molar ratio of 1:3) followed by Decon 90 and tap and deionized water. Finally, they were dried at 150 °C using a high temperature vacuum oven.

4.3 Activation of Adsorbents and Purification of Solvents, Monomers, and Gases

All the related operations were carried out using standard Schlenk techniques and glovebox under an inert Argon environment. Solvent (Toluene) and alpha-olefins (1-hexene and 1-octene)

were passed through columns of Al₂O₃ (Aldrich), a Cu-oxygen scavenger supported on BASF R3-11G catalyst, and molecular sieves (Aldrich, 4Å).

Table 4.1: Research-related materials.

Items	Description
Alpha-olefin comonomers	1-hexene (bp 63 °C), and 1-octene (bp 121 °C) (Donated by UNITED)
Chemicals (precatalysts, cocatalysts, and reactor impurities scavenger)	▪ Dow CGC precatalyst: Dimethylsilylene(‘butylamido) (tetramethylcyclopentadienyl) titanium (IV) dichloride Me₂Si(Me₄Cp)N^tBuTiCl₂) ▪ Spaleck precatalyst: Dimethyl silyl bis(2-methyl-4-phenyl-indenyl) zirconium dichloride Me₂Si(2-Me-4-Ph-Ind)₂ZrCl₂ ▪ Cocatalysts: Methylaluminoxane MAO, trityltetrakis(pentafluorophenyl)borate (ion-paired trityl salt having triphenylcarbenium cation) TTB, and triisobutyl aluminum TIBA (also used as reactor impurities scavenger)
Solvents	Toluene, and 1,2,4-trichlorobenzene (TCB), Deuterated Dimethylsulfoxide (DMSO-d), Toluene-d
Gases	High grade (99.9995%) ethylene (monomer) and argon
Scavengers and scavenging columns	▪ BASF catalyst oxygen scavenger (R3-11G) and 4Å molecular sieve (M524-500) impurities scavenger ▪ Aluminum oxide (Al₂O₃) Oxygen and moisture scavenging columns
GPC solvent stabilizer	▪ Antioxidant 2,6-Di-tert-butyl-4-methylphenol (BHT)

4.3.1 Activation/regeneration of BASF R3-11G Adsorbent Catalyst and Oxygen Removal Mechanism

Activated BASF R3-11G adsorbent catalyst removed oxygen from the experimental solvent and the comonomers used. The oxygen, unless removed as required, will poison the copolymerization catalyst system.

The above BASF catalyst activation and regeneration procedure is listed below:

- Pack the fritted column with BASF catalyst and place inside the heating jacket.

- ii. Preheat the bed with 3,000 Nm³/h of argon and gradually increase the inlet temperature by heating for three hours up to 230 °C. Maintain this argon flow rate throughout the reduction step.
- iii. Close the argon cylinder and begin dosing H₂ 10 %/Aargon mixture. This generates a moderate exotherm. Hold the inlet temperature up to 230°C during the reduction period.
- iv. After completion of the reduction, disconnect the H₂ 10%/argon supply. The production of water at the outlet stream approaches zero when the reduction process completes.
- v. Cool slowly using at least 3,000 Nm³ /h of argon flow until the bed temperature drops below 50 °C. Avoid catalyst deactivation due to contact with air.
- vi. Transfer the activated BASF catalyst to a one-neck Schlenk flask under argon flow. Continue argon flow for some time and finally close the flask with a rubber septum.
- vii. Save the activated catalyst under argon until it is used for the purification step (see Section 4.3.4).

Figure 4.1 illustrates the BASF adsorbent catalyst activation and regeneration mechanism while Figure 4.2 shows how it removes the oxygen [75].

4.3.2 Activation of Molecular Sieve (4Å)

Molecular sieve (MoS) 4Å adsorbs water, methanol, ethanol, sulfur compounds, carbon dioxide, peroxides, etc. [76, 77]. It was, therefore, used to remove moisture from the experimental solvent and the comonomers used. MoS 4Å is basically a synthetic Na-form type A zeolite. See Figure 4.3. This is a 3D uniform size and shape crystalline microporous aluminosilicate, composed of AlO₄ (acidic Al³⁺) and SiO₄ (basic O²⁻) tetrahedral network linked via oxygen bridges. Figure 4.4 shows the mechanism of removing protic polar contaminants by activated MoS 4Å. It was

activated by heating twice overnight at 250 °C, first using a regular oven and next employing a high vacuum oven.

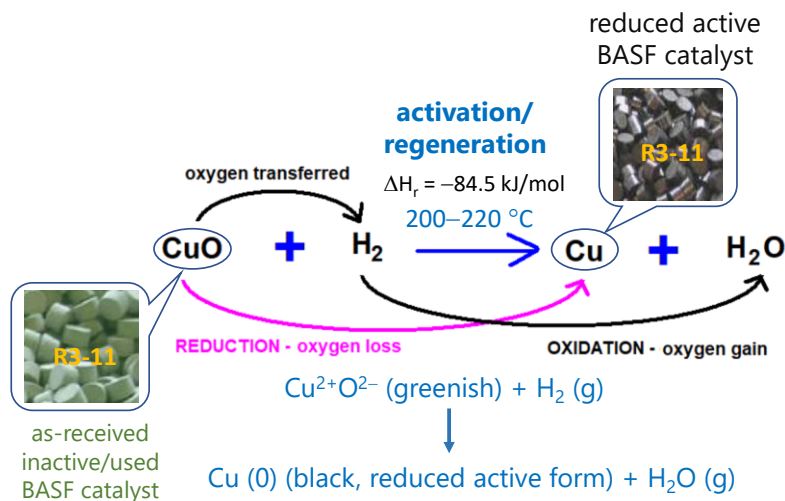


Figure 4.1: BASF adsorbent catalyst activation and regeneration mechanism.



Figure 4.2: O_2 removal mechanism by BASF adsorbent catalyst.

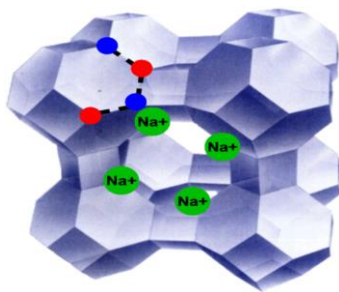


Figure 4.3: Shape and structure of MoS 4 Å.

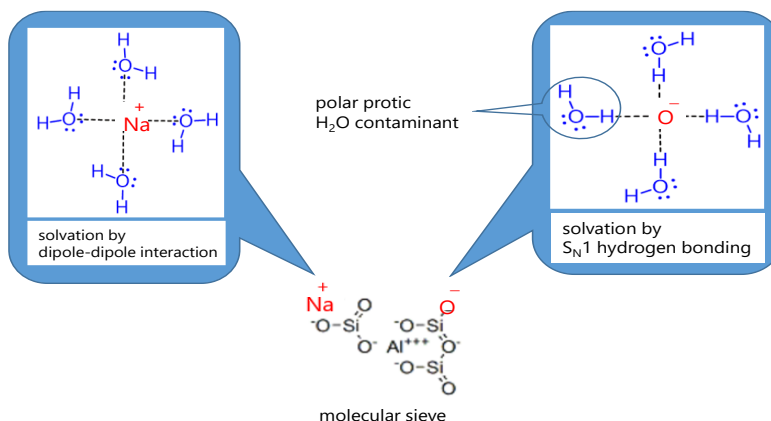


Figure 4.4: Mechanism of removing protic polar contaminants by activated MoS.

4.3.3 Activation of Basic Alumina

Activated basic alumina (Al_2O_3) removes polar protic contaminants, namely water, peroxides, methanol, 2-methoxy ethanol, and inhibitors such as BHT. It has high polarity $-\text{OH}$ group which forms hydrogen bonds. Figure 4.5 explains the mechanism of removing protic polar contaminants by activated basic alumina. The thermal activation procedure outlined in Section 4.3.2 also holds here.

4.3.4 Purification of Solvents, Monomers, and Gases

Argon and ethylene were purified by passing successively through two columns—a moisture-absorbing 4Å molecular sieve column (Column I) and an oxygen-scavenging column (Column II). Details follow.

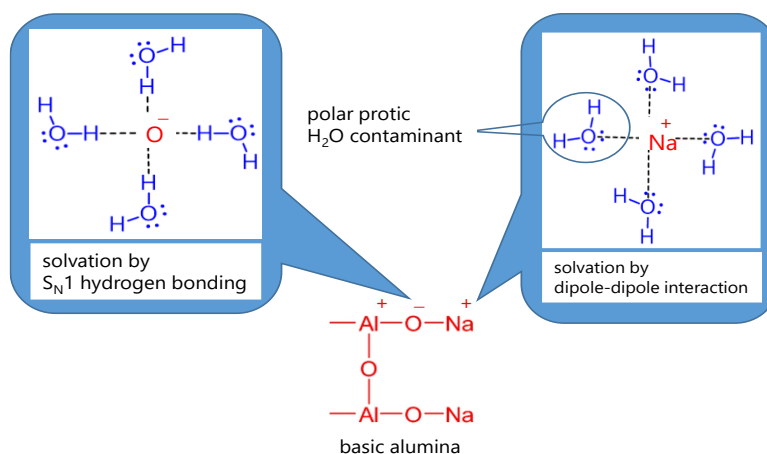


Figure 4.5: Mechanism of removing protic polar contaminants by activated basic alumina.

The as-received solvent and alpha-olefin comonomers were processed as follows [36, 78, 79, 80]:

- Take the solvent in an appropriate size Schlenk flask (Flask I) and de-moisturize it overnight using activated molecular sieve (4Å) with intermittent hand shaking. Next, determine the moisture content using a Karl Fischer (KF) coulometer.
- Pass the above solvent through a column filled with activated basic alumina (Column Al I) under argon pressure to further decrease the moisture content and contact the eluent over activated BASF catalyst (under shaking) in another Schlenk flask (Flask II) for 1 h to remove the dissolved oxygen (Figure 4.6).

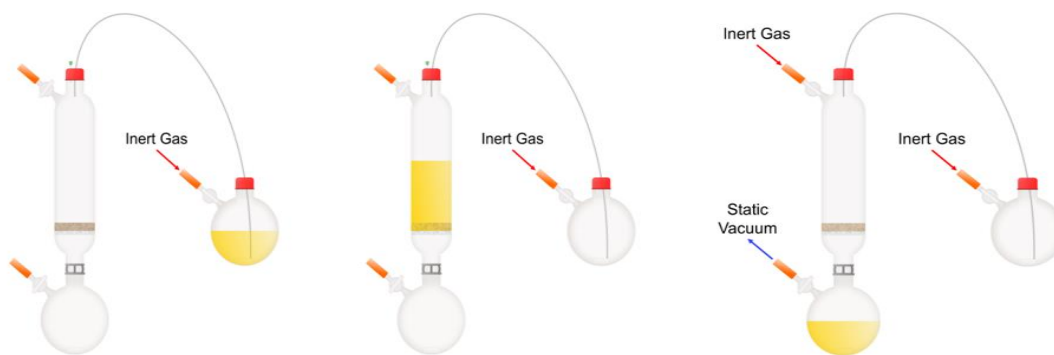


Figure 4.6: Successive removal of moisture and oxygen using activated basic alumina and BASF catalyst using Schlenk flask purification setup [81].

- iii. Pass, after 24 h, the deoxygenated solvent through another activated basic alumina column (Column Al II).
- iv. Collect the above solvent in another Schlenk flask (Flask III) over activated molecular sieve (4Å) and measure the moisture content using KF titration.
- v. Repeat the above operations until the moisture level becomes less than 5 ppm. Appendix E tabulates the measured solvent moisture levels.
- vi. Deoxygenate finally the dried solvent by purging purified argon through it for at least 30 min.

The preceding procedure equally applies to purifying the comonomers.

The above task is the heart of a successful elastomer synthesis polymerization trial. It prevents catalyst deactivation.

4.4 Precatalyst-cocatalyst Mixing Routes

Two methods prepared the preactivated precatalyst-cocatalyst mixtures. Method I mixes the precatalyst with the cocatalyst MAO while Method II contacts the precatalyst with primary and secondary cocatalysts TTB and TIBA, respectively. Both methods are elaborated below.

4.4.1 Precatalyst-MAO Cocatalyst Route

About 6.25 μmol of Spaleck or DOW CGC precatalyst was dissolved in a de-moisturized and deoxygenated toluene in a 20 ml vial. Next, 1250 μmol of 10 wt% or 30 wt% MAO in toluene was added to the above precatalyst solution. The precatalyst:cocatalyst (M:Al) molar ratio used was 1: 200. Note that the product data sheet net Al elemental analysis value and toluene density calculated this molar ratio. The final preactivated mixture was heated at 40 $^{\circ}\text{C}$ for 30 min. The color of the resulting solution changed from yellow to reddish-brown for Spaleck precatalyst. The color change was from yellow to yellowish for DOW CGC. See Figure 4.7.

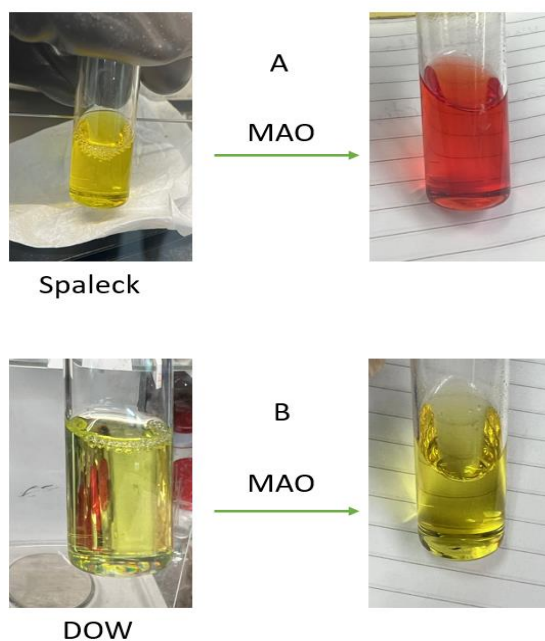


Figure 4.7: (A) Spaleck/MAO route. (B) DOW/MAO route.

4.4.2 Precatalyst-TTB-TIBA Cocatalyst Route

About 6.25 μmol of Spaleck or DOW CGC precatalyst and 12.5 μmol of TTB primary cocatalyst were dissolved in a de-moisturized and deoxygenated toluene in a 20 ml vial. The precatalyst:TTB molar ratio was 1:2. The solution was preheated at 40 $^{\circ}\text{C}$ for 30 min using a hot plate. Subsequently, 1250 μmol of TIBA secondary cocatalyst was introduced into the earlier

mixture. The precatalyst:secondary cocatalyst (M:TIBA) molar ratio used was 1: 200. The Spaleck precatalyst mixture transitioned from orange to dark green. But the DOW CGC mixture color changed from orange to light brown. The final preactivated mixture was heated at 40 °C for 30 min. This changed color from dark green to greenish brown for Spaleck and from light brown to greenish brown for DOW CGC. See Figure 4.8.

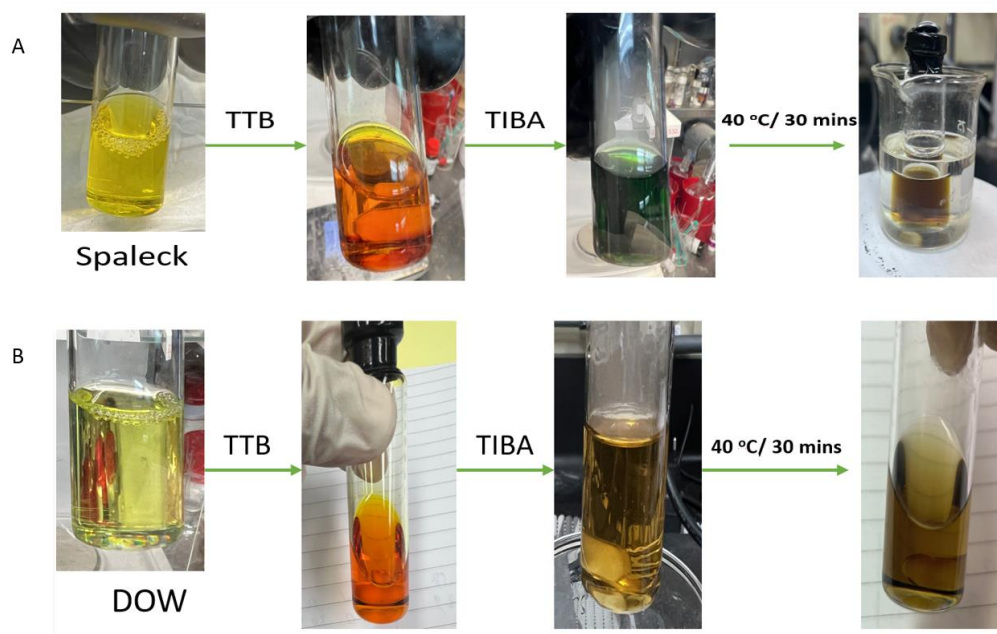


Figure 4.8: (A) Spaleck/TTB/TIBA route. (B) DOW/TTB/TIBA route.

4.5 Synthesis of Ethylene-Alpha-Olefin Copolymer Elastomers

A computer-operated HighTech polymerization system, having a 250 mL Buchi glass reactor, synthesized the target elastomers by copolymerizing ethylene with the experimental alpha-olefins in a toluene solvent environment. See Figure 4.9. The polymerization procedure is listed below:

- i. Fill two-third reactor vessel with de-moisturized and deoxygenated toluene and rinse the reactor inside at 40–60 °C for 60 min at 250 rpm. Then decant the toluene and reflux the vessel and dry it under argon flow.



Figure 4.9: Computer-operated HighTech polymerization reactor system.

- ii. Bake the glass reactor at 2 bar(g) argon pressure and 110 °C for 45 min, evacuate the argon using a high vacuum pump, and cool the reactor to 60 °C. Repeat this operation thrice.
- iii. Feed the reactor with the purified experimental solvent, alpha-olefin comonomer, and TIBA impurity scavenger (under adequate stirring) using the argon-operated closed loop liquid addition system.
- iv. Heat the reactor up to the set polymerization temperature.
- v. Saturate the reactor content with ethylene up to the set polymerization pressure of 4 bar(g) at 600 rpm impeller speed.
- vi. Introduce the preactivated precatalyst-cocatalyst mixture using the closed loop liquid addition system. See Section 4.4.

- vii. Open the ethylene valve to attain the set polymerization pressure. Continue polymerization till the reaction mixture remains free of ethylene starvation and micromixing effect [82, 83]. For the present copolymerization conditions, Average **20** min reaction time showed to be adequate. *Reaction time exceeding this value, because of viscosity build-up, will introduce serious error to polymerization trial performance and reliability.*
- viii. Quench the trial by venting ethylene, transferring the product to a collection beaker, and adding acidic methanol.
- ix. Separate the as-synthesized product by filtration. Purify the product by washing it several times using excess additional methanol. See Figure 4.10.
- x. Vacuum dry the product overnight and store it properly for subsequent characterization.
- xi. Calculate the catalyst activity using the product yield, catalyst concentration, and polymerization run time.



Figure 4.10: Separation and purification of as-synthesized elastomers.

4.6 Precatalyst-cocatalyst Interaction Evaluation and Ethylene–Alpha-Olefin Elastomer Characterization

The precatalyst-cocatalyst interaction and active transition metal cation (catalyst active site) generation were evaluated using primarily ^1H NMR spectroscopy. The as-synthesized elastomers were characterized in terms of the properties listed in Table 4.2 using the techniques listed therein. Table 4.2 also reports the relevant references for all the techniques used. The sample preparation method and the specific instrumental procedures of DSC, GPC, Crystaf, and ^1H NMR and ^{13}C NMR are described in the following sections.

4.6.1 Differential Scanning Calorimetry (DSC)

A TA Q2000 DSC instrument, having a RCS90 cooling system and an auto sampler, measured the as-synthesized copolymer thermal properties. The instrument was calibrated using indium.

About 4.0 mg sample was taken in a Tzero aluminium pan, which was tightly closed with the lid. A sealed pan was used as a reference. The samples and the reference were placed in the experimental carousel. The entire DSC analysis comprised 3 cycles; each cycle used $10\text{ }^\circ\text{C min}^{-1}$ thermal ramp under a nitrogen flow rate of 50 mL min^{-1} .

Cycle 1 heated the sample from room temperature to $160\text{ }^\circ\text{C}$. At this temperature, it was heated additionally for 5 min to remove the influence of the thermal history. Cycle 2 cooled the sample from 160 to $-85\text{ }^\circ\text{C}$ and kept it at this temperature for another 5 min. Cycle 3 heated the sample from $-85\text{ }^\circ\text{C}$ to $160\text{ }^\circ\text{C}$.

Table 4.2: Elastomer properties and characterization techniques.

Catalyst active site characteristics and elastomer properties	Techniques	References
Precatalyst-cocatalyst interaction and active metallocenium cation	Appropriate NMR techniques (predominantly ^1H NMR spectroscopy)	[25], [30], [36], [37], [38], [39], [59], [62], [84], [85], [86]
MW and MWD	GPC	[16], [87]
Copolymer composition distribution	Crystaf	[16], [87]
Thermal properties* (T_g , T_m , and %crystallinity)	DSC	[16], [87]
Average comonomer incorporation and microstructure (triad sequence, sequence length distribution, average sequence length, backbone defect, etc.)	^{13}C NMR	[16], [65], [87], [88], [89]

^1H NMR = Proton nuclear magnetic resonance; MW = Molecular weight; MWD = Molecular weight distribution; GPC = Gel permeation chromatography; ^{13}C NMR = Carbon nuclear magnetic resonance; DSC = Differential scanning calorimetry. *Depending on comonomer arrangement and configuration, the as-synthesized elastomer may show both T_g and T_m .

The TA explorer software acquired each cycle data and calculated the peak crystallization temperature T_{pc} using Cycle 2 scan, and glass transition temperature T_g and (peak melting temperature T_{pm} and %crystallinity X_c , if any) using Cycle 3 scan, respectively.

Cycle 3 scan determined T_g —the transition between glassy and rubbery states—using the following steps:

- Draw glassy and rubbery states onset (top) and endset (bottom) tangents, respectively,
- Intercept the inclined glassy to rubbery transition line by the above two tangents and determine the corresponding mid-point,
- Read T_g on the temperature X-axis that corresponds to the above mid-point.

Integrating Cycle 3 melting trace gave the heat of fusion H_f which, in turn, estimated %crystallinity $X_c = \frac{H_f}{H_{fo}} \times 100$ where H_{fo} is the heat of fusion of a perfectly crystalline polyethylene and this equals to 290.0 Jg^{-1} [87].

4.6.2 Gel Permeation Chromatography (GPC)

The elastomer molecular characteristics, such as weight-average molecular weight (MW) and molecular weight distributions (MWD), were analyzed using high-temperature gel permeation chromatography (Agilent Technology PL-GPC 220) having linear columns (PLgel Olexis, 300 mm $\times$ 7.5 mm) at 160 °C. To avoid high temperature oxidative polymer sample degradation, 0.0125 wt% BHT antioxidant was added to the 1,2,4-trichlorobenzene (TCB) mobile phase. Next, a 20 mg polymer sample was introduced into a 20 mL vial and dissolved in 10 mL of BHT-stabilized TCB according to the following procedure. The sample vials were placed into the heating chamber of the high temperature sample preparation apparatus (PL-SP 260) and maintained at 160 °C for about 1 hr. Duration this process, the instrument shaker agitated the vials and fully dissolved the samples. The sample solutions were transferred to 2 mL GPC vials using a hand pipettor fitted with a 0.5 μ m filter.

A refractive index (RI) detector measured the eluent polymer concentration. Before injecting the samples, the differential refractive index detector was purged for 4 hr using TCB (at a flow rate of 1 mL min⁻¹) to achieve a stable baseline. The injected sample amount and its flow rate were 100 μ L and 1.0 mL min⁻¹, respectively. The instrument was calibrated using a set of three polystyrene (PS) standards with 12 calibration points called EasiVial PS-H. The PS standard peak molecular weights varied from 600 to 6,000,000 g mol⁻¹. The PS calibration curve was converted into the corresponding polyethylene (PE) calibration curve using the Mark-Houwink constants ($\alpha = 0.725$ and $k = 40.6 \times 10^{-5}$) of PE [90]. Each sample run time was 20 mins. Agilent GPC/SEC software calculated the average molecular weight, MWD, and polydispersity index using the acquired chromatogram and the above PE calibration curve.

4.6.3 Crystallization Analysis Fractionation (Crystaf)

A Polymer Char Crystaf 100 determined the composition distribution of the as-synthesized copolymer elastomers. This instrument works as follows [87]. The dissolved polymer is sampled at an even time interval, and the polymer solution concentration is measured using an infrared detector by cooling the solution at a constant rate. A copolymer with lower co-monomer content crystallizes from the solution at a higher temperature than the one with a higher co-monomer content (more short-chain branches). The Crystaf crystallization profile shows the comonomer incorporation level in the copolymer.

Sample solutions of concentration of 0.1 mg/mL in TCB were prepared at 160 °C under stirring for 60 min. The solutions were equilibrated at 95 °C for 45 min. They were subsequently crystallized at a cooling rate of 0.2 °C min⁻¹ from 95 to 25 °C. The qualitative differential composition distribution (dw/dT versus T) was obtained by numerical differentiation of the integral analogue.

4.6.4 Carbon and Proton Nuclear Magnetic Resonance (¹H and ¹³C NMR) Spectroscopy

Two types of NMR analyses—¹H and ¹³C—were done using a 600 MHz JEOL instrument. ¹H NMR investigated precatalyst-cocatalyst interaction and catalyst active site formation. On the other hand, ¹³C NMR characterized the as-synthesized elastomers. They are summarized below.

The ¹H NMR spectra of the experimental precatalysts and cocatalysts were obtained at 50 °C and 70 °C using Teflon-capped 5 mm NMR tubes. Here, the same polymerization precatalyst to cocatalyst ratio was used. Refer to Section 4.4.

The as-synthesized elastomer samples were analyzed as follows. Approximately 25 mg of the sample were dissolved in a 9:1 v/v mixture of 1,2,4-trichlorobenzene (TCB) and DMSO-d at 130 °C using the GPC high temperature sample preparation unit (PL-SP 260) for 1 hr. The resulting solution was transferred to a 5 mm NMR tube using a warm glass pipette. The probe was set to 130 °C, and the spectra were recorded by collecting 4000 scans. The reinverse-gated NMR experiment acquired the analysis data using 90° pulse, 1.3 s acquisition time, and 6 s delay time. The triad mole fractions were calculated using Randall's regional collective assignment approach and the related algebraic expressions [88]. The resulting triad mole fractions estimated the average copolymer composition and the structural parameters. See Section 3.1.

CHAPTER 5

RESULTS AND DISCUSSION

We design Chapter 5 in terms of the following sections:

- Solution of ethylene solubility model equations (Section 5.1),
- Comparison of model predictions with experiments (Section 5.2),
- Solvent effect on ethylene solubility and temperature-dependent Henry's constant (Section 5.3),
- Catalyst-mediated copolymer/elastomer synthesis topical (major) results (Section 5.4) which include:
 - Catalyst activation and deactivation (macroscopic and microscopic perspectives) (Section 5.4.1),
 - As-synthesized elastomer chain growth, polydispersity index, and temperature effects (Section 5.4.2), and
 - Elastomer microstructures, morphology, and thermal properties (Section 5.4.3)

Sections 5.2 and 5.3 relate to model performance and prediction. On the other hand, Section 5.4 reports how the present catalyst-mediated ethylene– α -olefin elastomer synthesis and characterization work, supported by the model results, add novelty, new knowledge, and insight (as appropriate) to the concerned literature.

5.1 Solution of Ethylene Solubility Model Equations

Equations 3.7 and 3.8 (EoS cubic compressibility factor equations), and Equations 3.9 and 3.10 compose the four constitutive model equations. The latter two equations predict ethylene solubility in the subject polymerization solvent (1) or comonomer (2) using Z^V and Z^L estimated by the former ones. Note that none of these model equations uses component liquid phase activity coefficient, which itself is cumbersome to estimate. The present activity coefficient-free model equations, therefore, avoid this undesirable situation.

We solve the model equations simultaneously to achieve the following objectives:

- i. Calculate X [the ratio of molar concentrations of monomer 1 and monomer 2 (comonomer) in the binary polymerization liquids] applying the model-predicted gaseous monomer solubility mole fraction x_{M_1} (Equation 3.19) and Equation 3.23. Equations 3.4 and 3.5 use these X values to correctly estimate the reactivity ratios r_1 and r_2 . Otherwise, very significant errors will occur [6].
- ii. Predict catalyst active center residential environment, represented by Z_{1-2}^L (Equation 3.24), using model-predicted $Z_{M_1-1}^L$ and $Z_{M_1-2}^L$ (Equation 3.10). Section 3.2 elaborates this *new* Atiqullah et al. [2023] mathematical concept with reference to catalyst science, solution polymerization, and elastomer synthesis [6]. The catalyst active species reside in the liquid phase copolymerization medium. Hence, we specially treat and refer to the liquid phase model-predicted results.

The following factors should be reviewed to solve the model equations. They are implicitly nonlinear. Hence, we need a numerical algorithm (method) that robustly converges even when the initial guesses distance from the actual roots. Selecting/estimating all the initial guesses close to

the solution may not be possible. We also want to avoid an *ad hoc* or experience-based initial guess estimation method, usually reported in the literature. Such approach is cumbersome because it uses *a priori* assumptions and iterates on calculating vapor-liquid phase fraction, bubble point, and dew point [91, 92, 93]. The complexity increases as nonlinearity and the number of unknowns increase. Hence, we consider Levenberg-Marquardt algorithm (LMA) that has the following advantages:

- i. LMA combines the best features of the gradient descent (GD) and the Gauss-Newton (GN) methods, and
- ii. It better controls the computational effort (convergence speed) via judicious root initialization and damping parameter update.

We, therefore, solve the model equations applying the LMA-based MATLAB *fsolve* algorithm. We resolve the initial guess problem using the following approach, which has two parts (Part A and Part B). Part A is a *quasi*-ideal K factor method. This assumes that the vapor and liquid mixtures behave as ideal gas and solution, respectively. Hence, we derive Equation 5.1 applying Raoult [94] and Lewis-Randall ideal solution [95] laws as follows:

$$x_{10} = \frac{1 - K_2}{K_1 - K_2}; y_{10} = K_1 \frac{1 - K_2}{K_1 - K_2};$$

$$K_1 = \frac{P_{s1}}{P}; K_2 = \frac{P_{s2}}{P}; \text{ideal vapor and liquid mixture} \quad (5.1)$$

Antoine equation (Equation T30.1), Chen correlation (Equation T30.2), or Wilson equation (Equation 30.3) [92, 96, 97] can be used to calculate P_{s1} and P_{s2} and the corresponding K_1 and K_2 .

Part B guesses Z_0^V and Z_0^L . Here, we assume $Z_0^V \approx 1$ (ideal gas limit) and $Z_0^L \approx \frac{P(v_{solvent}^L \text{ Tait eqn})}{RT}$,

which makes a rational initial guess framework. Atiqullah et al. [2024] elaborates the overall model equation-solving algorithm in their recent *AIChE J* publication [6]. The present LMA

overall converges in 10 to 15 iterations. Section 5.2 compares the model-predicted solubilities with the corresponding experimental values for the three systems under consideration (ethylene–toluene, ethylene–1-hexene, and ethylene–1-octene).

Appendix F Tables F.1–F.4 list the data used in the present research modeling work.

5.2 Comparison of Model Predictions with Experiments

We evaluate the success of applying Atiqullah et al. [2023] initial guess method, Levenberg-Marquardt algorithm (LMA), and MATLAB *f*solve software to solve the model Equations 3.7–3.10 in two ways: using graphical presentation (see Figure 5.1) and Tables 5.1–5.3 (model results). They both show that model-predicted solubilities of ethylene (expressed in terms of mole fraction) in toluene [98, 99], 1-hexene [100], and 1-octene [100] as a function of laboratory to industrial level temperatures and pressures, very satisfactorily match the experimental values. Accordingly, we conclude that the present PR EoS solubility prediction model and the algorithm developed are very suitable, robust, efficient, and user friendly. Antoine, Chen, and Wilson vapor pressure equations give comparable results. But we recommend using the latter two which, unlike Antoine equation, apply only thermophysical properties and has no T_{max} limitation. Table 5.4 shows the applications of the model results reported in Tables 5.1–5.3.

Sections 5.4.1–5.4.3 use, as appropriate, Table 5.4 framework to elucidate the present study catalyst-mediated copolymer/elastomer synthesis topical results.

Table 5.1: Model versus experimental solubility of ethylene in toluene [98, 99].

Temperature (K)	Pressure (bar)	$x_{1\text{ }expt}$ (mole fraction)	$x_{1\text{ }model}$ (mole fraction)	$y_{1\text{ }model}$ (mole fraction)	Model-predicted ethylene- toluene mixture	
					Z^V	Z^L
323.15	4.7	0.0442	0.0452	0.9711	0.9700	0.0188
	9.1	0.0898	0.0878	0.9836	0.9500	0.0357
	13.9	0.1418	0.1334	0.9880	0.9200	0.0533
	19.1	0.1765	0.1819	0.9902	0.8955	0.0716
	24.5	0.2306	0.2312	0.9913	0.8653	0.0896
373.15	6.8	0.0444	0.0395	0.8809	0.9642	0.0250
	8.2	0.0502	0.0484	0.8990	0.9595	0.0301
	11.3	0.0754	0.0681	0.9230	0.9490	0.0411
	17.0	0.1165	0.1038	0.9439	0.9294	0.0609
	20.2	0.1355	0.1235	0.9502	0.9183	0.0717
	24.7	0.1666	0.1509	0.9561	0.9025	0.0867
	28.9	0.2007	0.1760	0.9597	0.8878	0.1003
423.15	6.7	0.0265	0.0202	0.5696	0.9392	0.0236
	10.5	0.0488	0.0393	0.7111	0.9345	0.0367
	14.9	0.0742	0.0610	0.7847	0.9260	0.0517
	19.4	0.0981	0.0830	0.8250	0.9161	0.0668
	24.7	0.1266	0.1086	0.8531	0.9038	0.0843
	28.8	0.1527	0.1282	0.8673	0.8940	0.0976
351.60	4.10	0.3067	0.2887	0.9804	0.8211	0.1393
373.70	4.8	0.3067	0.2863	0.9654	0.8201	0.1596
421.20	6.4	0.3067	0.2918	0.9080	0.8073	0.2056
475.30	7.9	0.3067	0.3020	0.7824	0.7593	0.2616
519.40	8.5	0.3067	0.3075	0.6049	0.6643	0.3195

$$\%AAD = \frac{100}{N} \sum_1^N \frac{|x_{exp} - x_{mod}|}{x_{exp}} = 15.83.$$

Table 5.2: Model versus experimental solubility of ethylene in 1-hexene [100].

Temperature (K)	Pressure (MPa)	$x_{1\text{ }expt}$ (mole fraction)	$x_{1\text{ }model}$ (mole fraction)	$y_{1\text{ }model}$ (mole fraction)	Model-predicted ethylene–1-hexene mixture	
					Z^V	Z^L
273.20	0.77	0.1180	0.1175	0.9687	0.9408	0.0363
	1.81	0.2890	0.2793	0.9835	0.8621	0.0783
	3.00	0.4820	0.4704	0.9870	0.7609	0.1170
	4.11	0.6810	0.6724	0.9872	0.6472	0.1456
	4.98	0.8390	0.8620	0.9861	0.5273	0.1748
	5.41	0.9130	0.9400	0.9851	0.5070	0.2758
	5.61	0.9440	0.9673	0.9833	0.4749	0.2531
332.90	0.93	0.0810	0.0876	0.8857	0.9363	0.0416
	2.50	0.2320	0.2456	0.9447	0.8543	0.1041
	2.52	0.2380	0.2476	0.9449	0.8532	0.1049
	3.75	0.3620	0.3677	0.9534	0.7833	0.1481
	5.19	0.5030	0.5075	0.9541	0.6928	0.1941
	7.01	0.6800	0.6955	0.9420	0.5515	0.2543
	7.53	0.7290	0.7576	0.9322	0.6247	0.2693
	8.06	0.7850	0.8388	0.9060	0.4151	0.3259
373.60	1.49	0.1050	0.0954	0.7638	0.8969	0.0644
	3.02	0.2270	0.2126	0.8560	0.8397	0.1252
	5.06	0.3740	0.3636	0.8827	0.7539	0.2004
	7.09	0.5150	0.5141	0.8787	0.6563	0.2741
	8.78	0.6320	0.6547	0.8495	0.7247	0.3306

$$\%AAD = \frac{100}{N} \sum_1^N \frac{|x_{exp} - x_{mod}|}{x_{exp}} = 3.57.$$

Table 5.3: Model versus experimental solubility of ethylene in 1-octene [91].

Temperature (K)	Pressure (MPa)	$x_{1 \text{ expt}}$ (mole fraction)	$x_{1 \text{ model}}$ (mole fraction)	$y_{1 \text{ model}}$ (mole fraction)	Model-predicted ethylene–1-octene mixture	
					Z^V	Z^L
303.0	1.08	0.194	0.1928	0.9962	0.9303	0.0598
	2.50	0.417	0.4146	0.9974	0.8327	0.1175
	4.00	0.616	0.6170	0.9972	0.7159	0.1595
	5.43	0.793	0.7899	0.9958	0.5781	0.1900
	6.33	0.909	0.9843	0.9844	0.3929	0.3929
342.4	1.00	0.117	0.1164	0.9772	0.9511	0.0539
	3.00	0.324	0.3255	0.9877	0.8593	0.1412
	5.00	0.499	0.5034	0.9873	0.7622	0.2081
	7.04	0.665	0.6608	0.9825	0.6546	0.2639
	8.97	0.807	0.9475	0.9475	0.4718	0.4718

$$\%AAD = \frac{100}{N} \sum_1^N \frac{|x_{exp} - x_{mod}|}{x_{exp}} = 3.00$$

Table 5.4: Applications of the model results.

Model results	Calculative applications	Reference equations
x_1 : Mole fraction solubility of gaseous monomer in a single liquid Z^L : Compressibility factor for dissolved gas-single liquid system	HCs : Henry's constants of ethylene-single solvent and ethylene-binary liquids	3.18
	x_{M_1} : Solubility of gaseous monomer in a binary liquid system	3.19
	r_1 : Reactivity ratio of monomer M_1	3.4
	r_2 : Reactivity ratio of monomer M_2	3.5
	X : Ratio of molar concentrations of monomer 1 and monomer 2 (comonomer)	3.23
	Z_{1-2}^L : Binary liquid phase compressibility factor Catalyst active center residential environment	3.24

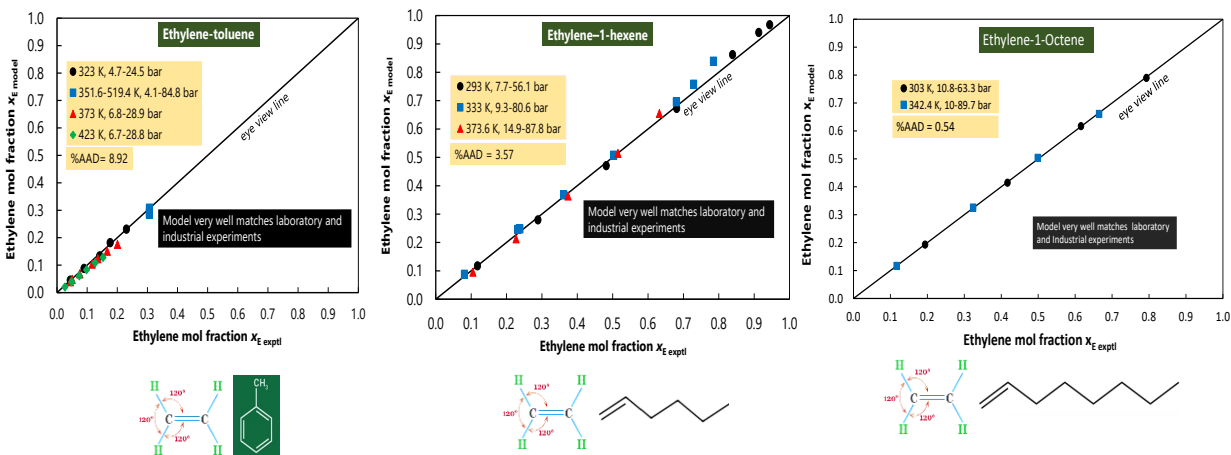


Figure 5.1: Comparison of experimental versus model-predicted solubilities of ethylene in toluene, 1-hexene, and 1-octene.

5.3 Solvent Effect on Ethylene Solubility and Temperature-Dependent Henry's Constant

The converged x_1 and y_1 values (Tables 5.1–5.3), predicted by PR EoS, confirm the phase equilibrium condition of equality of vapor and liquid phase fugacities and chemical potentials at a given experimental T and P . Hence, each P gives the liquid phase mixture vapor pressure P_{smix} for the corresponding T . We, therefore, revisit ethylene solubility in polymerization solvent (1) or comonomer (2) from Henry's law perspective.

We address how the model-predicted Henry's constants (HCs) at a single to varying temperatures illustrate ethylene solubility behavior in toluene, 1-hexene, and 1-octene. For example, Figure 5.2 shows that at 323 K, ethylene solubility, as a function of pressure, decreases as follows: $S_{E\ 1-octene} > S_{E\ 1-hexene} > S_{E\ toluene}$. This finding is inversely related to the corresponding Henry's constant order: $HC_{E\ 1-octene} < HC_{E\ 1-hexene} < HC_{E\ toluene}$. This means that ethylene solubility decreases as HC increases. We recognize that the intra- and intermolecular interactions between ethylene and liquid solvent molecules affect solubility as well. The more is this interaction; the more is the solubility and the less is HC . Hence, $I_{E\ 1-octene} >$

$I_{E\ 1-hexene} > I_{E\ toluene}$, which can be attributed to ethylene-liquid structural differences. In this regard, ethylene-liquid interactions can be listed as follows:

- *Ethylene–1-hexene and ethylene–1-octene*: interaction between a two carbon π -bonded unsaturated smaller olefin, and a six carbon as well as eight carbon π -bonded unsaturated higher linear olefin, and
- *Ethylene–toluene*: interaction between a two carbon π -bonded unsaturated smaller olefin and a six carbon π -bonded unsaturated aromatic ring.

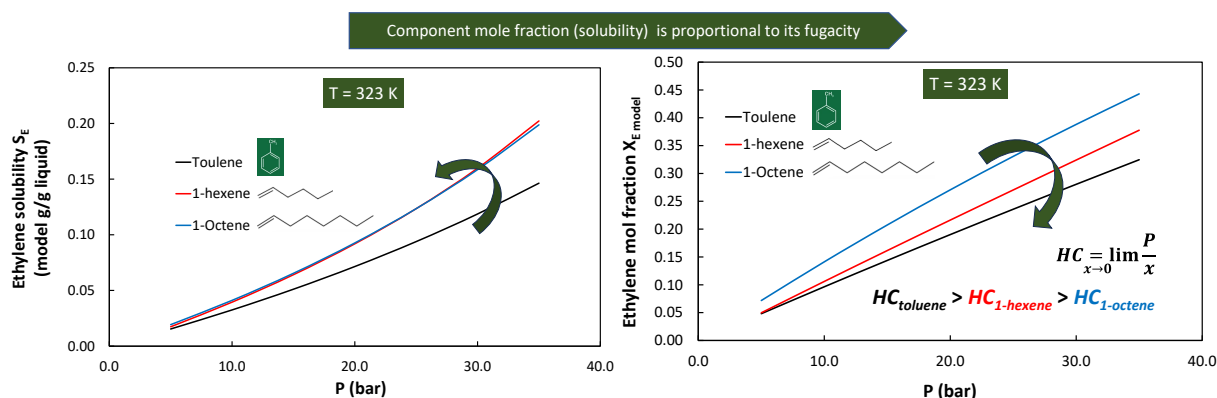


Figure 5.2: Varying solvent effects on ethylene solubility illustrated by Henry's law.

Now, we address the Arrhenius temperature-dependence of Henry's constant. The inverse of the slope of ethylene mole fraction solubility versus the experimental pressure [101] determines $H_{gL}(T)$ at a given temperature. We consider only the linear part of this plot. Interestingly, all the three systems showed approximately linear x - P relation from laboratory to industrial level pressures. Next, we evaluate the temperature-dependent Henry's constant $H_{gL}(T)$ using Equation 3.18 [102, 103, 104] Table 5.5 lists these Arrhenius HC relations for this study ethylene-liquid systems. The coefficient of determination r^2 in each case is high (0.9107–0.9934). They can, therefore, also be used to estimate the practical case solubility.

What has been summarized above also illustrates how an EoS such PR can determine Henry's constant as a function of temperature. Section 5.4.1 uses them in Shulgin-Ruckenstein activity coefficient– HC formalism [105] to estimate ethylene solubility x_{M_1} in binary solvents/liquids of our interest (toluene–1-hexene and toluene–1-octene).

Table 5.5: Developed Arrhenius Henry's constant relations for selected ethylene-single liquid systems.

Ethylene-liquid pair	Temperature (K)					Arrhenius relation for Henry's constant HC	r^2	%AAD
	273.15	293.15	323.15	333.15	423.15			
	Henry's constants (bar)							
Ethylene-toluene	161.63	81.16*	106.47	117.31*	204.69	$H_{gL} = H_0 \exp\left(-\frac{898.74}{T}\right)$ $H_0 = \exp(7.46)$	0.9934	5.21
Ethylene-1-hexene	131.34	55.72	82.72*	96.87	196.04*	$H_{gL} = H_0 \exp\left(-\frac{1179.40}{T}\right)$ $H_0 = \exp(8.07)$	0.9907	8.86
Ethylene-1-octene	Temperature (K)					$H_{gL} = H_0 \exp\left(-\frac{820.75}{T}\right)$ $H_0 = \exp(7.04)$	0.9107	7.37
	303.00	323.15	332.15	342.40	423.15			
	76.22*	90.25*	96.68*	104.10*	164.48*			

*Determined using the developed relations. Unit of H_0 and H_{gL} is bar. $\%AAD = \frac{100}{N} \sum_1^N \frac{|x_{exp} - x_{HC}|}{x_{exp}}$. Equations 3.18 and 3.19 calculate ethylene mole fraction x_{HC} (HC = Henry's constant) and the corresponding ethylene solubility in the liquids (solvent and comonomer) listed above, respectively. r^2 = coefficient of determination.

5.4 Present Study Catalyst-Mediated Copolymer/Elastomer Synthesis Topical Results

This is the core section of this MS thesis report. We, therefore, divide this part into the following three subsections (5.4.1–5.4.3). The major findings herein have been first underscored with reference to the appropriate figures and tables that originate from the modeling and experimental work (catalyst-mediated elastomer synthesis and characterization). Next, we explain them as scholastically as possible to add novelty, new knowledge, and insight (as appropriate) to the concerned literature.

Table 5.6 summarizes the design of the experimental copolymerization trials. Factors such as precatalyst, cocatalyst, and comonomer types, cocatalyst to precatalyst molar ratios, precatalyst and comonomer concentrations, temperature, pressure, and reactor operational mode form this design foundation.

Table 5.6: Design of the experimental copolymerization trials.

Precatalyst types	Cocatalyst types	Cocatalyst:precatalyst molar ratios	Comonomer types	Copolymerization temperatures (°C)
▪ Spaleck	▪ MAO ▪ TTB (primary) and TIBA (secondary)	▪ Al (in MAO excluding free-TMA):M = 200:1 ▪ M:TTB (primary):TIBA (secondary) = 1:2:200	▪ 1-hexene ▪ 1-octene	▪ 40.00 ▪ 50.00 ▪ 60.00 ▪ 70.00
▪ Dow CGC	▪ MAO ▪ TTB (primary) and TIBA (secondary)			

Reactor vessel = 250 mL cylindrical round-bottom Buchi reactor. Reactor liquid volume = Toluene solvent + comonomer = (140 + 10.5) or (160 + 11.4) = 150.5 or 171.4 mL. Precatalyst concentration: 36.46–50.52 $\mu\text{mol/L}$. Ethylene monomer feeding pressure = 4 barg. Reactor operational mode = Semicontinuous feeding of ethylene (without monomer starvation). Polymerization type: Solution polymerization that dissolves the as-synthesized elastomer and forms a single phase. Impeller speed = 600 rpm. Total successful copolymerization trials = 2 precatalysts $\times$ 2 comonomers $\times$ 2 cocatalysts $\times$ 4 temperatures = 32.

According to Table 5.6 17, we have the following four as-synthesized elastomers, corresponding to both E–1-hexene and E–1-octene copolymers:

- Spaleck/MAO E–1-hexene and E–1-octene elastomers,
- Spaleck/(TTB + TIBA) E–1-hexene and E–1-octene elastomers,
- Dow CGC/MAO E–1-hexene and E–1-octene elastomers, and
- Dow CGC/(TTB + TIBA) E–1-hexene and E–1-octene elastomers.

Sections 5.4.1 to 5.4.3 discuss the results, following the above order for each copolymer type. The discussion focuses on effects of precatalyst and cocatalyst structure, catalyst active center, temperature, and ethylene solubility (monomer concentration) on E–1-hexene and E–1-octene copolymerization and the resulting elastomer properties. We consider E–1-hexene and E–1-octene copolymers in parallel, as appropriate. The data originating from the thirty-two (32) polymerization trials and the subsequent characterization work are voluminous. We, therefore,

report here only the summarized tables while the relevant appendices contain the corresponding detailed tabulated data and results.

5.4.1 Catalyst Activation and Deactivation (Macroscopic and Microscopic Perspectives)

The coordination catalysis related to ethylene- α -olefin elastomer synthesis comprises chemical as well as physical phenomena. Chemical phenomena, dictated by precatalyst-cocatalyst structures, address concepts such as catalyst activity (reactivity), activation and time-dependent deactivation, ion-pair properties—(cation-anion) formation, structure, interaction, separation and stability, and match—as well as arene coordination (by an aromatic solvent such as toluene). On the other hand, the physical phenomena include ethylene solubility in the binary solvent-comonomer system, and their intra- and intermolecular separation and interaction, predicted by the corresponding liquid compressibility factor Z_{1-2}^L . Chapter 3 Section 3.2 correlates ethylene solubility to Z_{1-2}^L which is next translated into catalyst active site residential environment parameter. We first published this concept in our 2023 report for an ethylene-single liquid system [6]. Now, the present research extends this to an ethylene-binary liquid (solvent + comonomer) system.

The concepts listed by the chemical phenomena are interrelated but also have subtle differences. Modeling and quantifying the above physical phenomena and separating them from the chemical ones can improve our understanding of overall ethylene- α -olefin coordination catalysis. This can develop high-performance catalysts and processes. However, this has not been done yet.

To complete the above description, we summarize the structures of both cocatalyst systems as follows. The MAO cocatalyst, according to the progressive studies, has a cage structure having

varying sizes. Each cage Al center also does not have the same Lewis acidity (LA). MAO, therefore, has size and LA distributions while the latter is more important from the catalyst activity perspective. Consequently, some of the Al centers have strong Lewis acidity to abstract a Cl^- from L_2ZrMeCl (or a Me^- from in-situ formed L_2ZrMe_2) and to form ion-pair structures such as $\text{L}_2\text{ZrMe}^+\text{Cl}[-\text{Al}(\text{Me})\text{O}-]_n^-$ or $\text{L}_2\text{ZrMe}^+\text{Me}[-\text{Al}(\text{Me})\text{O}]_n$ [25]. The requisite strong and narrow LA distribution depends on the manufacture process technology.

For the (TTB + TIBA) cocatalyst, the TTB-TIBA reaction product— $[\text{Al}^i\text{Bu}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ balanced by the borate anion—acts as the in-situ cocatalyst and it has a defined molecular structure [36, 37]. See Figure 2.10.

The active catalyst center, generated by both precatalyst systems, is strictly speaking $\text{L}_n\text{M}^+\text{R}(\text{polyolefin} \Rightarrow (\text{CH}_2-\text{CH}_2)_n\text{H}$ with and without chain branching) that includes the inserted olefin and growing polyolefin chain. Its steric and electronic environments differ from those of the customary form of catalyst active site $\text{L}_n\text{M}^+\text{Me}$ because the former has varying alkyl steric encumbrances, agostic interactions, and cation-anion interactions. The environment around the nascent (embryonic) active metal cation constantly changes with (i) the mass transfer processes associated with the incoming monomers and (ii) the growth and termination of the polymer chains. As a result, the ion-pair thermodynamic stability as well as ion-pair solution structure and structural dynamics are affected [25, 106].

Based on the preceding discussions, the resulting catalyst active center, generated by all precatalyst-cocatalyst systems, is *polyalkyl* and it may be rated as *pseudo*-single site (SS) but not an *ideal* SS one which features constant coordination environment. Note that the real situations do not satisfy the latter requirement. We, therefore, explain and discuss Section 5.4.1 overall findings

applying the following major concepts: polyalkyl *pseudo*-single site (SS) catalyst active center, selected ion-pair properties, and catalyst active site residential environment parameter Z_{1-2}^L .

Figure 5.3 shows how the time-average catalyst productivity varies as a function of the following: temperature, precatalyst-cocatalyst structure, and copolymerization monomer-comonomer pair (E-1-hexene and E-1-octene). It was prepared using the relevant experimental data summarized in Appendix G Tables G.1 to G.8. Because of using time-average catalyst productivity, we define Figure 5.3 catalyst productivity-temperature profiles as macroscopic representation of catalyst stability and deactivation.

We first consider particularly the effect of temperature. Here, the observation related to average catalyst productivity is divided into two groups. Group I refers to E-1-hexene copolymerization in the presence of Spaleck precatalyst, and MAO and (TTB + TIBA) cocatalysts. Group II includes (i) E-1-hexene copolymerization in the presence of Dow CGC precatalyst, and MAO and (TTB + TIBA) cocatalysts, and (ii) E-1-octene copolymerization in the presence of Spaleck and Dow CGC precatalysts and the above cocatalysts.

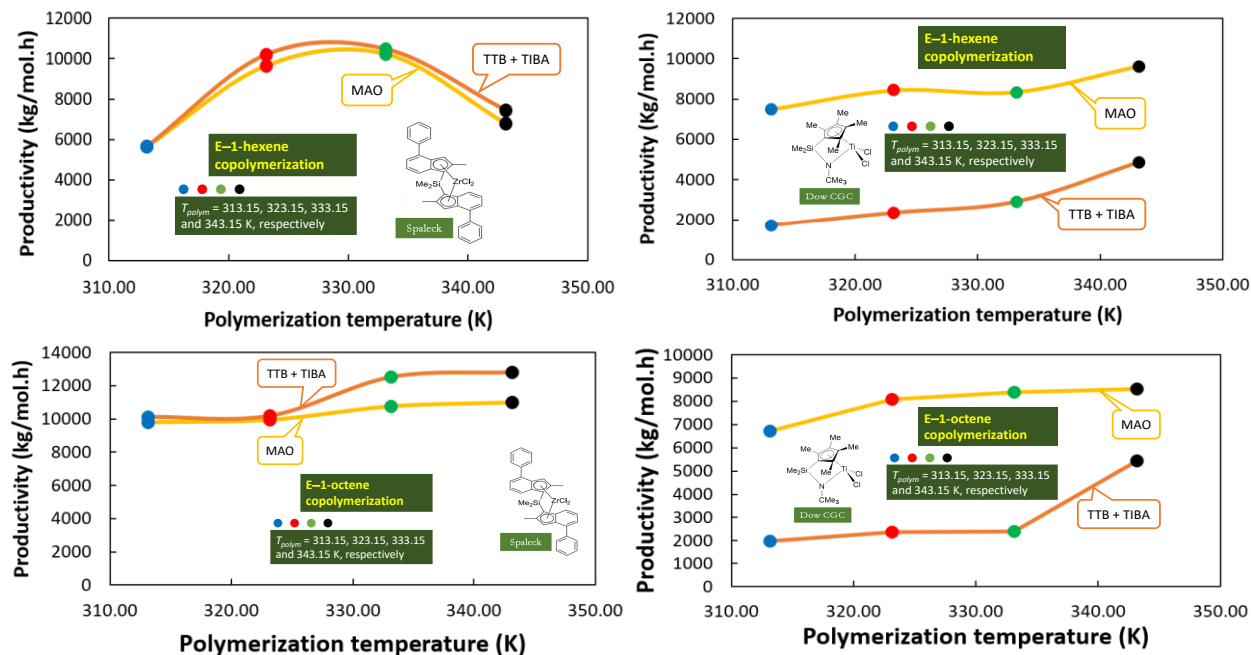


Figure 5.3: Time-average macroscopic stability of Spaleck and Dow CGC precatalysts in ethylene copolymerization with 1-hexene and 1-octene as a function of precatalyst-cocatalyst type and temperature.

Group I shows a maximum E-1-hexene average productivity with increasing copolymerization temperature for both cocatalysts. This behavior may be ascribed to hindered ion-pair interaction and catalyst deactivation. The productivity profile also fairly overlaps expressing negligible cocatalyst effect. The Al:Zr molar ratio, in each case, is 200. Group II, on the other hand, demonstrates, unlike Group I, increasing productivity with temperature. For both groups, the above diverse productivity-temperature behavior occurs under the following:

- Decreasing ethylene solubility and concentration in toluene- α -olefin (1-hexene or 1-octene) binary liquid phase, under the experimental polymerization conditions, as the temperature increases (Figure 5.4), and
- Practically constant catalyst active site residential environment parameter Z_{1-2}^L (Figure 5.5).

Ethylene solubility/concentration and Z_{1-2}^L were calculated using the model and procedure reported in Section 3.2 and Appendix F Tables F.1–F.4 data.

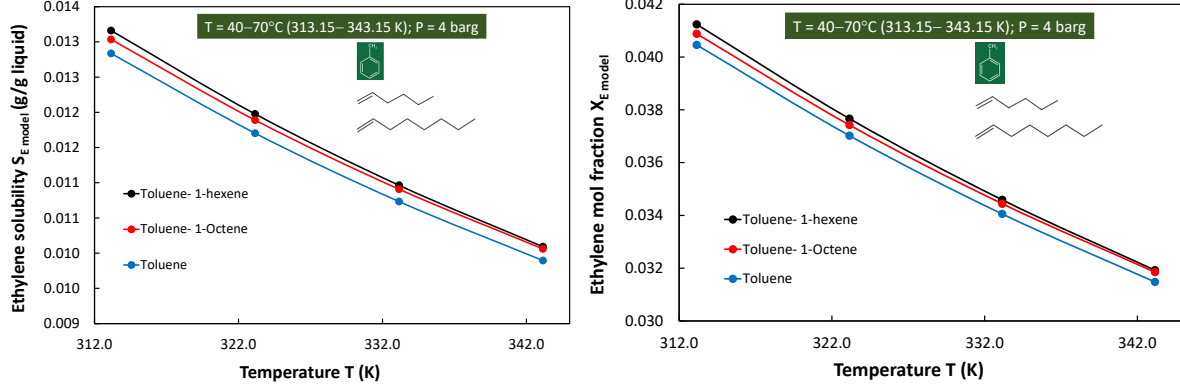


Figure 5.4: Predicted temperature effect on ethylene solubility and concentration in solvent- α -olefin binary liquid phase under the experimental polymerization conditions.

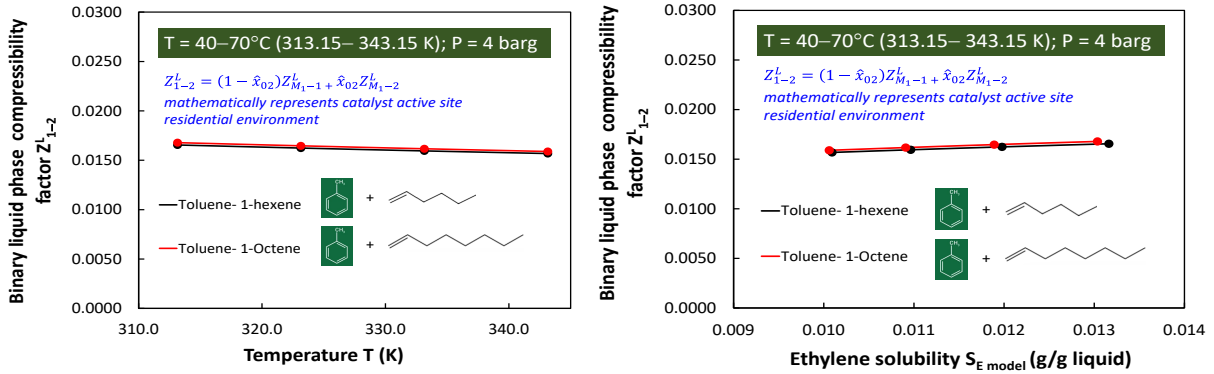


Figure 5.5: Temperature and ethylene solubility effects on model-predicted binary liquid phase compressibility factor Z_{1-2}^L (catalyst active center residential environment parameter) under the experimental polymerization conditions.

This research, via introducing the concept of Z_{1-2}^L (Figure 5.5), shows how to achieve the following:

- Design polymerization trials under the same to varying catalyst active site residential environments, and

- Separate the influence of physical phenomena, such as gaseous monomer solubility in solvent-comonomer binary liquid as well as their intra- and intermolecular separation and interaction, from the ion-pair chemical phenomena listed earlier.

To the best of our knowledge, the above approach to studying gas-liquid copolymerization is not reported in the literature. It is, therefore, new, insightful, and novel. It equally applies to laboratory to industrial polymerization conditions.

The overlapping productivity profile in Group I E–1-hexene copolymerization indicates that the polyalkyl *pseudo*-single site (SS) catalyst active center $L_nM^+R(\text{polyolefin} \Rightarrow (\text{CH}_2\text{--CH}_2)_n\text{H})$ and the corresponding ion-pair properties (listed earlier) for each cocatalyst system are comparable and they vary, as a function of temperature, in a similar fashion despite $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ is less coordinating than MAOCl^- [25]. For Group II, such variations—*intra-group* and *inter-group*—are different. Next, we discuss Figure 5.3 Group II results. The following observations are evident. The temperature-dependent productivity of E–1-hexene copolymerization, for the Spaleck precatalyst and the given two cocatalyst systems, differs from the corresponding E–1-octene analogue. E–1-hexene shows a maximum productivity while E–1-octene demonstrates mildly increasing productivity. The temperature-dependent comonomer effect on productivity, hence, is noticeably varying. On the contrary, for the Dow CGC precatalyst and the above cocatalyst systems, the E–1-hexene and E–1-octene productivity variation trends are similar. Here, the previous differing comonomer effect does not exist. With reference to Figure 5.3, we, therefore, particularly address the following questions:

- Why does MAO offer higher productivity than (TTB + TIBA) for both copolymerizations?

(Q1)

- Why do Spaleck/MAO and Spaleck/(TTB + TIBA) give more E-1-octene copolymerization productivity than the corresponding Dow CGC analogue? (**Q2**)

Two factors decide the overall productivity. One is the π -ligand steric bulk and electronic effects plus the metal center coordinative unsaturation (Factor I). Factor I fundamentally relates to the precatalyst structural characteristics, partially affected by the surrounding anion. The other is cumulative ion-pair properties (Factor II) which we listed earlier. The productivity is a complex interplay and competition between Factor I and Factor II. It is more for a given copolymerization and precatalyst-cocatalyst system if one or both factors are greater than the corresponding factors of the comparing system. We now answer the above questions from the perspective of Factor I and Factor II, as appropriate.

MAO is a much stronger Lewis acid than (TTB + TIBA). It, therefore, creates a strongly electron-deficient metal center (coordinatively more unsaturated metal cation). This phenomenon is particularly important for electron rich higher α -olefins which, unlike ethylene, very slowly incorporate into the growing polyethylene chain. The resulting MAOCl^- is more coordinating than the tetrakisborate $\text{B}(\text{C}_6\text{F}_5)_4^-$ and at the same time sufficiently weak and labile which allows ethylene and comonomer to displace the anion from its coordination site for rapid enchainment. These properties strengthen the *ion pairing* and stabilize the highly electron-deficient metal center which are reflected in the higher productivity by MAO over (TTB + TIBA). This answers **Q1**. We also refer to this argument while discussing the next figure.

Q2 relates to monomer insertion barrier. For MAOCl^- and $\text{B}(\text{C}_6\text{F}_5)_4^-$ (which refer to MAO and (TTB + TIBA), respectively), the monomer insertion barrier in Spaleck precatalyst is less than that in Dow CGC despite the latter is coordinatively more open. The electron deficiency and

coordinative unsaturation at the Spaleck Zr^+ center are more than those at the Dow CGC Ti^+ center. All these arguments reply to **Q2**.

Figure 5.3 findings originate from temperature-dependent time-average E-1-hexene and E-1-octene copolymerization productivities. It, therefore, does not show the influence of time on precatalyst-cocatalyst interaction that happens during polymerization in the reactor. Figure 5.6 that plots ethylene flow rate as a function of polymerization time addresses this subject. This figure, in other words, demonstrates the dynamics of qualitative copolymerization rate. Hence, it can describe catalyst deactivation from a microscopic perspective and reveal several aspects that macroscopic deactivation Figure 5.3 cannot.

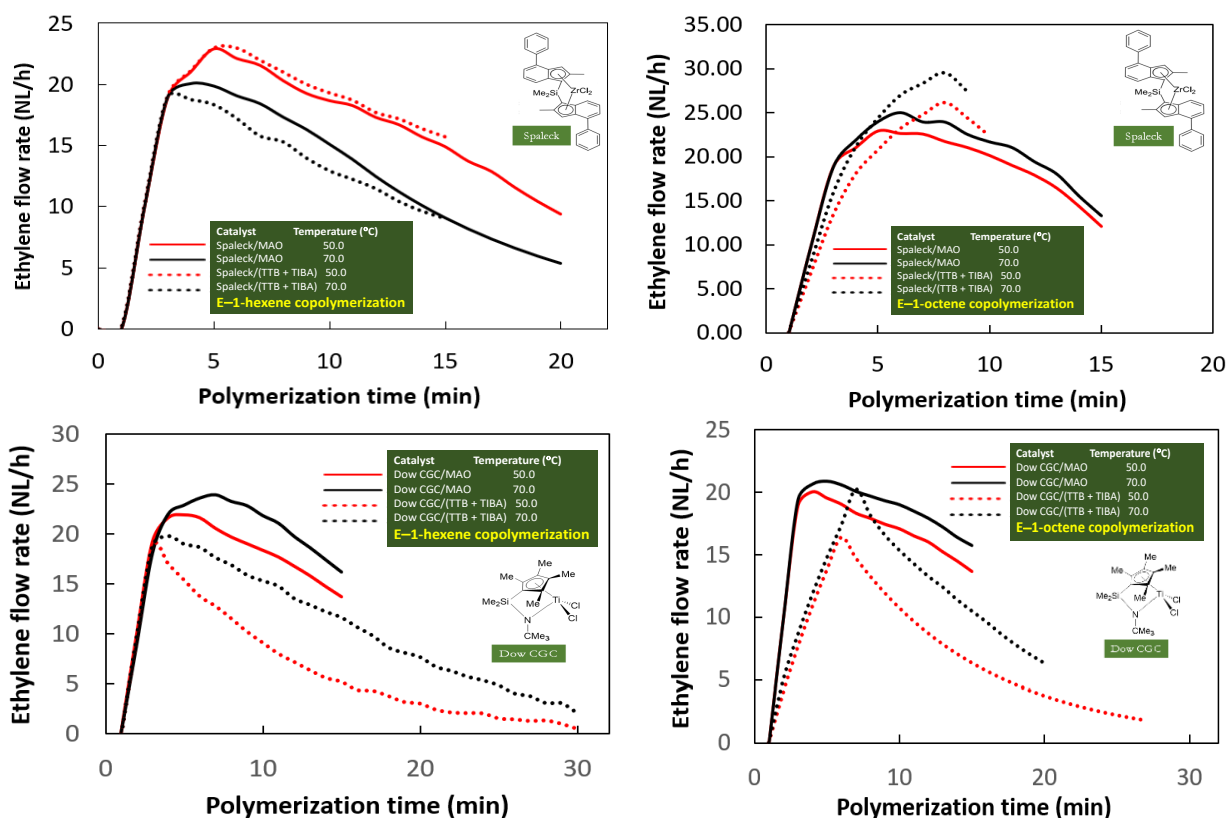


Figure 5.6: Microscopic deactivation behavior of Spaleck and Dow CGC precatalysts in ethylene copolymerization with 1-hexene and 1-octene as a function of cocatalyst type and temperature.

In Figure 5.6, the E-flow rate-time curve for Spaleck E-1-hexene copolymerization complements the corresponding Figure 5.3 productivity-temperature curve. The 50 °C productivity is higher than the 70 °C value. Figure 5.6 shows that the 70 °C flow curves for both cocatalyst systems are lower than the 50 °C ones. This also helps explain the above productivity difference. All the Spaleck E-1-hexene copolymerization flow curves are of decay type and feature a maximum copolymerization rate. This observation globally applies to Figure 5.6. This confirms that microscopic partial catalyst deactivation occurs in each case in a practically invariant catalyst active site residential environment. See also Figure 5.5. Catalyst instability is prevalent. The aliased effect of ethylene pressure and solubility, and polymerization temperature are decoupled from the catalyst deactivation phenomenon. *The current approach to studying catalyst microscopic deactivation is novel, new, and insightful. It also applies to industrial polymerization conditions. This is a seminal contribution of this research to the relevant catalyst literature.*

Now we focus on the genesis of the above microscopic catalyst deactivation using ^1H NMR spectroscopy. Maximum and minimum Spaleck E-1-hexene productivities are shown at 50 °C and 70 °C, respectively. The preactivated precatalyst-cocatalyst fed the reactor. Hence, we design the NMR experiments as presented in Figures 5.7 to 5.10. These figures show the following:

- All spectra at 50 °C and 70 °C are identical.
- The experimental precatalysts and cocatalysts do not decompose and show thermal stability.
- Free TMA and excess TIBA exist in the preactivated precatalyst-cocatalyst mixture.
- The preactivation generates the active catalyst site via reaction between a given precatalyst-cocatalyst system.

The free TMA, being less Lewis acidic, does not activate the experimental precatalysts. MAO, on the other hand, has the following properties [25]:

- It is a superior alkylating agent and Lewis acid, having a greater capacity to produce and stabilize cation-like complexes.
- The resulting anion is far less coordinating than TMA.
- The activation equilibrium involved with MAO, unlike TMA, lies far to the right.

Hence, it acts as the real cocatalyst. But the active role of TMA changes as the copolymerization proceeds and the trial temperature increases. The same remark holds for excess TIBA. They both participate to deactivate the catalyst active site thru formation of M^+-Al heterodinuclear adduct that blocks olefin insertion [50, 51, 52, 55, 58, 60, 61]. See Figure 5.11.

The deactivation role played by the free TMA and the excess TIBA is, in principle, like arene coordination (by an aromatic solvent such as toluene) to the catalyst active site that especially happens for a CGC cation such as $[(Me_4Cp)SiMe_2(N^tBu)]ZrMe^+$ in the presence of *only* $B(C_6F_5)_4^-$ anion [25, 53, 107, 108]. Both phenomena prevent the incoming olefin from insertion into the vacant coordination site.

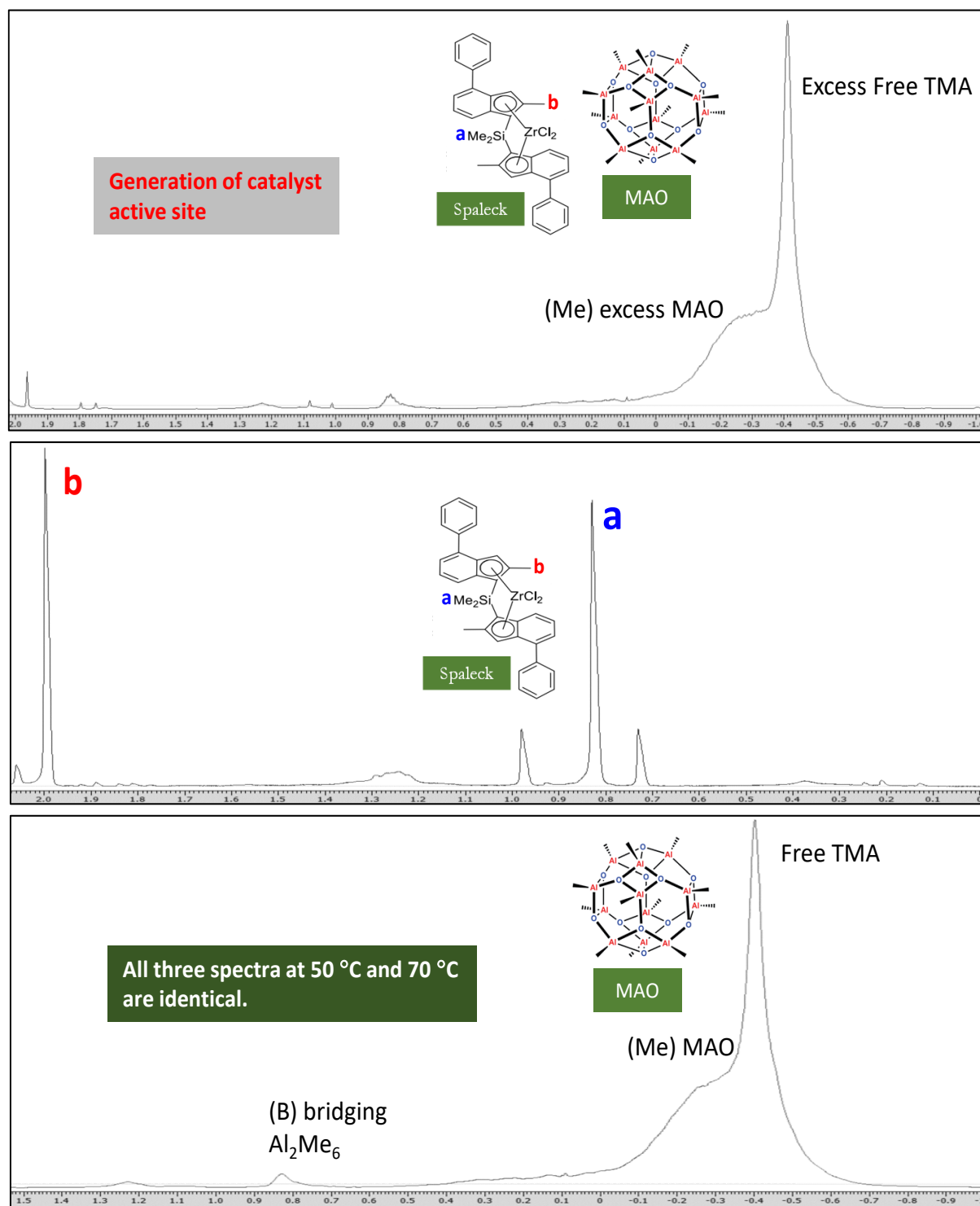


Figure 5.7: Thermal stability of Spaleck precatalyst and MAO cocatalyst, their mutual interaction, and generation of catalyst active sites evaluated using ^1H NMR spectroscopy.

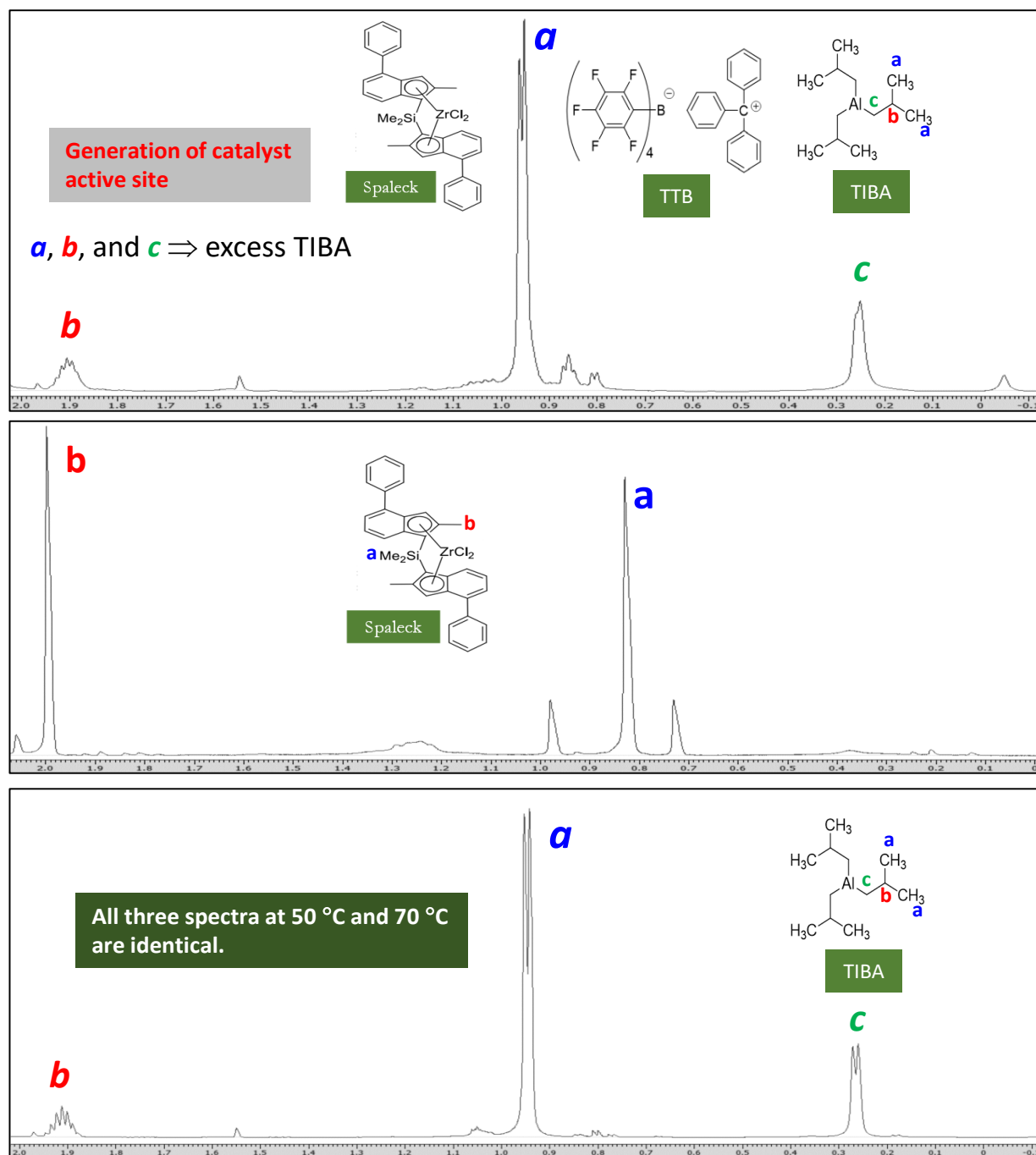


Figure 5.8: Thermal stability of Spaleck precatalyst and (TTB + TIBA) cocatalyst, their mutual interaction, and generation of catalyst active sites evaluated using ^1H NMR spectroscopy.

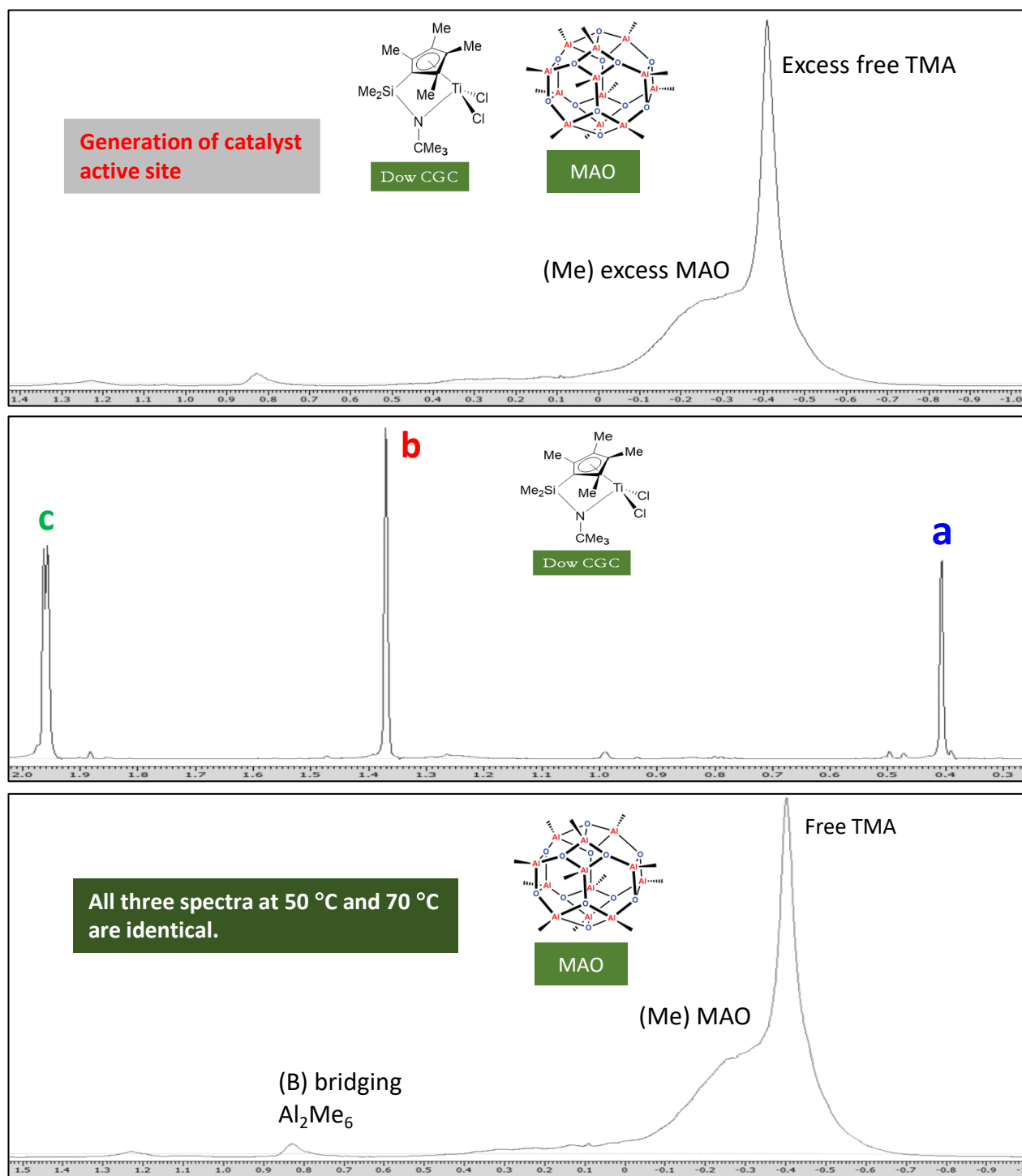


Figure 5.9: Thermal stability of Dow CGC precatalyst and MAO cocatalyst, their mutual interaction, and generation of catalyst active sites evaluated using ^1H NMR spectroscopy.

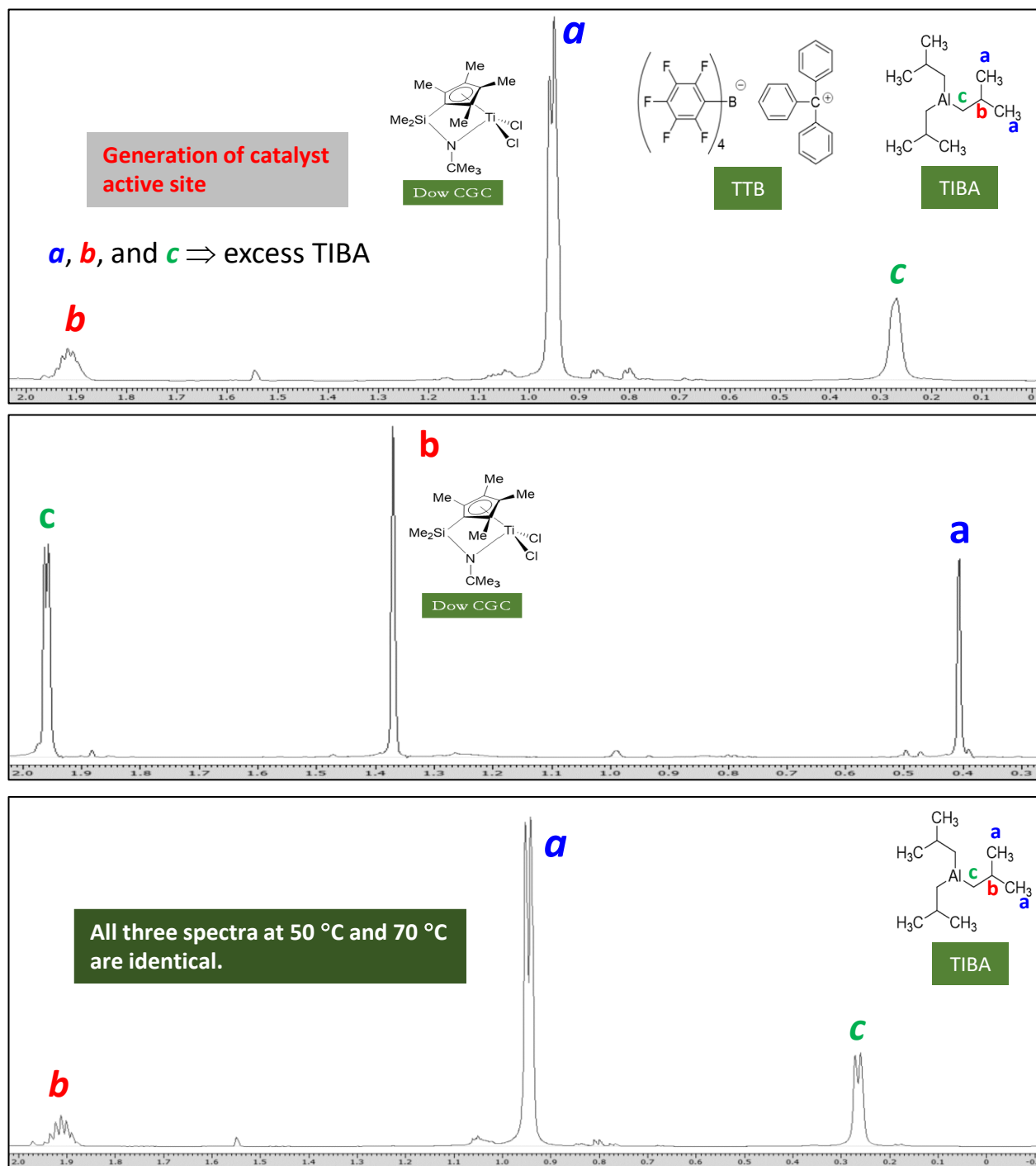


Figure 5.10: Thermal stability of Dow CGC precatalyst and (TTB + TIBA) cocatalyst, their mutual interaction, and generation of catalyst active sites evaluated using ^1H NMR spectroscopy.

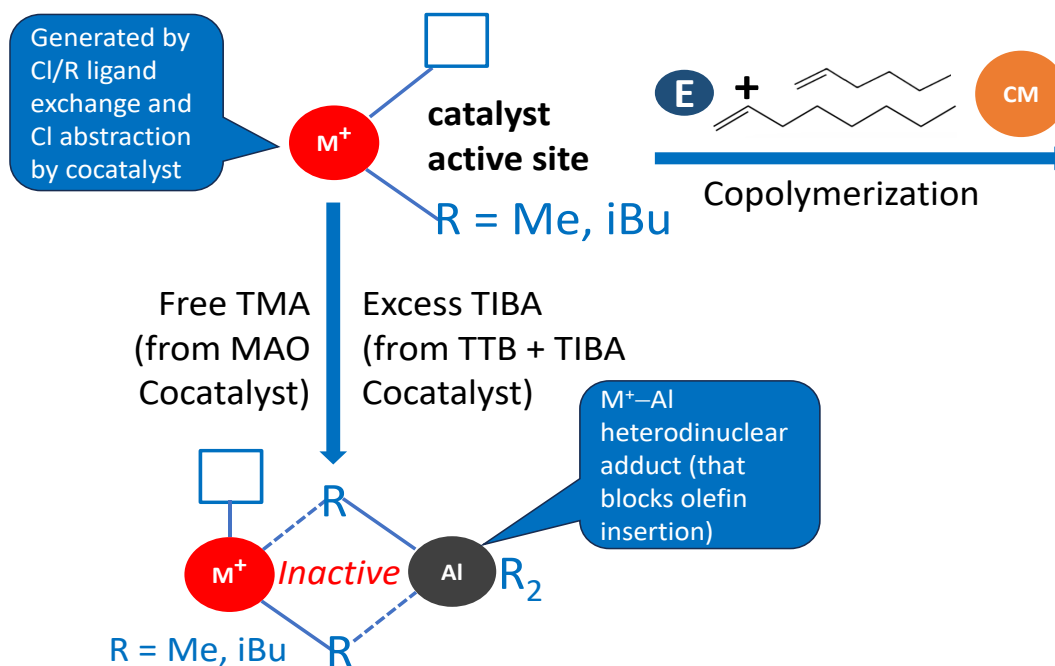


Figure 5.11: Catalyst active site deactivation by MAO free TMA and (TTB + TIBA) cocatalyst excess TIBA.

Figure 5.12 concludes this section discussion. It illustrates how the model-predicted catalyst active site residential environment parameter Z_{1-2}^L concept can be applied to develop catalyst as well as ethylene- α -olefin solution copolymerization process to make better elastomers. It is now possible to depict the polymerization mixture molecular ensemble as a function of the process conditions. *This has not been reported in the literature before.*

5.4.2 Elastomer Chain Growth, Polydispersity Index, and Temperature Effects

The present Spaleck- and Dow CGC-mediated synthesis of elastomers fall under addition polymerization. Here, the development of MW and MWD completes in the very early part of polymerization (1 to several seconds). Increasing polymerization time increases conversion but does not significantly affect average MW. Our MW and MWD report, therefore, holds though the polymerization trials were completed at different run times. Tables 5.7–5.8 summarize the as-

synthesized E–1-hexene and E–1-octene elastomers MWs and PDIs (MWDs) as a function of the experimental precatalyst-cocatalyst systems and temperature. The detailed data are available in Appendix G Tables G.1 to G.8 which have been used to prepare Figure 5.13 and Figure 5.14 originates from the data acquired by the GPC instrument.

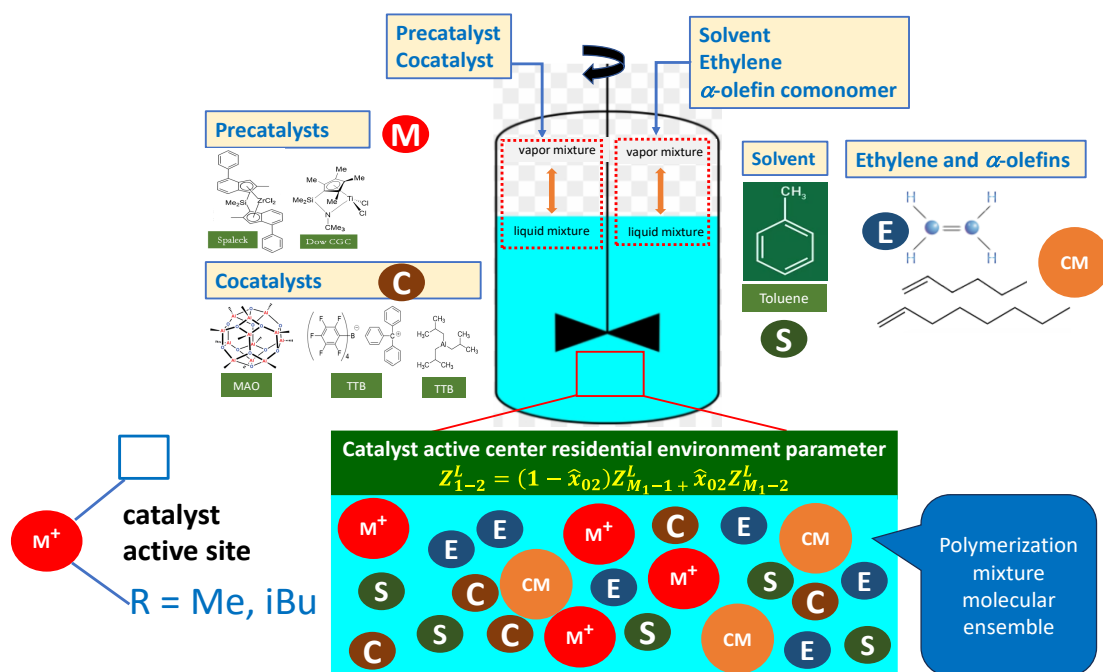


Figure 5.12: Application perspective of model-predicted catalyst active site residential environment parameter Z_{1-2}^L .

Based on the above tables and figures, we list the following common findings:

- M_w overall varies from 100,000 to 300,000 g/mol which reflects the experimental precatalyst chain growth behavior. Under the experimental conditions, all the precatalyst-cocatalyst systems, therefore, make industrial MW level E–1-hexene and E–1-octene elastomers.
- M_w consistently decreases as a function of polymerization temperature.

- PDI (MWD) varies from 2.20 to 5.73 and widens as a function of precatalyst-cocatalyst systems and polymerization temperature. However, strict differentiation, in certain cases, is difficult.

Table 5.7: Summary of as-synthesized E-1-hexene elastomers MWs and PDIs (MWDs).

Precatalyst/cocatalyst system	AICHE J model-predicted X values	M_n (g/mol)	M_w (g/mol)	PDI
Spaleck/MAO	0.7177, 0.6848, 0.6270, and 0.5771.	55,265–99,269	157,067–270,574	2.73–2.84
Spaleck/(TTB + TIBA)		17,875–60,621	102,372–247,737	3.56–5.73
Dow/MAO		29,438–73,982	101,036–198,357	2.68–3.43
Dow/(TTB + TIBA)		50,957–123,373	145,347–270,889	2.20–2.85

Details are available in Appendix G (Tables G.1 to G.4). Pressure = 4 barg. Polymerization temperatures (K) = 313.15, 323.15, 333.15, and 343.15. X , M_n , and M_w are decreasing functions of temperature.

Table 5.8: Summary of as-synthesized E-1-octene elastomers MWs and PDIs (MWDs).

Precatalyst/cocatalyst system	AICHE J model-predicted X values	M_n (g/mol)	M_w (g/mol)	PDI
Spaleck/MAO	0.7177, 0.6848, 0.6270, and 0.5771.	22,978–56,040	123,299–211,860	3.78–5.37
Spaleck/(TTB + TIBA)		23,3462–53,591	120,256–189,323	3.53–5.18
Dow/MAO		40,474–140,332	134,459–322,051	2.30–3.32
Dow/(TTB + TIBA)		57,179–135,518	158,752–308,021	2.27–2.78

Details are available in Appendix G (Tables G.5 to G.8). Pressure = 4 barg. Polymerization temperatures (K) = 313.15, 323.15, 333.15, and 343.15. X , M_n , and M_w are decreasing functions of temperature.

Do the above findings, particularly the latter two, add any new insight to metallocene and post-metallocene catalyst science? We address this question as follows.

Our ^1H NMR experiments show that the preactivated mode of precatalyst-cocatalyst feeding completes the generation of catalyst active sites, and the process is instantaneous. Hence, the rate of generation of catalyst active sites can be considered independent of temperature. On the other hand, the electron rich higher α -olefins, unlike ethylene, very slowly incorporate into the growing polyethylene chain via hindered coordination to the strongly electron-deficient catalyst active site [109]. Under such simplifications, the following can be written [110]: Average MW $\propto$

$\left(\frac{\text{Propagation rate constant}}{\sqrt{\text{Chain transfer rate constant}}} \right) \times [E]$. Here, the first term is temperature-increasing (due to positive comonomer effect [87, 109]) whereas $[E]$ (ethylene concentration) is strongly temperature-decreasing (see Figure 5.4). Note that this type of copolymerization rate-accelerating α -olefin effect occurs due to (i) enhanced olefin diffusion thru the dissolved amorphous elastomer in solvent-comonomer binary liquid and (ii) activation of M^+-H dormant sites. Hence, the effect of $[E]$ is more dominating than the first term which argues for decrease of M_w with temperature. Figure 5.15 illustrates the various ethylene- α -olefin copolymerization chain transfer/termination mechanisms. *This explanation adds new insight to the literature and underscores the merits of the present (i) preactivated precatalyst-cocatalyst feeding mode, (ii) 1H NMR assay, and (iii) binary liquid ethylene solubility modeling work.*

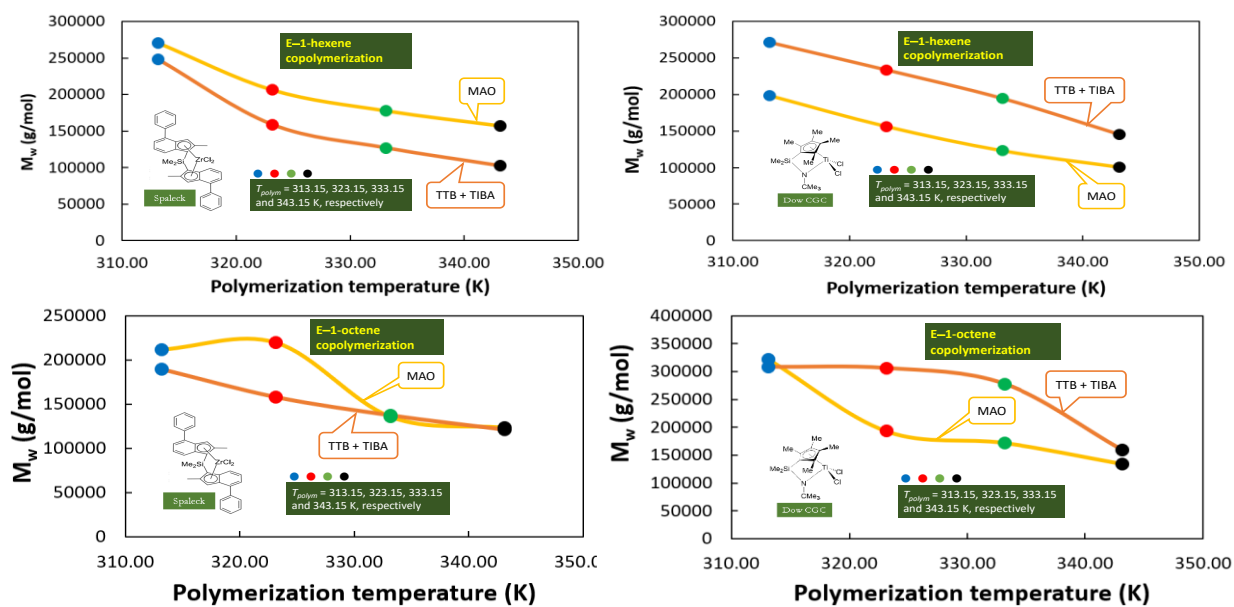


Figure 5.13: Effect of precatalyst-cocatalyst type and temperature on M_w of as-synthesized Spaleck and Dow CGC E-1-hexene and 1-octene elastomers.

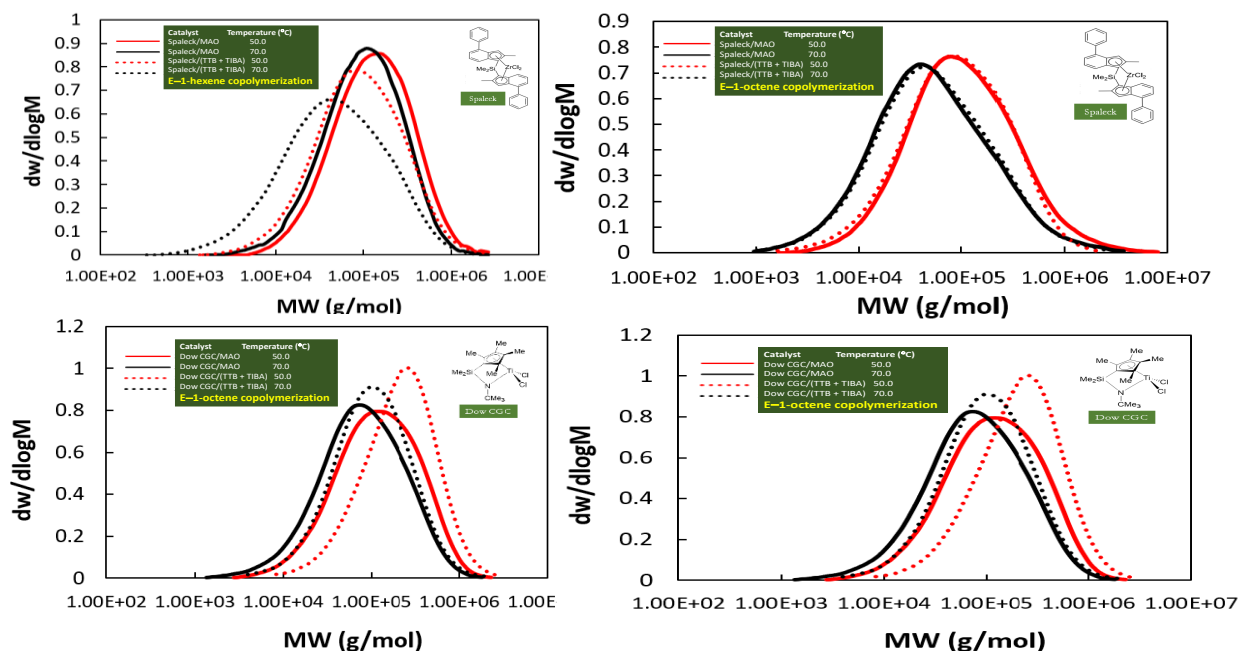


Figure 5.14: Variation of MWD of as-synthesized Spaleck and Dow CGC E-1-hexene and E-1-octene elastomers as a function of precatalyst-cocatalyst type and temperature.

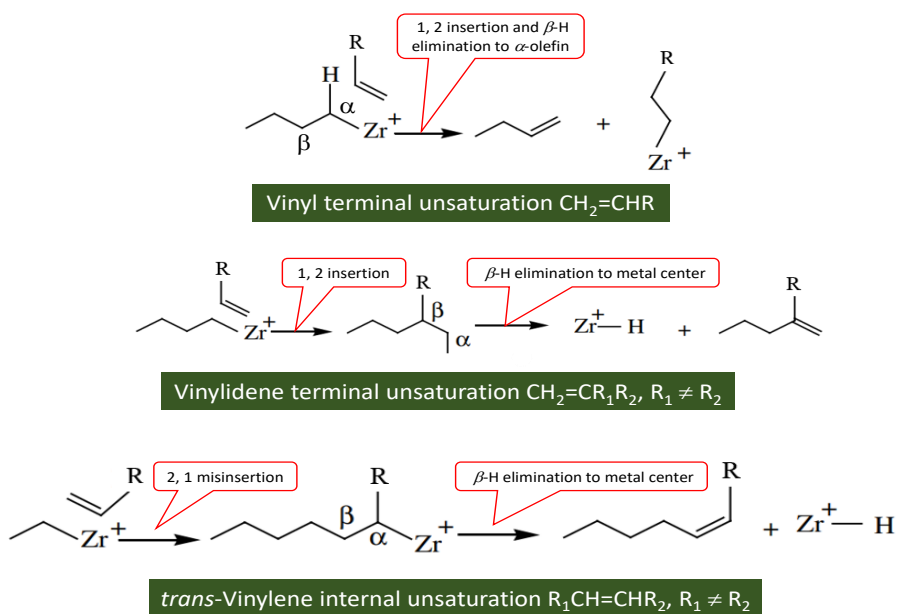


Figure 5.15: Chain termination mechanisms in ethylene- α -olefin copolymerization.

This study PDI (MWD) varies from 2.20 to 5.73. This exceeds Schulz-Flory (SF) most probable value of 2 which is customarily used in the literature to conclude single site (SS) behavior of metallocene and post-metallocene precatalysts. An ideal SS precatalyst has constant rates of

propagation and termination [24]. It is difficult to achieve this in a changing macromolecular environment. The literature reports deconvoluting an experimental MWD into several SF components to predict the existence of multiple catalyst sites [16, 87] and explain the situation $PDI > 2$.

The above literature approaches are subject to criticism. The most probable PDI value (2) fundamentally derives from the mechanism of step growth polymerization [111], *ignoring active monomer functionality deactivation as well as kinetic and mass transfer effects*. The coordination addition polymerization mechanism significantly differs from that of step growth polymerization. Hence, to apply the step growth SF PDI to evaluate SS or multiple site precatalyst is pretty subjective. We, therefore, revisit this situation as follows.

Refer to Figure 5.11 and Figure 5.15 that represent catalyst active site generation and chain termination, respectively. In each case, kinetic and mass transfer effects are involved. The kinetic effect originates from interaction of the incoming olefins with the polyalkyl *pseudo*-single site (SS) catalyst active center $L_nM^+R(\text{polyolefin} \Rightarrow (\text{CH}_2\text{--CH}_2)_n\text{H})$. The mass transfer effect is generated by the transport of the olefins, particularly ethylene thru the dissolved amorphous elastomer in the solvent-comonomer binary liquid. This prompts us to introduce the *kinetic- and diffusion-controlled pseudo single-site catalyst center* concept (*having dynamic steric and electronic environment*). This analysis retains the original SS catalyst function with changing kinetic and mass transfer effects. The PDI reflects the competition between chain propagation rate and chain termination rate [24]. The positive comonomer effect [87, 109] increases the former while the various chain transfer reactions (see Figure 5.15) add to the latter. $PDI > 2$ happens when propagation rate exceeds chain termination rate, mediated by the polyalkyl *pseudo*-single site (SS)

catalyst active center. This argument aligns with the previous decreasing M_w –temperature explanation.

5.4.3 Catalyst-Mediated Elastomer Microstructures, Morphology, and Thermal Properties

We design this section as follows:

- Summarize the ^{13}C NMR triad mole fractions of the as-synthesized E–1-hexene elastomers (Table 5.9), and their microstructural parameters (Tables 5.10A and 5.10B),
- Summarize the ^{13}C NMR triad mole fractions of the as-synthesized E–1-octene elastomers (Table 5.11), and their microstructural parameters (Tables 5.12A and 5.12B),
- Elucidate the copolymerization mechanism and mass transfer effect on the relevant microstructural parameters and catalyst active site type using Tables 5.9 to 5.12 data,
- Illustrate the precatalyst-cocatalyst structural effect on ethylene sequence length distributions $w_1(n)$ (Figure 5.16) and 1-hexene sequence length distributions $w_2(n)$ (Figure 5.17) of the as-synthesized E–1-hexene elastomers,
- Illustrate the precatalyst-cocatalyst structural effect on ethylene sequence length distributions $w_1(n)$ (Figure 5.18) and 1-octene sequence length distributions $w_2(n)$ (Figure 5.19) of the as-synthesized E–1-octene elastomers,
- Highlight the novel and new insight added to the creation of amorphous E– α -olefin elastomer morphology (Figures 5.20, 5.21, and 5.22),
- Summarize the peak melting and peak crystalline temperatures, glass transition temperatures, and Crystaf results of the as-synthesized E–1-hexene elastomers (Table 5.13),

- Summarize the peak melting and peak crystalline temperatures, glass transition temperatures, and Crystaf results of the as-synthesized E–1-octene elastomers (Table 5.14),
- Illustrate the precatalyst-cocatalyst structural effect on glass transition temperature T_g of the as-synthesized E-1-hexene elastomers (Figure 5.23),
- Illustrate the precatalyst-cocatalyst structural effect on glass transition temperature T_g of the as-synthesized E–1-octene elastomers (Figure 5.24), and
- Compare the DSC experimental T_g s with those calculated by the Gordon–Taylor relation [112] and elucidate the difference and the role that the free volume theory plays in this regard.

Table 5.9: Summary of ^{13}C NMR triad mole fractions of as-synthesized E–1-hexene elastomers determined using Randall method.

Precatalyst/cocatalyst system	EEE	EEH	HEH	EHE	EHH	HHH	E	H
Spaleck/MAO	0.32–0.54	0.21–0.27	0.04–0.11	0.13–0.15	0.07–0.10	0.01–0.06	0.69–0.79	0.21–0.31
Spaleck/(TTB + TIBA)	0.41–0.59	0.14–0.21	0.06–0.10	0.08–0.11	0.09–0.13	0.05–0.11	0.68–0.78	0.22–0.32
Dow/MAO	0.41–0.55	0.21–0.26	0.03–0.06	0.08–0.12	0.08–0.13	0.03–0.05	0.71–0.80	0.20–0.29
Dow/(TTB + TIBA)	0.43–0.51	0.24–0.26	0.03–0.05	0.10–0.14	0.08–0.11	0.01–0.02	0.74–0.79	0.21–0.26

Details are available in Appendix G (Tables G.9 to G.12). E = Ethylene (mole fraction), H = 1-hexene (mole fraction). Polymerization temperatures (K) = 313.15, 323.15, 333.15, and 343.15.

Table 5.10A: Summary of Group A ^{13}C NMR microstructural parameters for as-synthesized E–1-hexene elastomers.

Precatalyst/cocatalyst system	Eqn 3.4 $r_1(X)$	$r_1 \neq f(X)^*$	Eqn 3.5 $r_2(X)$	$r_2 \neq f(X)^*$	$r_1(X) \times r_2(X)$	χ	$\langle r_1(X)r_2(X) \rangle \neq f(X)$	ρ
Spaleck/MAO	3.15–6.89	2.26–3.98	0.17–0.38	0.29–0.53	1.15–1.21	0.98–0.96	1.01–1.25	0.89–1.10
Spaleck/(TTB + TIBA)	4.40–9.15	3.01–5.28	0.42–0.88	0.70–1.17	2.10–4.15	0.68–0.84	1.92–3.88	1.10–1.38
Dow/MAO	4.12–9.52	2.95–5.24	0.33–0.44	0.60–0.61	1.80–3.15	0.79–0.87	1.84–2.80	1.10–1.36
Dow/(TTB + TIBA)	4.11–7.60	2.95–4.18	0.21–0.27	0.37–0.45	1.08–1.71	0.90–0.98	1.14–1.66	1.01–1.08

Details are available in Appendix G (Tables G.13A, G.14A, G.15A, and G.16A). *Copolymerization propagation rate-exclusive statistical approach or $X = 1$ (incorrect). X = Ratio of molar concentrations of monomer 1 and monomer 2 (comonomer). Polymerization temperatures (K) = 313.15, 323.15, 333.15, and 343.15.

Table 5.10B: Summary of Group B ^{13}C NMR microstructural parameters for as-synthesized E-1-hexene elastomers.

Precatalyst/cocatalyst system	Eqn T9.2a $L_1 \text{ NAV}$	Eqn T9.11 $n_1 \text{ NAV}$	Eqn T9.2b $L_2 \text{ NAV}$	Eqn T9.11 $n_2 \text{ NAV}$	Eqn T9.12 $n_1 \text{ WAV}$	Eqn T9.12 $n_2 \text{ WAV}$	CI	MD
Spaleck/MAO	3.26–4.98	3.26–4.98	1.29–1.53	1.29–1.53	5.53–8.95	1.58–2.07	9.91–10.80	70.40–74.95
Spaleck/(TTB + TIBA)	4.01–6.28	4.01–6.28	1.70–2.17	1.70–2.17	7.02–11.57	2.40–4.80	12.63–16.21	47.76–61.62
Dow/MAO	3.95–6.24	3.95–6.24	1.60–1.61	1.60–1.61	6.91–11.47	2.20–2.22	11.97–16.19	58.39–66.33
Dow/(TTB + TIBA)	3.95–5.18	3.95–5.18	1.37–1.45	1.37–1.45	6.90–9.37	1.73–1.90	10.23–13.64	70.15–74.13

Details are available in Appendix G (Tables G.13B, G.14B, G.15B, and G.16B). CI = Cluster index; MD = Monomer dispersity. Polymerization temperatures (K) = 313.15, 323.15, 333.15, and 343.15.

Table 5.11: Summary of ^{13}C NMR triad mole fractions of as-synthesized E-1-octene elastomers determined using Randall method.

Precatalyst/cocatalyst system	EEE	EEO	OEO	EOE	EOO	OOO	E	O
Spaleck/MAO	0.38–0.52	0.18–0.24	0.08–0.14	0.10–0.11	0.08–0.12	0.02–0.05	0.71–0.74	0.22–0.29
Spaleck/(TTB + TIBA)	0.32–0.46	0.19–0.25	0.07–0.09	0.09–0.14	0.12–0.14	0.06–0.08	0.64–0.73	0.27–0.36
Dow/MAO	0.45–0.64	0.16–0.29	0.00–0.06	0.10–0.13	0.07–0.11	0.01–0.03	0.77–0.80	0.20–0.23
Dow/(TTB + TIBA)	0.48–0.53	0.22–0.25	0.03–0.05	0.11–0.13	0.06–0.08	0.01–0.02	0.80–0.82	0.18–0.20

Details are available in Appendix G (Tables G.17 to G.20). E = Ethylene (mole fraction), O = 1-octene (mole fraction). Polymerization temperatures (K) = 313.15, 323.15, 333.15, and 343.15.

Table 5.12A: Summary of Group A ^{13}C NMR microstructural parameters for as-synthesized E-1-octene elastomers.

Precatalyst/cocatalyst system	Eqn 3.4 $r_1(X)$	$r_1 \neq f(X)^*$	Eqn 3.5 $r_2(X)$	$r_2 \neq f(X)^*$	$r_1(X) \times r_2(X)$	χ	$\langle r_1(X)r_2(X) \rangle \neq f(X)$	ρ
Spaleck/MAO	3.81–5.81	3.09–4.30	0.33–0.54	0.49–0.66	1.52–2.10	0.85–0.91	0.94–2.06	0.70–1.18
Spaleck/(TTB + TIBA)	2.52–5.87	2.05–3.68	0.47–0.56	0.69–0.80	1.42–2.95	0.77–0.92	1.53–2.48	1.03–1.23
Dow/MAO	4.64–8.24	3.76–5.16	0.28–0.32	0.35–0.46	1.30–2.32	0.85–0.95	1.40–3.95	0.93–1.97
Dow/(TTB + TIBA)	4.79–6.95	3.89–4.46	0.17–0.24	0.25–0.38	1.02–1.68	0.91–1.00	0.92–1.62	0.89–1.07

Details are available in Appendix G (Tables G.21A, G.22A, G.23A, and G.24A). *Copolymerization propagation rate-exclusive statistical approach or $X = 1$ (incorrect). X = Ratio of molar concentrations of monomer 1 and monomer 2 (comonomer). Polymerization temperatures (K) = 313.15, 323.15, 333.15, and 343.15.

Table 5.12B: Summary of Group B ^{13}C NMR microstructural parameters for as-synthesized E-1-octene elastomers.

Precatalyst/cocatalyst system	Eqn T9.2a $L_{1\text{ NAV}}$	Eqn T9.11 $n_{1\text{ NAV}}$	Eqn T9.2b $L_{2\text{ NAV}}$	Eqn T9.11 $n_{2\text{ NAV}}$	Eqn T9.12 $n_{1\text{ WAV}}$	Eqn T9.12 $n_{2\text{ WAV}}$	CI	MD
Spaleck/MAO	4.40–5.30	4.40–5.30	1.49–1.66	1.49–1.66	7.18–9.60	1.98–2.33	12.30–13.61	60.04–87.47
Spaleck/(TTB + TIBA)	3.05–4.68	3.05–4.68	1.69–1.80	1.69–1.80	5.09–8.35	2.39–2.61	10.16–14.22	56.62–62.20
Dow/MAO	4.76–4.88	4.76–4.88	1.35–1.46	1.35–1.46	8.52–8.77	1.69–1.93	11.03–13.85	70.92–76.57
Dow/(TTB + TIBA)	4.89–5.46	4.89–5.46	1.25–1.38	1.25–1.38	8.77–9.71	1.50–1.77	10.38–12.57	73.39–84.29

Details are available in Appendix G (Tables G.21B, G.22B, G.23B, and G.24B). CI = Cluster index; MD = Monomer dispersity. Polymerization temperatures (K) = 313.15, 323.15, 333.15, and 343.15.

Now we discuss the above Tables 5.9 to 5.12 results for the as-synthesized E-1-hexene and E-1-octene elastomers as follows.

- The triad mole fractions decrease as $\text{EEE} > \text{EEC} > \text{CEC}$, ECE , $\text{ECC} > \text{CCC}$ where C = 1-hexene (H) or 1-octene (O) α -olefin comonomer. Incorporation of the comonomer into the elastomer copolymer backbone varies from 20 mol% to 35 mol% (Tables 5.9 and 5.11).
- Ethylene reactivity ratios $r_1(X)$ s in E-1-hexene copolymerization vary from 3.15–9.52 while 1-hexene reactivity ratios $r_2(X)$ s range from 0.17–0.88. On the other hand, ethylene reactivity ratios $r_1(X)$ s in E-1-octene copolymerization vary from 2.52–8.24 while 1-octene reactivity ratios $r_2(X)$ s range from 0.17–0.56.
- Precatalyst-cocatalyst structures and types do not significantly affect what has been stated above.
- The common microstructural findings in both copolymerizations, fairly unaffected by precatalyst-cocatalyst structures and types, are listed below:

- Each $r_1 \neq f(X)$ is less than the corresponding $r_1(X)$ and each $r_2 \neq f(X)$ is greater than the corresponding $r_2(X)$. $r_1(X)$ and $r_2(X)$ derive from considering conditional probabilities, 1st order Markov statistical model, microkinetic terminal copolymerization model (MTCM) propagation rate expressions, and ethylene solubility X in the solvent-comonomer liquid mixture. $r_1 \neq f(X)$ and $r_2 \neq f(X)$ ignore the latter two factors. The above comparative remark underscores the resulting implications. The first situation underestimates r_1 while the second one overestimates r_2 . This can severely affect catalyst and copolymerization process development.
- $r_1(X) \times r_2(X) > 1$ and $\chi < 1$, both of which indicate blocky tendency with respect to E sequence and comparable EC randomness.
- Additional microstructural parameters for both copolymerizations are compared as follows:

Copolymer type	$L_{1\text{ NAV}} = n_{1\text{ NAV}}$	$L_{2\text{ NAV}} = n_{2\text{ NAV}}$	ρ	CI	MD
E-1H	3.26–6.28	1.29–2.17	0.89–1.38	9.91–16.21	47.76–74.95
E-1O	3.05–5.46	1.25–1.80	0.70–1.97	10.16–14.22	56.62–87.47

The cluster index $CI > 10$ indicates non-Bernoullian statistics. The monomer dispersity $MD < 100$. Hence, 1-hexene or 1-octene tends to sequence repeatedly or cluster but the comonomer sequence block is much shorter than the E sequence block. The corresponding $r_1(X)$ and $r_2(X)$ values support this finding and conclusion.

Figures 5.16 and 5.17 show the ethylene and 1-hexene sequence length distributions, respectively for the as-synthesized E-1-hexene elastomers. Figures 5.18 and 5.19 are analogues

for the E-1-octene elastomers. The findings for both copolymerizations are very similar. Each figure shows highly significant unreacted comonomer amount. The ethylene sequence distributions flatten with increasing polymerization temperature. Precatalyst-cocatalyst structures and types do not appreciably affect these findings.

Now we address the *core result* of this section that derives from the previous overall copolymer microstructural characterization. This relates to the origin of the amorphous elastomer morphology. Figure 5.20 compares the microstructural parameters of the experimental E- α -olefin elastomer copolymers with those of a literature semicrystalline E-1H copolymer (%crystalline = 53.0) [16]. It clearly shows that the amorphous morphology (phase) originates from (i) the significant decrease in crystalline (hard) EEE sequence (I), ethylene backbone mol%, and average ethylene sequence length, and (ii) appreciable increase in comonomer backbone mol%, and amorphous (soft) random EC enchainment (II), and (iii) drastic narrowing of the ethylene sequence length distribution (Figure 5.21). The very minor comonomer blocky CCC sequence (III), having the least backbone contribution, hardly contributes to developing the amorphous (soft) phase (III). The chain folding lamellar crystallization model (Figure 5.22) aligns with what we reported above. Short average ethylene sequence length ($L_{1\text{NAV}} = 3.05\text{--}6.28$), according to recent simulation study [113], resists the crystallization and movement of the copolymer backbones. We, therefore, notice zero to very negligible %crystallinity. This is a pervasive finding in this study with respect to elastomer morphology development and progression. The literature ascribes fringed micelle model (Figure 5.22) to this phenomenon [115]. *But the present study refutes this which is another novel, new, and insightful contribution to the literature.*

Tables 5.13 and 5.14 summarize the peak melting and peak crystalline temperatures, glass transition temperatures, and *Crystaf* results of the as-synthesized E-1-hexene and E-1-octene elastomers, respectively. The DSC %crystallinity values and *Crystaf* results confirm the formation of elastomers under the experimental conditions. However, *Crystaf* cannot differentiate an E-1-hexene elastomer from an E-1-octene one.

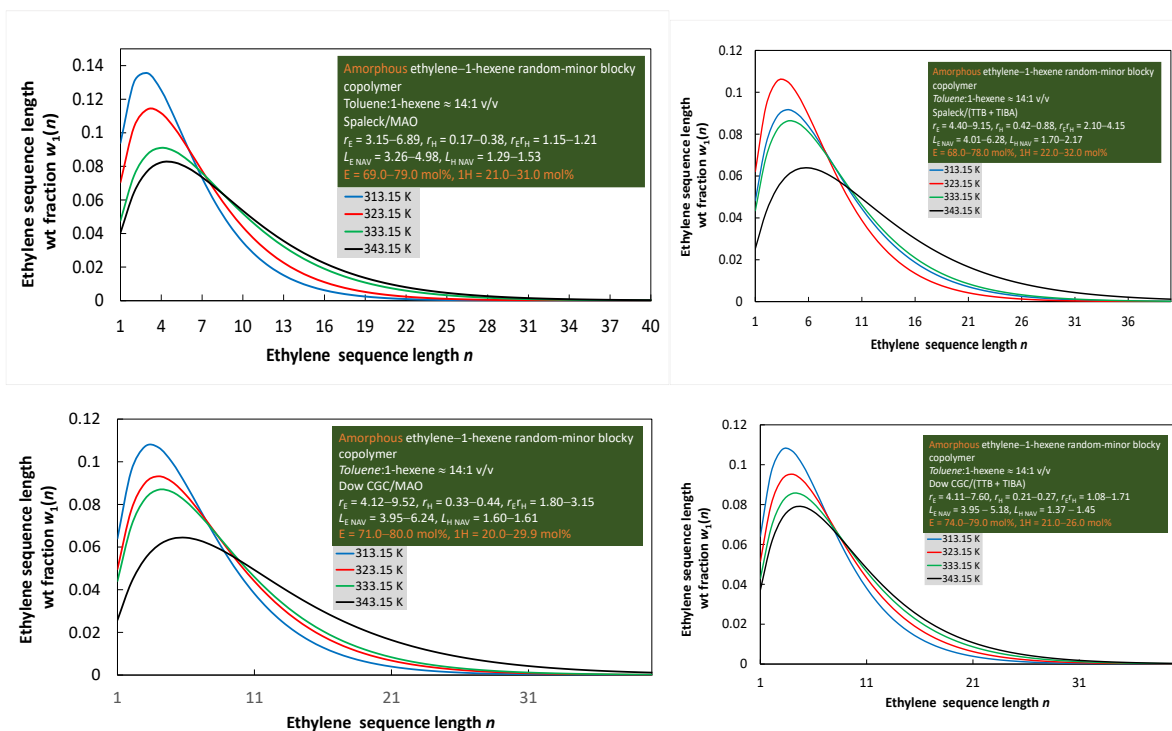


Figure 5.16: Precatalyst-cocatalyst structural effect on ethylene sequence length distributions $w_1(n)$ of the as-synthesized E-1-hexene elastomers.

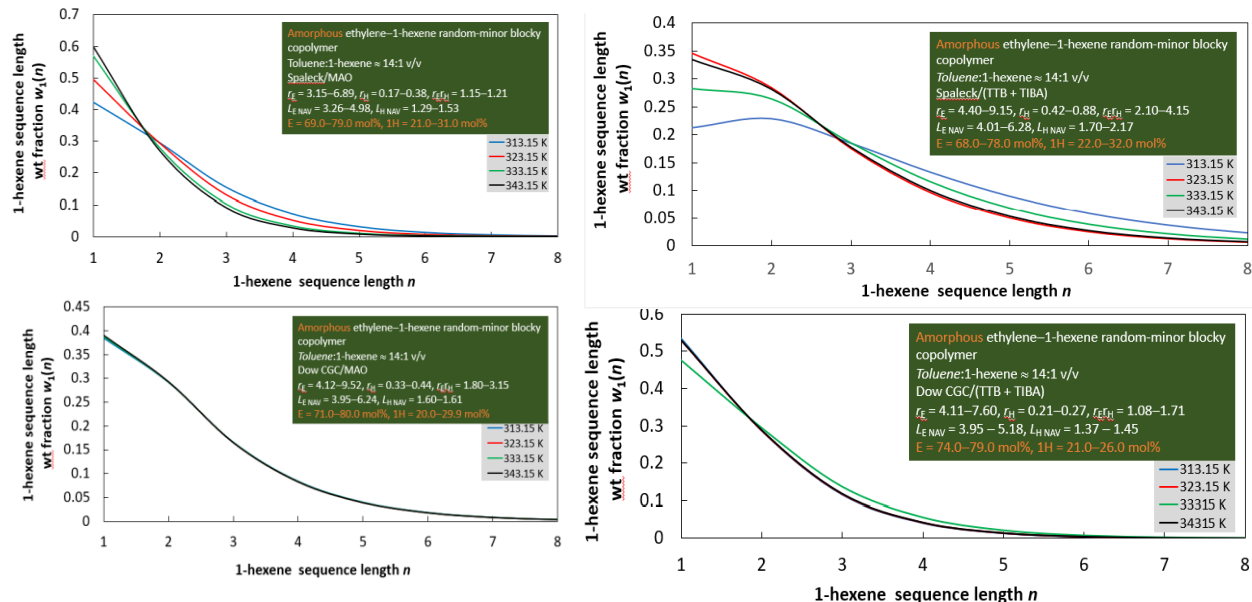


Figure 5.17: Precatalyst-cocatalyst structural effect on 1-hexene sequence length distributions $w_2(n)$ of the as-synthesized E-1-hexene elastomers.

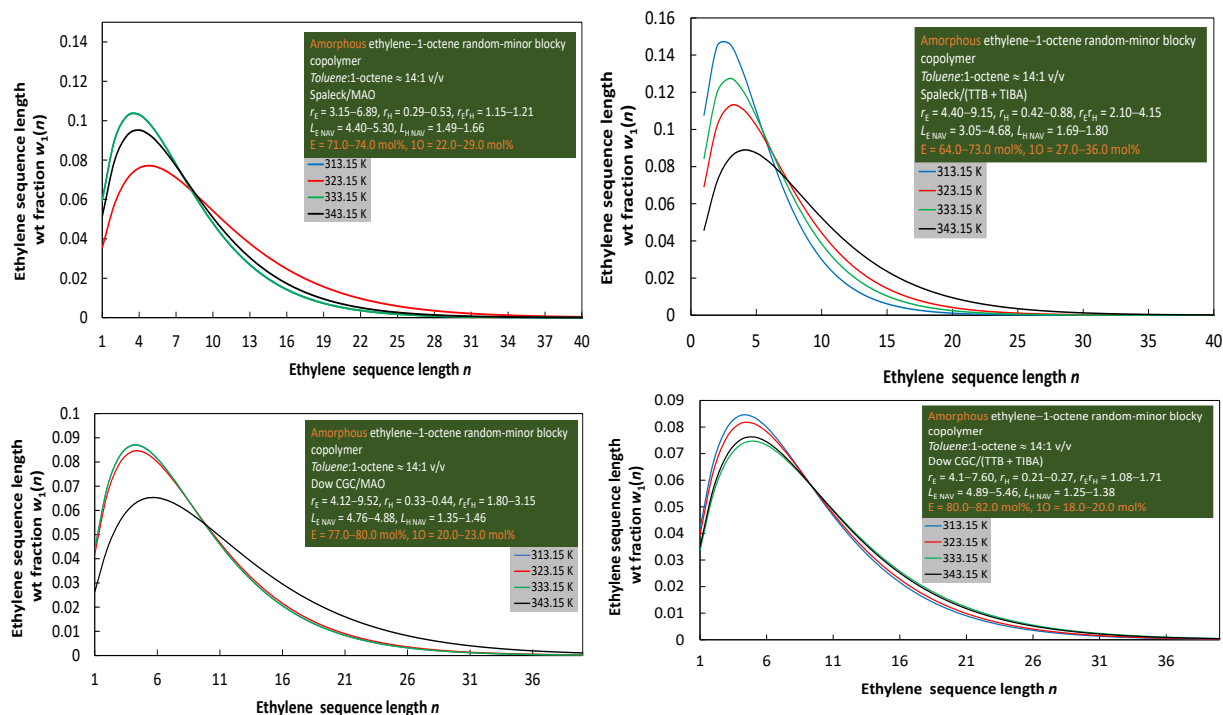


Figure 5.18: Precatalyst-cocatalyst structural effect on ethylene sequence length distributions $w_1(n)$ of the as-synthesized E-1-octene elastomers.

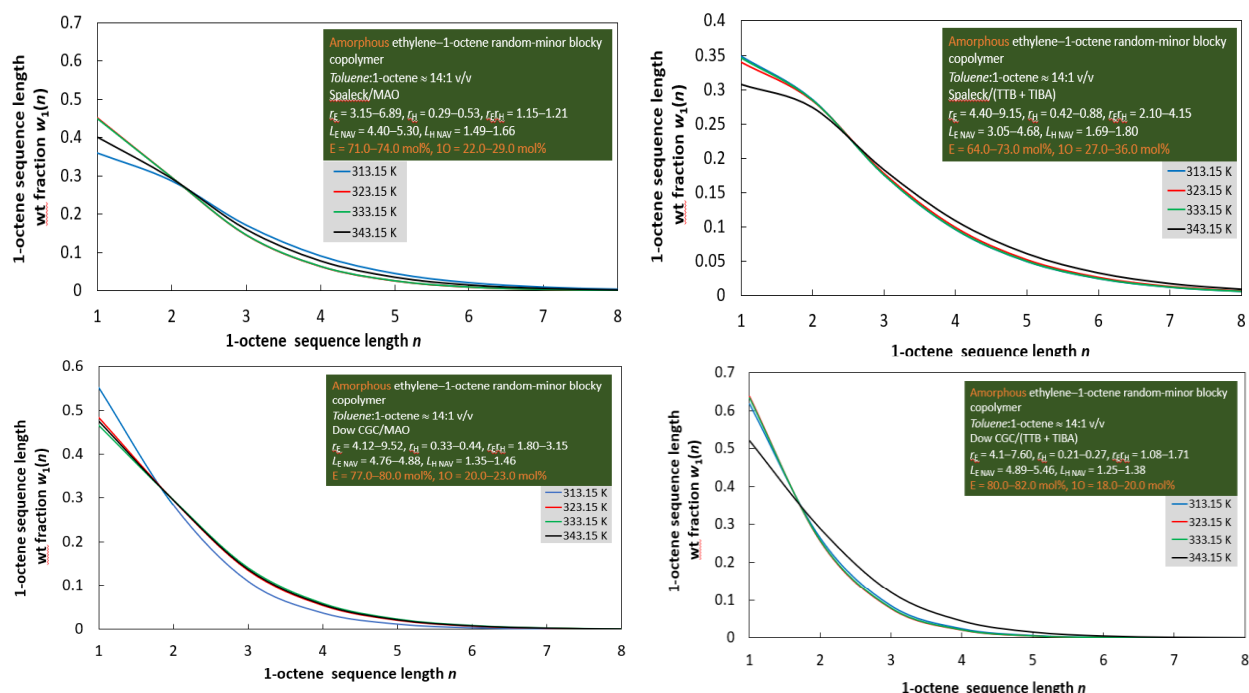


Figure 5.19: Precatalyst-cocatalyst structural effect on 1-octene sequence length distributions $w_2(n)$ of the as-synthesized E-1-octene elastomers.

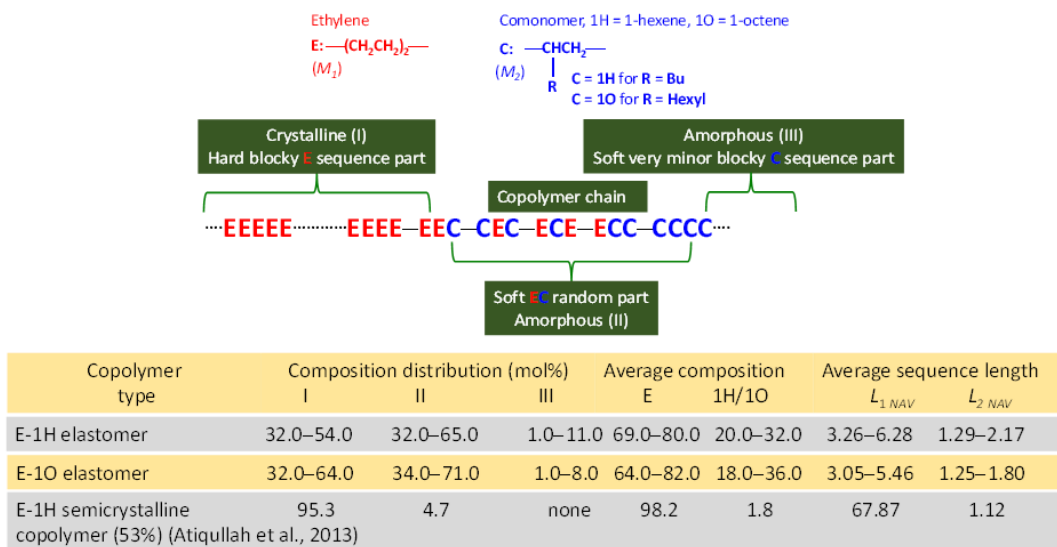


Figure 5.20: New insight regarding the role played by ethylene sequence length progression in creating amorphous E- α -olefin copolymeric elastomers.

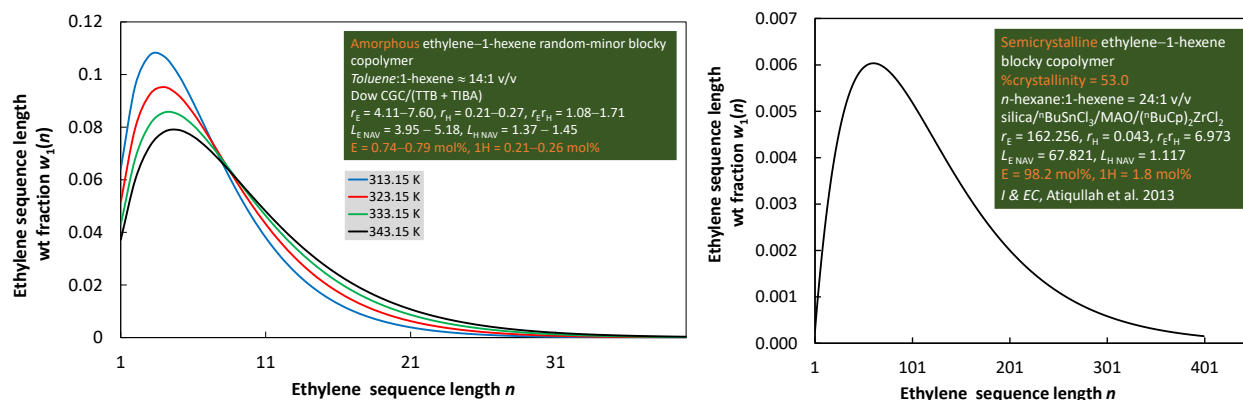


Figure 5.21: Comparison of ethylene sequence length distribution and microstructural parameters of a semicrystalline blocky E-1-hexene copolymer with those of selected as-synthesized amorphous E-1-hexene elastomers.

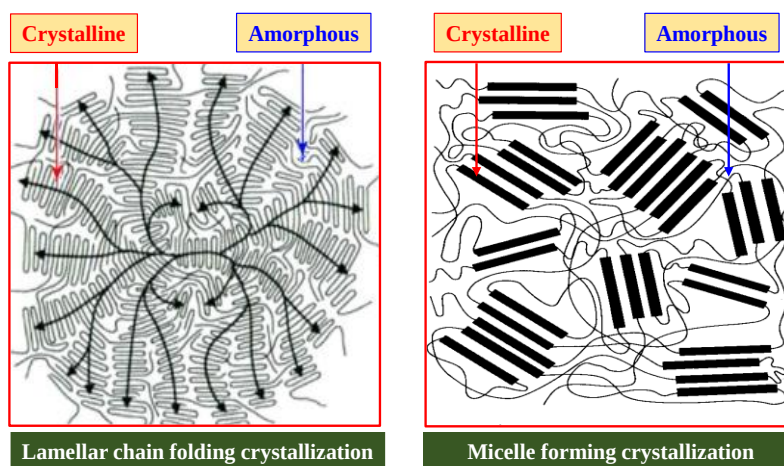


Figure 5.22: Chain folding lamellar model versus fringed model of polymer crystallization.

Figures 5.23 and 5.24 illustrate that precatalyst-cocatalyst structures do not affect glass transition temperature T_g of the as-synthesized E-1-hexene and E-1-octene elastomers, respectively. They also compare the DSC T_g values of both elastomers with those calculated by the Gordon–Taylor relation [72, 112]. The Gordon T_g values are consistently lower. The reason is that the as-synthesized E-1-hexene and E-1-octene elastomers are 30–70% random copolymer whereas Gordon relation applies to a fully random copolymer.

The average DSC T_g value of the as-synthesized E-1-hexene elastomer is $-64.0\text{ }^{\circ}\text{C}$ while that of E-1-octene one is $-69.0\text{ }^{\circ}\text{C}$. The lower E-1-octene T_g (by $-5.0\text{ }^{\circ}\text{C}$) can be attributed to the influence of side chain length, steric, and flexibility on the elastomer free volume. See Figure 5.25. Note that the continuity of ethylene sequence length controls the %crystallinity while the amount, size, and steric of the comonomer side chain regulates T_g . Controlling both properties develops versatile advanced elastomer applications.

Table 5.13: Summary of as-synthesized E-1-hexene elastomers peak melting and peak crystalline temperatures, glass transition temperatures, and Crystaf results.

Precatalyst/cocatalyst system	Peak melting temperature T_m ($^{\circ}\text{C}$)	Peak crystalline temperature T_c ($^{\circ}\text{C}$)	% crystallinity	Glass transition temperature T_g ($^{\circ}\text{C}$)	As-synthesized elastomer Crystaf results*
Spaleck/MAO	0.00–125.36	0.00–113.31	0.67–4.50	-64.19 to -65.13	Dissolved elastomer precipitation at $25 \leq T(^{\circ}\text{C}) \leq 30$
Spaleck/(TTB + TIBA)	0.00–124.31	0.00–114.27	1.09–11.04	-61.41 to -64.05	
Dow/MAO	0.00–105.74	0.00–85.34	0.00–3.83	-63.46 to -64.82	
Dow/(TTB + TIBA)	0.00–124.58	0.00–119.68	0.07–0.80	-62.92 to -65.58	

Details are available in Appendix G (Tables G.25 to G.32). * Cooling rate = $0.2\text{ }^{\circ}\text{C}/\text{min}$. Indicates liquid-solid phase separation. Polymerization temperatures (K) = 313.15, 323.15, 333.15, and 343.15.

Table 5.14: Summary of as-synthesized E-1-octene elastomers peak melting and peak crystalline temperatures, glass transition temperatures, and Crystaf results.

Precatalyst/cocatalyst system	Peak melting temperature T_m ($^{\circ}\text{C}$)	Peak crystalline temperature T_c ($^{\circ}\text{C}$)	% crystallinity	Glass transition temperature T_g ($^{\circ}\text{C}$)	As-synthesized elastomer Crystaf results*
Spaleck/MAO	122.64–124.76	96.81–113.18	3.99–10.03	-69.51 to -69.90	Dissolved elastomer precipitation at $25 \leq T(^{\circ}\text{C}) \leq 30$
Spaleck/(TTB + TIBA)	0.00–124.07	0.00–111.67	0.00–5.71	-68.68 to -70.54	
Dow/MAO	0.00–96.62	0.00–75.71	0.00–1.93	-67.00 to -67.87	
Dow/(TTB + TIBA)	0.00–124.71	0.00–112.88	0.00–1.13	-67.94 to -69.07	

Details are available in Appendix G (Tables G.33 to G.40). * Cooling rate = $0.2\text{ }^{\circ}\text{C}/\text{min}$. Indicates liquid-solid phase separation. Polymerization temperatures (K) = 313.15, 323.15, 333.15, and 343.15.

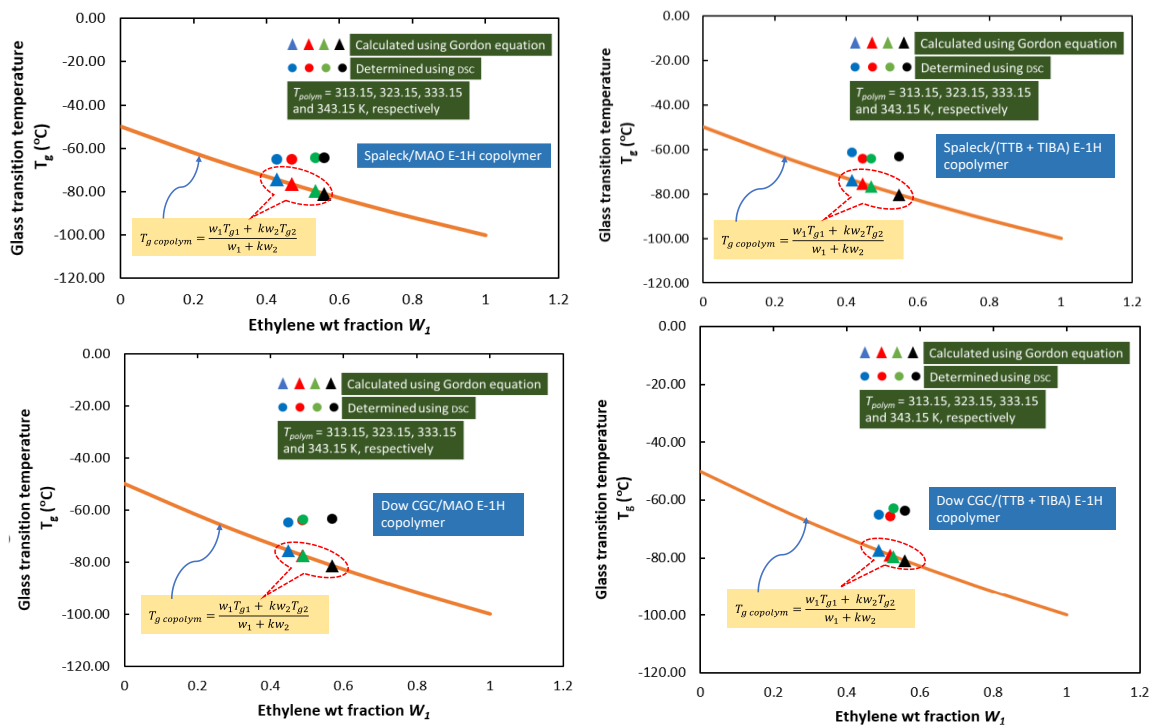


Figure 5.23: Precatalyst-cocatalyst structural effect on glass transition temperature T_g of the as-synthesized E-1-hexene elastomers.

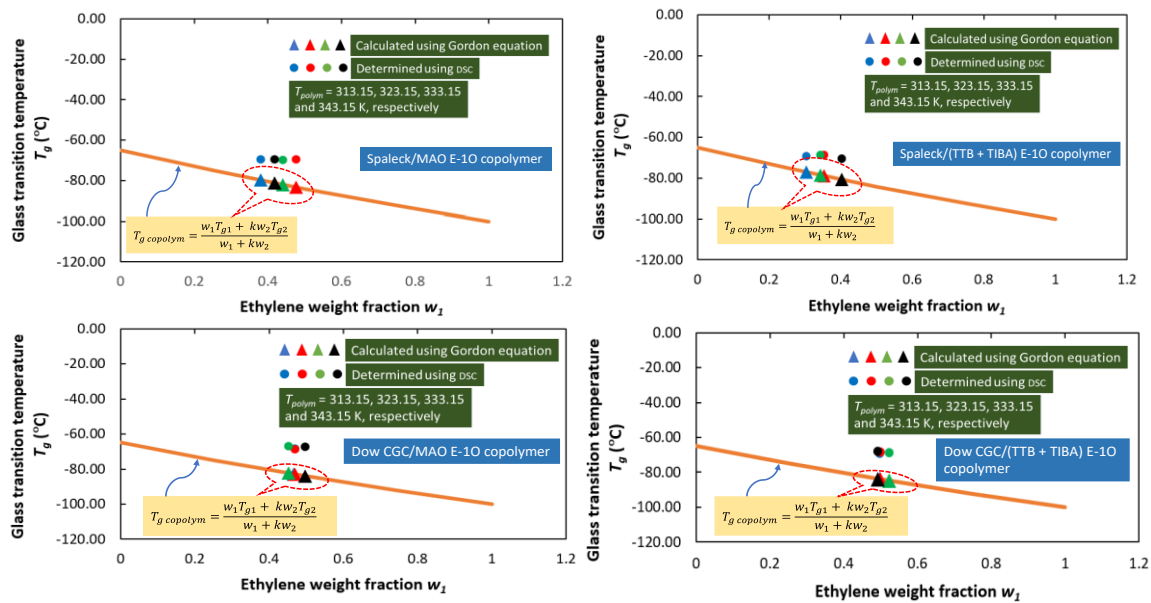


Figure 5.24: Precatalyst-cocatalyst structural effect on glass transition temperature T_g of the as-synthesized E-1-octene elastomers.

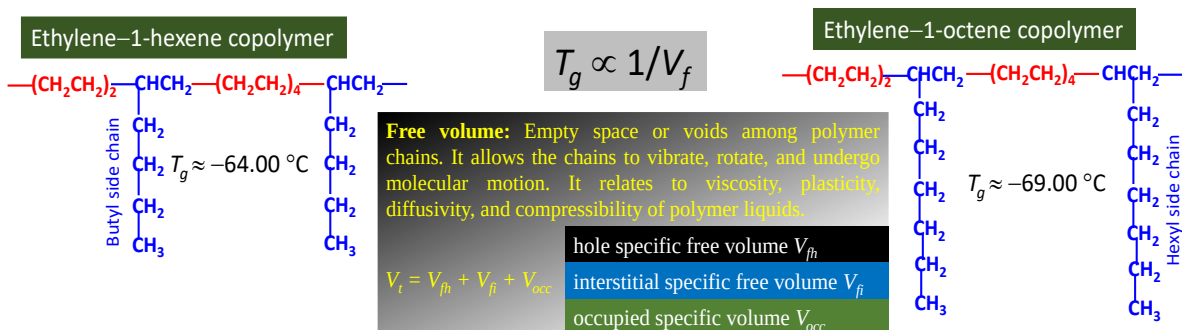


Figure 5.25: Effect of 1-hexene and 1-octene side chain length, steric, and flexibility on free volume and glass transition temperature T_g of the as-synthesized elastomers. |

CHAPTER 6

RECOMMENDATIONS FOR FUTURE WORK

The recommendations for future work are listed below:

- **Chain transfer reactions and mechanisms:** The present study did not investigate the various chain transfer reactions and mechanisms involved in E-1-hexene and E-1-octene semicrystalline to elastomeric copolymerizations. Include E-1-decene copolymerization as well. Evaluate them using FTIR and ^1H NMR spectroscopies and compare the findings against those of ethylene, 1-hexene, 1-octene, and 1-decene homopolymerizations, as well as investigate the ethylene and comonomer sequence and randomness effects on them. The proposed work is important from the viewpoint of polymer degradation and stabilization.
- **Higher temperature and pressure study:** This work considered elastomer synthesis at 40 °–70 °C and 4 bar(g). It introduced several new concepts and approaches such as catalyst active site environment parameter, *polyalkyl* pseudo single-site (SS) catalyst active center, copolymer elastomer morphology progression, and Gordon–Taylor T_g model. Evaluate them at higher temperatures (70 °C – 90 °C) and pressures (8–12 barg). This will better help process development.
- **Precatalyst-cocatalyst activation, and catalyst system stability and deactivation:** Design and fabricate a customized NMR-tube reactor. Investigate precatalyst-cocatalyst activation, and catalyst system stability and deactivation by conducting in-situ elastomeric copolymerization in it and acquiring the necessary ^1H NMR and ^{13}C NMR data. This will generate more realistic knowledge regarding catalyst activation, stability, and deactivation.

- **Application of emerging postmetallocenes precatalyst:** Postmetallocenes such as tridentate titanium [8, 11] and tetradentate zirconium postmetallocenes [11, 10] and Nomura (cyclopentadienyl)(aryloxy)titanium postmetallocenes [13] have been also reported in the literature to incorporate α -olefin comonomer as high as 50 mol%. Revisit the concerned copolymerization phenomena using the new concepts and approaches this study developed, such as catalyst active site environment parameter, *polyalkyl* pseudo single-site (SS) catalyst active center, copolymer elastomer morphology progression, and Gordon–Taylor T_g model. This will further elucidate precatalyst-cocatalyst structure versus performance relation.

- **Blending and miscibility study:** Determine how the comonomer short chain branching (SCB) and its structure affect blend compatibility and miscibility, morphology, and phase transformation. Model the dynamic thermal and phase transition behavior and morphology development of *i*-PP and random PP (a copolymer of propylene and a small amount of ethylene or α -olefin) and their blends with the as-synthesized elastomers using DSC. The resulting knowledge will add new insight to *i*-PP or random PP blend miscibility and compatibility, which will eventually lead to novel product and application development. Focus on the synthesis of elastomers, with such comonomer incorporation levels, that mix with *i*-PP or random PP at broad blend compositions. Develop blends that produce variable PP *spherulitic morphologies* and significantly improve impact property.

Appendix A

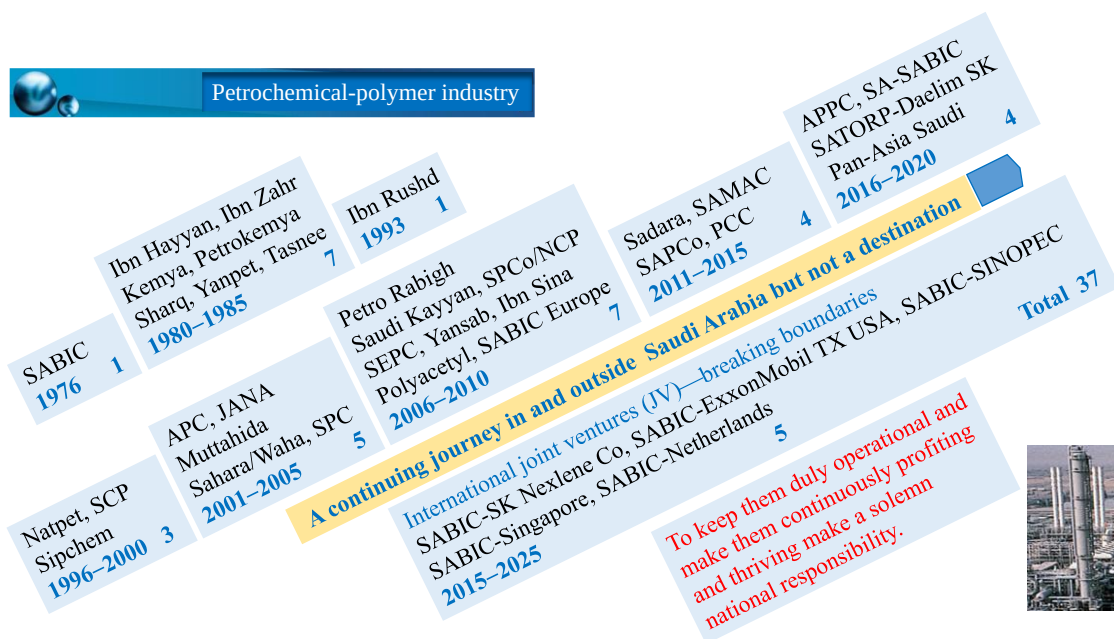
Research theme background and thesis committee

Yahya A. Rawas is a junior member of applied polyolefin catalyst research at SABIC Technical Center (STC) KAUST. SABIC wants him to grow as a future leader in this catalyst area because catalyst makes the heart of polyolefin synthesis, manufacture, process, and diverse applications, and hence meets the growing market needs. Mark Vlaar and Sensei Nicolaas Friederichs, both Senior Researchers, STC Geleen, The Netherlands (one of Europe's largest polymer research centers) are Yahya's current managers.

Dr. Muhammad Atiqullah, Ex-Senior Research Engineer of Research Institute Interdisciplinary Research Center for Refining & Advanced Chemicals (RI-IRCRAC) (and a Full Professor at KFUPM) devoted his 35-year research career to very successfully conducting (as the project manager) and leading a series of strategic metallocene and post-metallocene catalyst research projects for SABIC. During this period, Dr. Hassan A. Al-Muallem, Associate Professor, Department of Chemistry collaborated with Dr. Atiqullah, especially in the long-term metallocene project. In this continued lengthy catalyst research journey, Dr. Atiqullah actively collaborated with researchers at STCs Geleen, Riyadh, and Bangalore. Hence, Dr. Atieh Aburaqaba (SABIC Polyolefin Catalyst Research Senior Advisor). Vlaar, and Sensei Friederichs strongly advised Yahya to conduct his MS thesis research under the guidance of Dr. Atiqullah. Dr. Atiqullah, during his research career at IRCRAC, earned SAR 83.5 million (about USD 22.25 million) that results from his leadership. Accordingly, Dr. Al-Muallem serves as the advisor and Dr. Atiqullah, being external to the Department of Chemistry, as the co-advisor of this MS thesis. Other Chemistry faculty members who serve on this thesis committee are Distinguished Prof. S. Asrof Ali, Prof. Mohammed Abu Jafar Mazumdar, and Dr. Ahmed B. Al-Harbi.

Appendix B

Saudi petrochemical–polymer industry growth profile [114]



Saudi Polymer-Plastic Industries

Saudi petrochemical-polymer industries



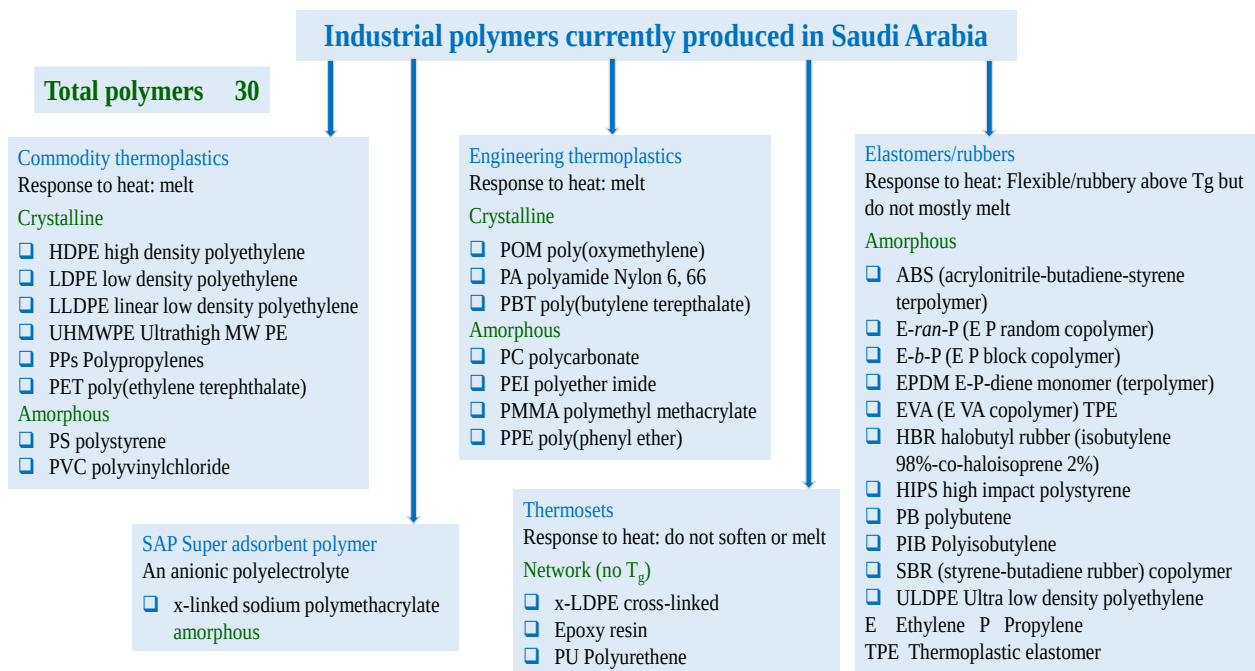
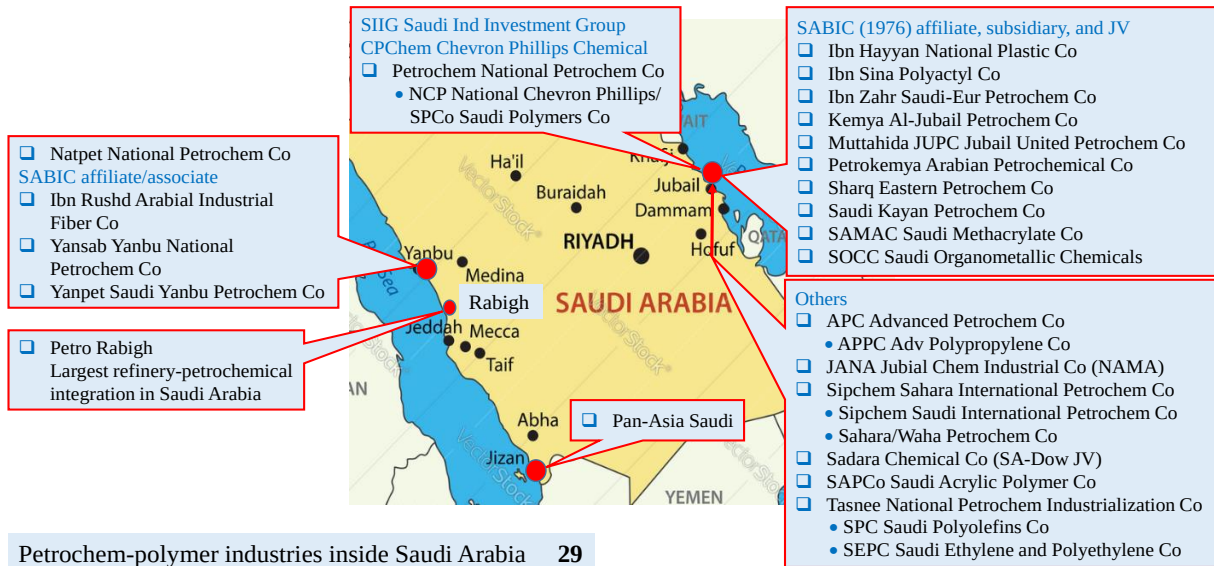
Polymer compound and additive masterbatch industries



Polymer processors/converters and plastic industries

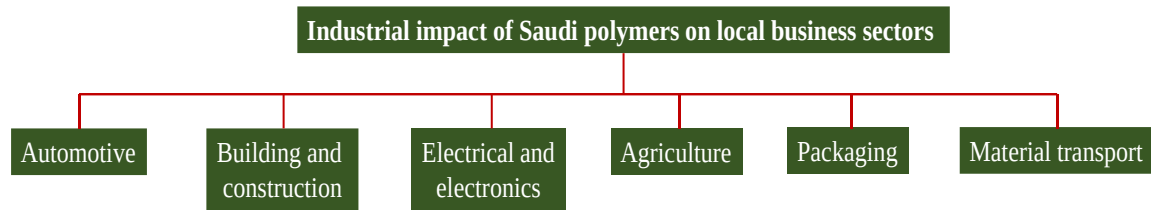


Saudi petrochemical–polymer industry geographical distribution [114]



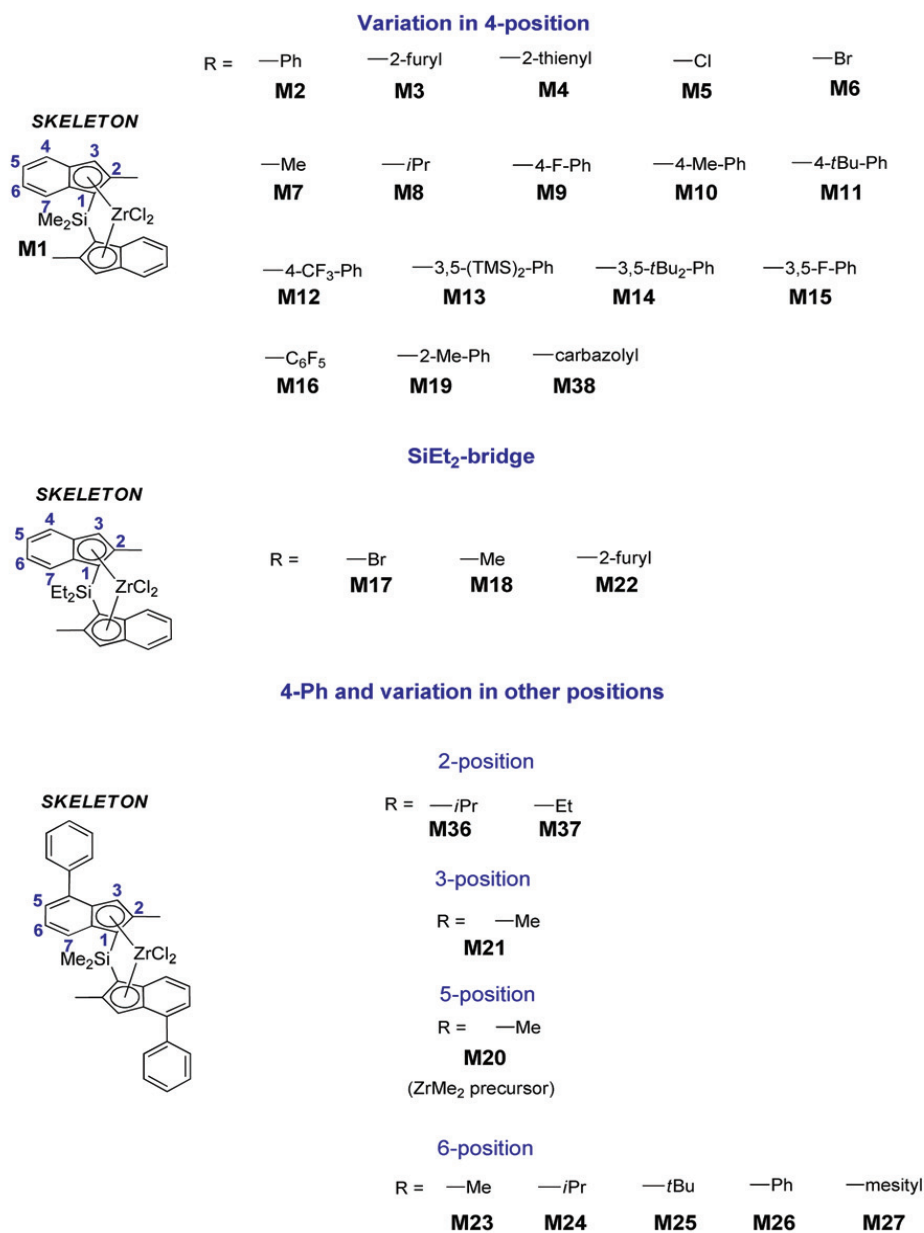
Ranking of Saudi polymers by production volume [114]

Polymer type	Production vol (kmtpa)	Rank	Polymer type	Production vol (kmtpa)	Rank
Polyethylenes	9520	1	Polystyrene	335	8
Polypropylenes	6725	2	Epoxy resin	120	9
PET	2570	3	SAP	80	10
PVC	750	4	PBT	63	11
Elastomer	680	5	POM	50	12
Polycarbonate	520	6	Nylon	50	12
Polyurethane	400	7	PMMA	40	13



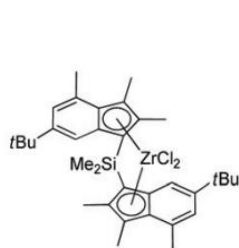
Appendix C

Spaleck's zirconocenes used by Ehm et al. [2020] to evaluate positional substitution effect on ethylene-1-hexene copolymerization [21]

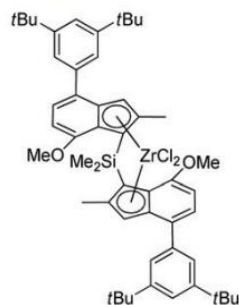


Spaleck's zirconocenes used by Ehm et al. to evaluate positional substitution effect on ethylene–1-hexene copolymerization [21]

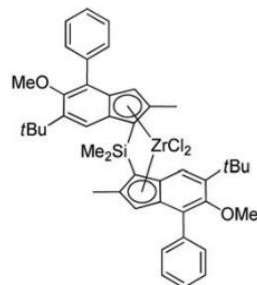
Complex Variations



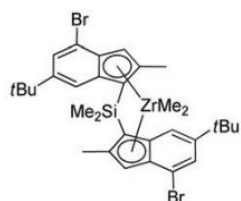
M28



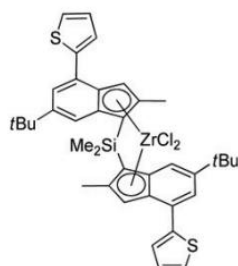
M29



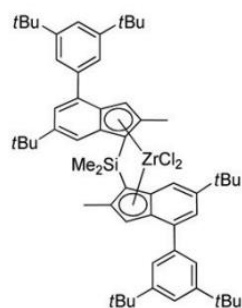
M30



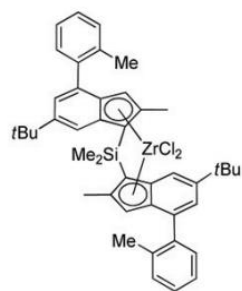
M31



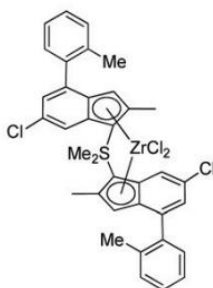
M32



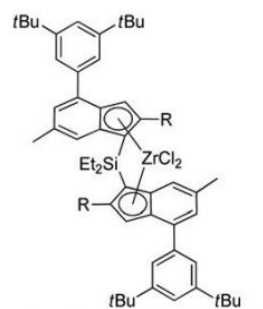
M33



M34



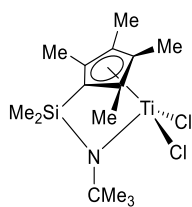
M35



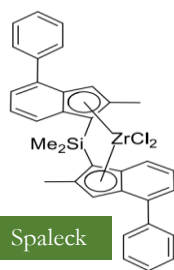
R = Me (**M39**) or Et (**M40**)

Appendix D

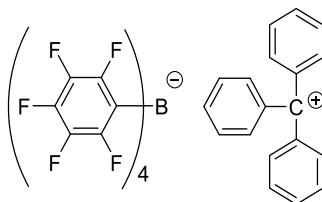
Structures of proposed precatalysts, cocatalysts, and reactor impurities scavenger



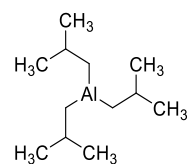
Dow CGC



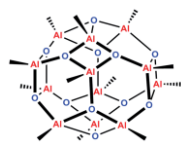
Spaleck



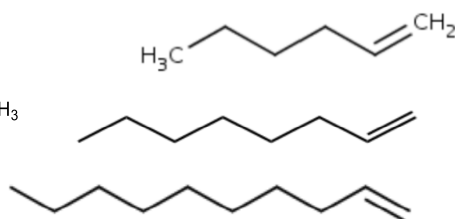
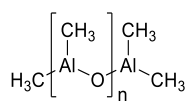
TTB



TIBA



MAO



1-hexene

1-octene

1-decene

Appendix E

Measured solvent and comonomer moisture levels

Table E.1: Solvent and olefins moisture level measured by KF titration.

Solvents and comonomers	Batch number	Amount (L)	Initial moisture level (ppm)	Moisture level with MoS (ppm)	Moisture level (ppm) after first alumina oxide pass to BASF catalyst	Moisture level (ppm) after second alumina oxide with MoS
Toluene	Toluene-01	2.0	57	6.7-8.2	7.6	4.9
1-Hexene	Hexene-01	1.0	7.7	7.5	10.6	5
Toluene	Toluene-02	2.0	45	10.3	9.1	3.5
Toluene	Toluene-03	2.0	66.2	20.6	15.4	3.9
1-Octene	Octene-01	1.00	35	13.4	8.7	4.8
Toluene	Toluene-04	2.0	54.4	6.8	7.8	4.8
Toluene	Toluene-05	2.0	54.4	6.4	11.2	4.7
Toluene	Toluene-06	2.0	30.6	12.9	11.6	4.1
Toluene	Toluene-07	2.0	42	8.2	11.6	3.3

Appendix F

Thermophysical properties, parametric values, and thermodynamic data used in model prediction

Table F.1: Vapor pressure-calculating correlations.

$\log(P_s) = \hat{A} - \frac{\hat{B}}{T + \hat{C}} \quad (\text{Antoine equation}) \quad (\text{T30.1})$ Antoine equation parameters $\hat{A}$, $\hat{B}$, and $\hat{C}$ are available in the literature [116, 117, 118, 119]. Note that their values specifically depend on the equation expression and the units of P_s and T. Hence, they should be carefully used. Also, precaution should be taken to extrapolate them beyond T_{max}. $\log(P_s) = \left[1 - \frac{\left(1 - \frac{T}{T_c}\right) \left(\frac{T_{nbp}}{T_c} + 0.2803 - 0.5211 \frac{T_{nbp}}{T_c}\right)}{\left(1 - \frac{T_{nbp}}{T_c}\right) \left(\frac{T}{T_c} + 0.2803 - 0.5211 \frac{T_{nbp}}{T_c}\right)} \right] \log P_c (\text{atm}) \quad (\text{Chen correlation}) \quad (\text{T30.2})$ Where T_b, T_c, and P_c are atmospheric boiling point, critical temperature, and critical pressure, respectively. Equation T30.2 calculates P_s using the above <i>liquid</i> pure component thermophysical properties. It reproduces that at $T = T_{nbp}$ (normal boiling), a <i>liquid</i> has 1 atm vapor pressure. The expression $(0.2803 - 0.5211 \frac{T_{nbp}}{T_c})$ results from the regression analysis of related thermophysical properties of 217 compounds over the widest possible range of $\frac{T_{nbp}}{T_c}$ [120]. $P_{Si} = P_{ci} \exp \left(\tilde{\alpha} \left(1 - \frac{T_{ci}}{T} \right) \right); \quad \tilde{\alpha} = 5.37(1 + \omega_i) \quad (\text{Wilson equation}) \quad (\text{T30.3})$ Wilson equation estimates saturation vapor pressure using pure component critical pressure P_c, temperature T_c, and Acentric factor ω [92, 96, 97].

Table F.2: Selected critical thermophysical properties and Antoine equation parameters for ethylene, toluene, 1-hexene and 1-octene.

Components	Boiling point	Critical temperature	Critical pressure	Acentric factor	Antoine equation $\log(P_s) = \hat{A} - \frac{\hat{B}}{T + \hat{C}}$ P_s (bar) and T (K)			Temperature range (K)
	T_b (K)	T_c (K)	P_c (bar)	ω	$\hat{A}$	$\hat{B}$	$\hat{C}$	
Ethylene	169.35	282.34	50.41	0.087	3.87261	584.146	-18.307	149.0–188.0
Toluene	383.80	593.00	41.00	0.262	4.07827	1343.943	-53.773	303.0–384.0
1-hexene	337.00	504.00	32.10	0.280	3.99063	1152.971	-47.301	289.0–337.0
1-octene	394.35	567.40	26.75	0.386	4.05752	1353.486	-60.386	318.0–395.4
References	[93, 100, 116, 117, 121, 122]				[117, 118, 119]			

Table F.3: Binary interaction parameters for ethylene-toluene, ethylene–1-hexene, and ethylene–1-octene mixtures.

Binary interaction parameter	Ethylene-toluene	Ethylene–1-hexene	Ethylene–1-octene
k_{12} (for a_{12})	0.03	0.069	0.011
l_{12} (for b_{12})	0.00	0.00	0.00
References	[91, 122, 123, 124]	[100]	[100]

Table F.4: Tait equations with parametric values for toluene, 1-hexene, and 1-octene.

Tait equation	Component and parametric values	References
$V \frac{L}{\text{mol}} = \frac{MW}{\rho} = \frac{MW}{\rho_0(T)} \times \left[1 - C \ln \frac{D(T)+P}{D(T)+P_0} \right] \quad (\text{T4.1})$ In the above equation, C is usually constant, or it may be sometimes a weak function of T.	Toluene ($273 \leq T \leq 373$ K; $564 \leq P \leq 1172$ bar) $C = 0.09143$ $P_0 = 0.1$ MPa (atmospheric) $\rho_0(T \text{ K}) \frac{\text{g}}{\text{L}} = 1103.06 - 0.68074T - 0.4229 \times 10^{-3}T^2$ $D(T) \text{ MPa} = 440.47 - 1.604T + 1.539 \times 10^{-3}T^2$	[125]
	1-hexene ($298 \leq T \leq 473$ K; $1 \leq P \leq 2451.6$ bar) $C = -0.0556 + 0.00056T$ $P_0 = 0.1$ MPa (atmospheric) $\rho_0(T \text{ K}) \frac{\text{g}}{\text{L}} = 945.54111 - 0.92629T$ $D(T) \text{ MPa} = 93.6898 - 0.1205T$	[126]
	1-octene ($298 \leq T \leq 373$ K; $1 \leq P \leq \sim 3150$ bar) $C = 0.21$ $P_0 = 0.1$ MPa (atmospheric) $\rho_0(T \text{ K}) \frac{\text{g}}{\text{L}} = 417.4 + 2.6061T - 4.7 \times 10^{-3}T^2$ $D(T) \text{ MPa} = 181.404 - 0.3760T$	[127]

Appendix G

Experimental data and calculated results

Table G.1: Spaleck/MAO E-1-hexene copolymerization productivity and resulting elastomer MW and PDI.

Polymerization trials	Catalyst concentration ($\mu\text{mol/L}$)	Atiqullah et al.* model-predicted X values	Polymerization temperature (K)	Polymer yield (g)	Average productivity (kg/mol.h)	M_n (g/mol)	M_w (g/mol)	PDI
YR-005	44.20	0.7177	313.15	9.37	5,629	99,269	270,574	2.73
YR-008	40.70	0.6848	323.15	13.45	9,641	74,226	206,281	2.78
YR-010	37.90	0.6270	333.15	13.27	10,208	63,027	177,642	2.82
YR-009	41.60	0.5771	343.15	14.48	6,766	55,265	157,067	2.84

Reactor vessel = 250 mL cylindrical round-bottom Buchi reactor. Reactor liquid volume = Toluene solvent + comonomer = (140 + 10.5) or (160 + 11.4) = 150.5 or 171.4 mL. Precatalyst concentration: 36.46–50.52 $\mu\text{mol/L}$. Ethylene monomer feeding pressure = 4 barg. Reactor operational mode = Semicontinuous feeding of ethylene (without monomer starvation). Polymerization type: Solution polymerization that dissolves the as-synthesized elastomer and forms a single phase. Impeller speed = 600 rpm. X = Ratio of molar concentrations of monomer 1 (ethylene) and monomer 2 (1-hexene comonomer). *See Section 3.2.

Table G.2: Spaleck/(TTB + TIBA) E-1-hexene copolymerization productivity and resulting elastomer MW and PDI.

Polymerization trials	Catalyst concentration ($\mu\text{mol/L}$)	Atiqullah et al.* model-predicted X values	Polymerization temperature (K)	Polymer yield (g)	Average productivity (kg/mol.h)	M_n (g/mol)	M_w (g/mol)	PDI
YR-006	42.50	0.7525	313.15	10.28	5,639	60,621	247,737	4.09
YR-015	37.00	0.6848	323.15	11.86	10,202	44,561	158,765	3.56
YR-016	41.60	0.6270	333.15	11.82	10,465	26,906	126,775	4.71
YR-014	41.60	0.5771	343.15	13.30	7,435	17,875	102,372	5.73

Reactor vessel = 250 mL cylindrical round-bottom Buchi reactor. Reactor liquid volume = Toluene solvent + comonomer = (140 + 10.5) or (160 + 11.4) = 150.5 or 171.4 mL. Precatalyst concentration: 36.46–50.52 $\mu\text{mol/L}$. Ethylene monomer feeding pressure = 4 barg. Reactor operational mode = Semicontinuous feeding of ethylene (without monomer starvation). Polymerization type: Solution polymerization that dissolves the as-synthesized elastomer and forms a single phase. Impeller speed = 600 rpm. X = Ratio of molar concentrations of monomer 1 (ethylene) and monomer 2 (1-hexene comonomer). *See Section 3.2.

Table G.3: Dow CGC/MAO E-1-hexene copolymerization productivity and resulting elastomer MW and PDI.

Polymerization trials	Catalyst concentration ($\mu\text{mol/L}$)	Atiqullah et al.* model-predicted X values	Polymerization temperature (K)	Polymer yield (g)	Average productivity (kg/mol.h)	M_n (g/mol)	M_w (g/mol)	PDI
YR-024	45.10	0.7177	313.15	10.16	7,483	73,982	198,357	2.68
YR-023	43.30	0.6531	323.15	10.07	8,428	51,445	156,405	3.04
YR-025	50.50	0.5979	333.15	12.16	8,344	38,895	123,312	3.17
YR-026	43.30	0.5503	343.15	12.55	9,628	29,438	101,036	3.43

Reactor vessel = 250 mL cylindrical round-bottom Buchi reactor. Reactor liquid volume = Toluene solvent + comonomer = (140 + 10.5) or (160 + 11.4) = 150.5 or 171.4 mL. Precatalyst concentration: 36.46–50.52 $\mu\text{mol/L}$. Ethylene monomer feeding pressure = 4 barg. Reactor operational mode = Semicontinuous feeding of ethylene (without monomer starvation). Polymerization type: Solution polymerization that dissolves the as-synthesized elastomer and forms a single phase. Impeller speed = 600 rpm. X = Ratio of molar concentrations of monomer 1 (ethylene) and monomer 2 (1-hexene comonomer). *See Section 3.2.

Table G.4: Dow CGC/(TTB + TIBA) E-1-hexene copolymerization productivity and resulting elastomer MW and PDI.

Polymerization trials	Catalyst concentration ($\mu\text{mol/L}$)	Atiqullah et al.* model-predicted X values	Polymerization temperature (K)	Polymer yield (g)	Average productivity (kg/mol.h)	M_n (g/mol)	M_w (g/mol)	PDI
YR-032	43.30	0.7177	313.15	5.04	1,718	123,373	270,889	2.20
YR-033	43.30	0.6531	323.15	6.63	2,348	95,268	233,362	2.45
YR-030	48.70	0.5979	333.15	7.44	2,900	84,278	194,294	2.31
YR-034	50.50	0.5503	343.15	12.33	4,865	50,957	145,347	2.85

Reactor vessel = 250 mL cylindrical round-bottom Buchi reactor. Reactor liquid volume = Toluene solvent + comonomer = (140 + 10.5) or (160 + 11.4) = 150.5 or 171.4 mL. Precatalyst concentration: 36.46–50.52 $\mu\text{mol/L}$. Ethylene monomer feeding pressure = 4 barg. Reactor operational mode = Semicontinuous feeding of ethylene (without monomer starvation). Polymerization type: Solution polymerization that dissolves the as-synthesized elastomer and forms a single phase. Impeller speed = 600 rpm. X = Ratio of molar concentrations of monomer 1 (ethylene) and monomer 2 (1-hexene comonomer). *See Section 3.2.

Table G.5: Spaleck/MAO E-1-octene copolymerization productivity and resulting elastomer MW and PDI.

Polymerization trials	Catalyst concentration ($\mu\text{mol/L}$)	Atiqullah et al.* model-predicted X values	Polymerization temperature (K)	Polymer yield (g)	Average productivity (kg/mol.h)	M_n (g/mol)	M_w (g/mol)	PDI
YR-039	43.20	0.8115	313.15	11.68	9,802	56,040	211,860	3.78
YR-036	42.10	0.7402	323.15	12.62	9,951	50,921	219,640	4.31
YR-037	44.20	0.6791	333.15	11.95	10,769	32,284	135,843	4.21
YR-040	44.20	0.6263	343.15	11.60	11,003	22,978	123,299	5.37

Reactor vessel = 250 mL cylindrical round-bottom Buchi reactor. Reactor liquid volume = Toluene solvent + comonomer = (140 + 10.5) or (160 + 11.4) = 150.5 or 171.4 mL. Precatalyst concentration: 36.46–50.52 $\mu\text{mol/L}$. Ethylene monomer feeding pressure = 4 barg. Reactor operational mode = Semicontinuous feeding of ethylene (without monomer starvation). Polymerization type: Solution polymerization that dissolves the as-synthesized elastomer and forms a single phase. Impeller speed = 600 rpm. X = Ratio of molar concentrations of monomer 1 (ethylene) and monomer 2 (1-octene comonomer).
*See Section 3.2.

Table G.6: Spaleck/(TTB + TIBA) E-1-octene copolymerization productivity and resulting elastomer MW and PDI.

Polymerization trials	Catalyst concentration ($\mu\text{mol/L}$)	Atiqullah et al.* model-predicted X values	Polymerization temperature (K)	Polymer yield (g)	Average productivity (kg/mol.h)	M_n (g/mol)	M_w (g/mol)	PDI
YR-055	45.30	0.8115	313.15	11.5	10,122	53,591	189,323	3.53
YR-054	44.20	0.7402	323.15	11.3	10,183	41,428	157,702	3.81
YR-053	49.50	0.6791	333.15	14.0	12,527	31,685	137,161	4.33
YR-052	44.20	0.6263	343.15	12.8	12,816	23,362	120,956	5.18

Reactor vessel = 250 mL cylindrical round-bottom Buchi reactor. Reactor liquid volume = Toluene solvent + comonomer = (140 + 10.5) or (160 + 11.4) = 150.5 or 171.4 mL. Precatalyst concentration: 36.46–50.52 $\mu\text{mol/L}$. Ethylene monomer feeding pressure = 4 barg. Reactor operational mode = Semicontinuous feeding of ethylene (without monomer starvation). Polymerization type: Solution polymerization that dissolves the as-synthesized elastomer and forms a single phase. Impeller speed = 600 rpm. X = Ratio of molar concentrations of monomer 1 (ethylene) and monomer 2 (1-octene comonomer).
*See Section 3.2.

Table G.7: Dow CGC/MAO E-1-octene copolymerization productivity and resulting elastomer MW and PDI.

Polymerization trials	Catalyst concentration ($\mu\text{mol/L}$)	Atiqullah et al.* model-predicted X values	Polymerization temperature (K)	Polymer yield (g)	Average productivity (kg/mol.h)	M_n (g/mol)	M_w (g/mol)	PDI
YR-041	41.50	0.8115	313.15	7.68	6,707	140,332	322,051	2.30
YR-042	46.90	0.7402	323.15	11.41	8,080	62,519	193,001	3.09
YR-043	45.10	0.6791	333.15	11.38	8,381	60,797	172,121	2.83
YR-044	50.50	0.6263	343.15	12.97	8,529	40,474	134,459	3.32

Reactor vessel = 250 mL cylindrical round-bottom Buchi reactor. Reactor liquid volume = Toluene solvent + comonomer = (140 + 10.5) or (160 + 11.4) = 150.5 or 171.4 mL. Precatalyst concentration: 36.46–50.52 $\mu\text{mol/L}$. Ethylene monomer feeding pressure = 4 barg. Reactor operational mode = Semicontinuous feeding of ethylene (without monomer starvation). Polymerization type: Solution polymerization that dissolves the as-synthesized elastomer and forms a single phase. Impeller speed = 600 rpm. X = Ratio of molar concentrations of monomer 1 (ethylene) and monomer 2 (1-octene comonomer). *See Section 3.2.

Table G.8: Dow CGC/(TTB + TIBA) E-1-octene copolymerization productivity and resulting elastomer MW and PDI.

Polymerization trials	Catalyst concentration ($\mu\text{mol/L}$)	Atiqullah et al.* model-predicted X values	Polymerization temperature (K)	Polymer yield (g)	Average productivity (kg/mol.h)	M_n (g/mol)	M_w (g/mol)	PDI
YR-056	46.90	0.8115	313.15	7.01	1,986	135,518	308,021	2.27
YR-049	41.50	0.7402	323.15	6.70	2,384	120,552	306,035	2.54
YR-050	43.30	0.6791	333.15	6.76	23,94	104,596	277,547	2.65
YR-051	45.10	0.6263	343.15	12.3	54,35	57,179	158,752	2.78

Reactor vessel = 250 mL cylindrical round-bottom Buchi reactor. Reactor liquid volume = Toluene solvent + comonomer = (140 + 10.5) or (160 + 11.4) = 150.5 or 171.4 mL. Precatalyst concentration: 36.46–50.52 $\mu\text{mol/L}$. Ethylene monomer feeding pressure = 4 barg. Reactor operational mode = Semicontinuous feeding of ethylene (without monomer starvation). Polymerization type: Solution polymerization that dissolves the as-synthesized elastomer and forms a single phase. Impeller speed = 600 rpm. X = Ratio of molar concentrations of monomer 1 (ethylene) and monomer 2 (1-octene comonomer). *See Section 3.2.

Table G.9: ^{13}C NMR-determined triad mole fractions of as-synthesized Spaleck/MAO E-1-hexene elastomers using Randall method.

Polymerization trials	Polymerization temperature (K)	EEE	EEH	HEH	EHE	EHH	HHH	E	H
YR-005	313.15	0.32	0.27	0.11	0.15	0.10	0.06	0.69	0.31
YR-008	323.15	0.41	0.25	0.07	0.13	0.12	0.02	0.73	0.27
YR-010	333.15	0.49	0.23	0.05	0.13	0.08	0.02	0.78	0.23
YR-009	343.15	0.54	0.21	0.04	0.13	0.07	0.01	0.79	0.21

E = Ethylene (mole fraction), H = 1-hexene (mole fraction).

Table G.10: ^{13}C NMR-determined triad mole fractions of as-synthesized Spaleck/(TTB + TIBA) E-1-hexene elastomers using Randall method.

Polymerization trials	Polymerization temperature (K)	EEE	EEH	HEH	EHE	EHH	HHH	E	H
YR-006	313.15	0.45	0.14	0.09	0.08	0.13	0.11	0.68	0.32
YR-015	323.15	0.41	0.21	0.08	0.11	0.13	0.06	0.71	0.29
YR-016	333.15	0.47	0.16	0.10	0.08	0.12	0.07	0.73	0.27
YR-014	343.15	0.59	0.14	0.06	0.08	0.09	0.05	0.78	0.22

E = Ethylene (mole fraction), H = 1-hexene (mole fraction).

Table G.11: ^{13}C NMR-determined triad mole fractions of as-synthesized Dow CGC/MAO E-1-hexene elastomers using Randall method.

Polymerization trials	Polymerization temperature (K)	EEE	EEH	HEH	EHE	EHH	HHH	E	H
YR-024	313.15	0.41	0.24	0.06	0.12	0.13	0.05	0.71	0.29
YR-023	323.15	0.44	0.26	0.05	0.10	0.11	0.04	0.74	0.26
YR-025	333.15	0.50	0.21	0.04	0.09	0.13	0.03	0.74	0.26
YR-026	343.15	0.55	0.22	0.03	0.08	0.08	0.03	0.80	0.20

E = Ethylene (mole fraction), H = 1-hexene (mole fraction).

Table G.12: ^{13}C NMR-determined triad mole fractions of as-synthesized Dow CGC/(TTB + TIBA) E-1-hexene elastomers using Randall method.

Polymerization trials	Polymerization temperature (K)	EEE	EEH	HEH	EHE	EHH	HHH	E	H
YR-032	313.15	0.43	0.26	0.05	0.14	0.10	0.02	0.74	0.26
YR-033	323.15	0.45	0.26	0.05	0.12	0.10	0.02	0.76	0.24
YR-030	333.15	0.48	0.24	0.04	0.10	0.11	0.01	0.77	0.23
YR-034	343.15	0.51	0.25	0.03	0.11	0.08	0.02	0.79	0.21

E = Ethylene (mole fraction), H = 1-hexene (mole fraction).

Table G.13A: Group A ^{13}C NMR microstructural parameters for as-synthesized Spaleck/MAO E-1-hexene elastomers.

Polymerization trials	Polymerization temperature (K)	Eqn 3.4 $r_1(X)$	$r_1 \neq f(X)^*$	Eqn 3.5 $r_2(X)$	$r_2 \neq f(X)^*$	$r_1(X) \times r_2(X)$	χ	$\langle r_1(X)r_2(X) \rangle \neq f(X)$	ρ
YR-005	313.15	3.15	2.26	0.38	0.53	1.21	0.96	1.01	0.89
YR-008	323.15	4.04	2.77	0.29	0.42	1.17	0.97	1.16	1.03
YR-010	333.15	5.71	3.58	0.20	0.32	1.16	0.97	1.18	1.04
YR-009	343.15	6.89	3.98	0.17	0.29	1.15	0.98	1.25	1.10

*Copolymerization propagation rate-exclusive statistical approach or $X = 1$ (incorrect). X = Ratio of molar concentrations of monomer 1 and monomer 2 (comonomer).

Table G.13B: Group B ^{13}C NMR microstructural parameters for as-synthesized Spaleck/MAO E-1-hexene elastomers.

Polymerization trials	Polymerization temperature (K)	Eqn T9.2a $L_1 \text{ NAV}$	Eqn T9.11 $n_1 \text{ NAV}$	Eqn T9.2b $L_2 \text{ NAV}$	Eqn T9.11 $n_2 \text{ NAV}$	Eqn T9.12 $n_1 \text{ WAV}$	Eqn T9.12 $n_2 \text{ WAV}$	CI	MD
YR-005	313.15	3.26	3.26	1.53	1.53	5.53	2.07	9.91	71.47
YR-008	323.15	3.77	3.77	1.42	1.42	6.53	1.84	10.80	70.40
YR-010	333.15	4.58	4.58	1.32	1.32	8.16	1.65	10.57	74.95
YR-009	343.15	4.98	4.98	1.29	1.29	8.95	1.58	10.44	74.64

CI = Cluster index; MD = Monomer dispersity.

Table G.14A: Group A ^{13}C NMR microstructural parameters for as-synthesized Spaleck/(TTB + TIBA) E-1-hexene elastomers.

Polymerization trials	Polymerization temperature (K)	Eqn 3.4 $r_1(X)$	$r_1 \neq f(X)^*$	Eqn 3.5 $r_2(X)$	$r_2 \neq f(X)^*$	$r_1(X) \times r_2(X)$	χ	$\langle r_1(X)r_2(X) \rangle \neq f(X)$	ρ
YR-006	313.15	4.72	3.55	0.88	1.17	4.15	0.68	3.88	1.38
YR-015	323.15	4.40	3.01	0.48	0.70	2.10	0.84	1.92	1.10
YR-016	333.15	6.06	3.80	0.55	0.88	3.34	0.74	2.76	1.13
YR-014	343.15	9.15	5.28	0.42	0.73	3.83	0.74	3.80	1.34

*Copolymerization propagation rate-exclusive statistical approach or $X = 1$ (incorrect). X = Ratio of molar concentrations of monomer 1 and monomer 2 (comonomer).

Table G.14B: Group B ^{13}C NMR microstructural parameters for as-synthesized Spaleck/(TTB + TIBA) E-1-hexene elastomers.

Polymerization trials	Polymerization temperature (K)	Eqn T9.2a $L_1 \text{ NAV}$	Eqn T9.11 $n_1 \text{ NAV}$	Eqn T9.2b $L_2 \text{ NAV}$	Eqn T9.11 $n_2 \text{ NAV}$	Eqn T9.12 $n_1 \text{ WAV}$	Eqn T9.12 $n_2 \text{ WAV}$	CI	MD
YR-006	313.15	4.55	4.55	2.17	2.17	8.11	3.33	13.87	47.76
YR-015	323.15	4.01	4.01	1.70	1.70	7.02	2.40	12.63	61.62
YR-016	333.15	4.80	4.80	1.88	1.88	8.59	4.80	14.78	58.81
YR-014	343.15	6.28	6.28	1.73	1.73	11.57	2.45	16.21	58.20

CI = Cluster index; MD = Monomer dispersity.

Table G.15A: Group A ^{13}C NMR microstructural parameters for as-synthesized Dow CGC/MAO E-1-hexene elastomers.

Polymerization trials	Polymerization temperature (K)	Eqn 3.4 $r_1(X)$	$r_1 \neq f(X)^*$	Eqn 3.5 $r_2(X)$	$r_2 \neq f(X)^*$	$r_1(X) \times r_2(X)$	χ	$\langle r_1(X)r_2(X) \rangle \neq f(X)$	ρ
YR-024	313.15	4.12	2.95	0.44	0.61	1.80	0.87	1.84	1.17
YR-023	323.15	5.34	3.49	0.39	0.60	2.10	0.85	1.95	1.10
YR-025	333.15	6.30	3.77	0.36	0.61	2.28	0.83	2.61	1.36
YR-026	343.15	9.52	5.24	0.33	0.60	3.15	0.79	2.80	1.14

*Copolymerization propagation rate-exclusive statistical approach or $X = 1$ (incorrect). X = Ratio of molar concentrations of monomer 1 and monomer 2 (comonomer).

Table G.15B: Group B ^{13}C NMR microstructural parameters for as-synthesized Dow CGC/MAO E-1-hexene elastomers.

Polymerization trials	Polymerization temperature (K)	Eqn T9.2a $L_1 \text{ NAV}$	Eqn T9.11 $n_1 \text{ NAV}$	Eqn T9.2b $L_2 \text{ NAV}$	Eqn T9.11 $n_2 \text{ NAV}$	Eqn T9.12 $n_1 \text{ WAV}$	Eqn T9.12 $n_2 \text{ WAV}$	CI	MD
YR-024	313.15	3.95	3.95	1.61	1.61	6.91	2.22	11.97	61.42
YR-023	323.15	4.49	4.49	1.60	1.60	7.98	2.20	13.20	64.86
YR-025	333.15	4.77	4.77	1.61	1.61	8.53	2.21	14.14	58.39
YR-026	343.15	6.24	6.24	1.60	1.60	11.47	2.20	16.19	66.33

CI = Cluster index; MD = Monomer dispersity.

Table G.16A: Group A ^{13}C NMR microstructural parameters for as-synthesized DowCGC/(TTB + TIBA) E-1-hexene elastomers.

Polymerization trials	Polymerization temperature (K)	Eqn 3.4 $r_1(X)$	$r_1 \neq f(X)^*$	Eqn 3.5 $r_2(X)$	$r_2 \neq f(X)^*$	$r_1(X) \times r_2(X)$	χ	$\langle r_1(X)r_2(X) \rangle \neq f(X)$	ρ
YR-032	313.15	4.11	2.95	0.26	0.37	1.08	0.98	1.14	1.06
YR-033	323.15	5.21	3.40	0.24	0.37	1.27	0.96	1.22	1.01
YR-030	333.15	6.40	3.83	0.27	0.45	1.71	0.90	1.66	1.08
YR-034	343.15	7.60	4.18	0.21	0.37	1.57	0.92	1.54	1.07

*Copolymerization propagation rate-exclusive statistical approach or $X = 1$ (incorrect). X = Ratio of molar concentrations of monomer 1 and monomer 2 (comonomer).

Table G.16B: Group B ^{13}C NMR microstructural parameters for as-synthesized Dow CGC/(TTB + TIBA) E-1-hexene elastomers.

Polymerization trials	Polymerization temperature (K)	Eqn T9.2a $L_1 \text{ NAV}$	Eqn T9.11 $n_1 \text{ NAV}$	Eqn T9.2b $L_2 \text{ NAV}$	Eqn T9.11 $n_2 \text{ NAV}$	Eqn T9.12 $n_1 \text{ WAV}$	Eqn T9.12 $n_2 \text{ WAV}$	CI	MD
YR-032	313.15	3.95	3.95	1.37	1.37	6.90	1.73	10.23	71.42
YR-033	323.15	4.40	4.40	1.37	1.37	7.81	1.74	11.34	74.13
YR-030	333.15	4.83	4.83	1.45	1.45	8.65	1.90	13.64	70.15
YR-034	343.15	5.18	5.18	1.37	1.37	9.37	1.75	12.60	73.27

CI = Cluster index; MD = Monomer dispersity.

Table G.17: ^{13}C NMR-determined triad mole fractions of as-synthesized Spaleck/MAO E-1-octene elastomers using Randall method.

Polymerization trials	Polymerization temperature (K)	EEE	EEO	OEO	EOE	EOO	OOO	E	O
YR-039	313.15	0.45	0.18	0.08	0.11	0.12	0.05	0.71	0.29
YR-036	323.15	0.52	0.20	0.06	0.10	0.08	0.03	0.78	0.22
YR-037	333.15	0.38	0.24	0.14	0.10	0.12	0.02	0.76	0.24
YR-040	343.15	0.45	0.22	0.08	0.11	0.11	0.04	0.74	0.26

E = Ethylene (mole fraction); O = 1-Octene (mole fraction).

Table G.18: ^{13}C NMR-determined triad mole fractions of as-synthesized Spaleck/(TTB + TIBA) E-1-octene elastomers using Randall method.

Polymerization trials	Polymerization temperature (K)	EEE	EEO	OEO	EOE	EOO	OOO	E	O
YR-055	313.15	0.32	0.23	0.08	0.14	0.14	0.08	0.64	0.36
YR-054	323.15	0.41	0.20	0.07	0.12	0.13	0.07	0.69	0.31
YR-053	333.15	0.34	0.25	0.09	0.13	0.13	0.07	0.68	0.32
YR-052	343.15	0.46	0.19	0.08	0.09	0.12	0.06	0.73	0.27

E = Ethylene (mole fraction); O = 1-Octene (mole fraction).

Table G.19: ^{13}C NMR-determined triad mole fractions of as-synthesized Dow CGC/MAO E-1-octene elastomers using Randall method.

Polymerization trials	Polymerization temperature (K)	EEE	EEO	OEO	EOE	EOO	OOO	E	O
YR-041	313.15	0.53	0.19	0.06	0.13	0.08	0.02	0.78	0.22
YR-042	323.15	0.45	0.29	0.04	0.10	0.11	0.01	0.78	0.22
YR-043	333.15	0.46	0.26	0.04	0.11	0.10	0.02	0.77	0.23
YR-044	343.15	0.64	0.16	0.00	0.10	0.07	0.03	0.80	0.20

E = Ethylene (mole fraction); O = 1-Octene (mole fraction).

Table G.20: ^{13}C NMR-determined triad mole fractions of as-synthesized Dow/(TTB + TIBA) E-1-octene elastomers using Randall method.

Polymerization trials	Polymerization temperature (K)	EEE	EEO	OEO	EOE	EOO	OOO	E	O
YR-056	313.15	0.48	0.27	0.05	0.12	0.07	0.01	0.80	0.20
YR-049	323.15	0.53	0.22	0.04	0.13	0.07	0.01	0.80	0.20
YR-050	333.15	0.53	0.25	0.03	0.12	0.06	0.01	0.82	0.18
YR-051	343.15	0.52	0.25	0.03	0.11	0.08	0.02	0.80	0.20

E = Ethylene (mole fraction); O = 1-Octene (mole fraction).

Table G.21A: Group A ^{13}C NMR microstructural parameters for as-synthesized Spaleck/MAO E-1-octene elastomers.

Polymerization trials	Polymerization temperature (K)	Eqn 3.4 $r_1(X)$	$r_1 \neq f(X)^*$	Eqn 3.5 $r_2(X)$	$r_2 \neq f(X)^*$	$r_1(X) \times r_2(X)$	χ	$\langle r_1(X)r_2(X) \rangle \neq f(X)$	ρ
YR-039	313.15	3.81	3.09	0.54	0.66	2.06	0.85	2.06	1.18
YR-036	323.15	5.81	4.30	0.36	0.49	2.10	0.86	1.88	1.05
YR-037	333.15	4.55	3.09	0.33	0.49	1.52	0.91	0.94	0.70
YR-040	343.15	5.44	3.40	0.36	0.58	1.96	0.86	1.74	1.04

*Copolymerization propagation rate-exclusive statistical approach or $X = 1$ (incorrect). X = Ratio of molar concentrations of monomer 1 and monomer 2 (comonomer).

Table G.21B: Group B ^{13}C NMR microstructural parameters for as-synthesized Spaleck/MAO E-1-octene elastomers.

Polymerization trials	Polymerization temperature (K)	Eqn T9.2a $L_1 \text{ NAV}$	Eqn T9.11 $n_1 \text{ NAV}$	Eqn T9.2b $L_2 \text{ NAV}$	Eqn T9.11 $n_2 \text{ NAV}$	Eqn T9.12 $n_1 \text{ WAV}$	Eqn T9.12 $n_2 \text{ WAV}$	CI	MD
YR-039	313.15	4.09	4.09	1.66	1.66	7.19	2.33	12.30	60.04
YR-036	323.15	5.30	5.30	1.49	1.49	9.60	1.98	13.54	71.05
YR-037	333.15	4.09	4.09	1.49	1.49	7.18	1.98	13.61	87.47
YR-040	343.15	4.40	4.40	1.58	1.58	7.81	2.15	12.86	67.44

CI = Cluster index; MD = Monomer dispersity.

Table G.22A: Group A ^{13}C NMR microstructural parameters for as-synthesized Spaleck/(TTB + TIBA) E-1-octene elastomers.

Polymerization trials	Polymerization temperature (K)	Eqn 3.4 $r_1(X)$	$r_1 \neq f(X)^*$	Eqn 3.5 $r_2(X)$	$r_2 \neq f(X)^*$	$r_1(X) \times r_2(X)$	χ	$\langle r_1(X)r_2(X) \rangle \neq f(X)$	ρ
YR-055	313.15	2.52	2.05	0.56	0.69	1.42	0.92	1.55	1.17
YR-054	323.15	3.79	2.80	0.53	0.72	2.01	0.85	2.10	1.23
YR-053	333.15	3.60	2.44	0.47	0.70	1.70	0.88	1.53	1.03
YR-052	343.15	5.87	3.68	0.50	0.80	2.95	0.77	2.48	1.10

*Copolymerization propagation rate-exclusive statistical approach or $X = 1$ (incorrect). X = Ratio of molar concentrations of monomer 1 and monomer 2 (comonomer). 1 = ethylene, 2 = 1-octene.

Table G.22B: Group B ^{13}C NMR microstructural parameters for as-synthesized Spaleck/(TTB + TIBA) E-1-octene elastomers.

Polymerization trials	Polymerization temperature (K)	Eqn T9.2a $L_1 \text{ NAV}$	Eqn T9.11 $n_1 \text{ NAV}$	Eqn T9.2b $L_2 \text{ NAV}$	Eqn T9.11 $n_2 \text{ NAV}$	Eqn T9.12 $n_1 \text{ WAV}$	Eqn T9.12 $n_2 \text{ WAV}$	CI	MD
YR-055	313.15	3.05	3.05	1.69	1.69	5.09	2.39	10.16	56.62
YR-054	323.15	3.80	3.80	1.72	1.72	6.60	2.43	11.80	57.00
YR-053	333.15	3.44	3.44	1.70	1.70	5.89	2.40	11.27	62.20
YR-052	343.15	4.68	4.68	1.80	1.80	8.35	2.61	14.22	60.79

CI = Cluster index; MD = Monomer dispersity.

Table G.23A: Group A ^{13}C NMR microstructural parameters for as-synthesized Dow CGC/MAO E-1-octene elastomers.

Polymerization trials	Polymerization temperature (K)	Eqn 3.4 $r_1(X)$	$r_1 \neq f(X)^*$	Eqn 3.5 $r_2(X)$	$r_2 \neq f(X)^*$	$r_1(X) \times r_2(X)$	χ	$\langle r_1(X)r_2(X) \rangle \neq f(X)$	ρ
YR-041	313.15	4.64	3.77	0.28	0.35	1.30	0.95	1.40	1.12
YR-042	323.15	5.25	3.88	0.32	0.44	1.70	0.90	1.42	0.93
YR-043	333.15	5.54	3.76	0.32	0.46	1.75	0.89	1.62	1.04
YR-044	343.15	8.24	5.16	0.28	0.45	2.32	0.85	3.95	1.97

*Copolymerization propagation rate-exclusive statistical approach or $X = 1$ (incorrect). X = Ratio of molar concentrations of monomer 1 and monomer 2 (comonomer). 1 = ethylene, 2 = 1-octene.

Table G.23B: Group B ^{13}C NMR microstructural parameters for as-synthesized Dow CGC/MAO E-1-octene elastomers.

Polymerization trials	Polymerization temperature (K)	Eqn T9.2a $L_1 \text{ NAV}$	Eqn T9.11 $n_1 \text{ NAV}$	Eqn T9.2b $L_2 \text{ NAV}$	Eqn T9.11 $n_2 \text{ NAV}$	Eqn T9.12 $n_1 \text{ WAV}$	Eqn T9.12 $n_2 \text{ WAV}$	CI	MD
YR-041	313.15	4.77	4.77	1.35	1.35	8.53	1.69	11.03	71.80
YR-042	323.15	4.88	4.88	1.44	1.44	8.77	1.88	13.85	76.57
YR-043	333.15	4.76	4.76	1.46	1.46	8.52	1.93	12.86	70.92
YR-044	343.15	6.16	6.16	1.45	1.45	11.32	1.90	13.67	54.77

CI = Cluster index; MD = Monomer dispersity.

Table G.24A: Group A ^{13}C NMR microstructural parameters for as-synthesized Dow CGC/(TTB + TIBA) E-1-octene elastomers.

Polymerization trials	Polymerization temperature (K)	Eqn 3.4 $r_1(X)$	$r_1 \neq f(X)^*$	Eqn 3.5 $r_2(X)$	$r_2 \neq f(X)^*$	$r_1(X) \times r_2(X)$	χ	$\langle r_1(X)r_2(X) \rangle \neq f(X)$	ρ
YR-056	313.15	4.79	3.89	0.22	0.27	1.06	0.99	0.92	0.89
YR-049	323.15	5.45	4.03	0.19	0.25	1.02	1.00	1.06	1.04
YR-050	333.15	6.57	4.46	0.17	0.26	1.14	0.98	1.06	0.95
YR-051	343.15	6.95	4.36	0.24	0.38	1.68	0.91	1.62	1.07

*Copolymerization propagation rate-exclusive statistical approach or $X = 1$ (incorrect). X = Ratio of molar concentrations of monomer 1 and monomer 2 (comonomer). 1 = ethylene, 2 = 1-octene.

Table G.24B: Group B ^{13}C NMR microstructural parameters for as-synthesized Dow CGC/(TTB + TIBA) E-1-octene elastomers.

Polymerization trials	Polymerization temperature (K)	Eqn T9.2a $L_1 \text{ NAV}$	Eqn T9.11 $n_1 \text{ NAV}$	Eqn T9.2b $L_2 \text{ NAV}$	Eqn T9.11 $n_2 \text{ NAV}$	Eqn T9.12 $n_1 \text{ WAV}$	Eqn T9.12 $n_2 \text{ WAV}$	CI	MD
YR-056	313.15	4.89	4.89	1.27	1.27	8.77	1.54	10.80	84.29
YR-049	323.15	5.03	5.03	1.25	1.25	9.07	1.50	10.38	78.37
YR-050	333.15	5.46	5.46	1.26	1.26	9.92	1.51	11.25	82.59
YR-051	343.15	5.36	5.36	1.38	1.38	9.71	1.77	12.57	73.39

CI = Cluster index; MD = Monomer dispersity.

Table G.25: As-synthesized Spaleck/MAO E-1-hexene elastomers peak melting and peak crystalline temperatures and Crystaf results.

Polymerization trials	Polymerization temperature (K)	Peak melting temperature T_m (°C)	Peak crystalline temperature T_c (°C)	% crystallinity	As-synthesized elastomer Crystaf results*
YR-005	313.15	None	None	0.67	Elastomer precipitation at $25 \leq T(^{\circ}\text{C}) \leq 30$
YR-008	323.15	None	None	1.41	
YR-010	333.15	125.36	113.31	2.86	
YR-009	343.15	113.47	102.01	4.5	

* Cooling rate = 0.2 °C/min. Indicates liquid-solid phase separation.

Table G.26: As-synthesized Spaleck/(TTB+TIBA) E-1-hexene elastomers peak melting and peak crystalline temperatures and Crystaf results.

Polymerization trials	Polymerization temperature (K)	Peak melting temperature T_m (°C)	Peak crystalline temperature T_c (°C)	% crystallinity	As-synthesized elastomer Crystaf results*
YR-006	313.15	121.76	107.22	4.65	Elastomer precipitation at $25 \leq T(^{\circ}\text{C}) \leq 30$
YR-015	323.15	None	None	1.09	
YR-016	333.15	122.40	109.36	5.83	
YR-014	343.15	124.31	114.27	11.04	

* Cooling rate = 0.2 °C/min. Indicates liquid-solid phase separation.

Table G.27: As-synthesized Dow CGC/MAO E-1-hexene elastomers peak melting and peak crystalline temperatures and Crystaf results.

Polymerization trials	Polymerization temperature (K)	Peak melting temperature T_m (°C)	Peak crystalline temperature T_c (°C)	% crystallinity	As-synthesized elastomer Crystaf results*
YR-024	313.15	None	None	0.00	Elastomer precipitation at $25 \leq T(^{\circ}\text{C}) \leq 30$
YR-023	323.15	None	72.79	0.68	
YR-025	333.15	105.74	83.76	2.38	
YR-026	343.15	103.41	85.34	3.83	

*Cooling rate = 0.2 °C/min. Indicates liquid-solid phase separation.

Table G.28: As-synthesized Dow CGC/(TTB + TIBA) E-1-hexene elastomers peak melting and peak crystalline temperatures and Crystaf results.

Polymerization trials	Polymerization temperature (K)	Peak melting temperature T_m (°C)	Peak crystalline temperature T_c (°C)	% crystallinity	As-synthesized elastomer Crystaf results*
YR-032	313.15	124.58	119.63	0.80	Elastomer precipitation at $25 \leq T(^{\circ}\text{C}) \leq 30$
YR-033	323.15	124.46	118.80	0.78	
YR-030	333.15	124.19	119.68	0.30	
YR-034	343.15	None	None	0.07	

*Cooling rate = 0.2 °C/min. Indicates liquid-solid phase separation.

Table G.29: Comparison of experimental versus calculated T_g s of as-synthesized Spaleck/MAO E-1-hexene elastomers.

Ethylene weight fraction W_E	Glass transition temperature T_g (°C)	Polymerization trials	Polymerization temperature (K)	^{13}C NMR W_E	T_g calculated** for as-synthesized elastomers (°C)	T_g experimental (°C)
0.00	-50.00*	YR-005	313.15	0.43	-74.57	-65.13
0.25	-64.97**	YR-008	323.15	0.47	-76.60	-64.99
0.5	-78.09**	YR-010	333.15	0.53	-79.83	-64.19
0.75	-89.68**	YR-009	343.15	0.56	-80.98	-64.23
1.00	-100.00*		Average value		-78.00	-64.64

T_{g1} (Polyethylene) (K) = 173.15; T_{g2} [Poly(1-hexene)] (K) = 223.15; $K_{12} = 173.15/223.15 = 0.78$. *Literature value. **Gordon's relation (applicable to random copolymer).

Table G.30: Comparison of experimental versus calculated T_g s of as-synthesized Spaleck/(TTB + TIBA) E-1-hexene elastomers.

Ethylene weight fraction W_E	Glass transition temperature T_g (°C)	Polymerization trials	Polymerization temperature (K)	^{13}C NMR W_E	T_g calculated** for as-synthesized elastomers (°C)	T_g experimental (°C)
0.00	-50.00*	YR-006	313.15	0.42	-73.89	-61.41
0.25	-64.97**	YR-015	323.15	0.45	-75.45	-64.05
0.5	-78.09**	YR-016	333.15	0.47	-76.67	-64.04
0.75	-89.68**	YR-014	343.15	0.55	-80.49	-63.27
1.00	-100.00*		Average		-76.62	-63.19

T_{g1} (Polyethylene) (K) = 173.15; T_{g2} [Poly(1-hexene)] (K) = 223.15; K_{12} = 173.15/223.15 = 0.78. *Literature value. **Gordon's relation (applicable to random copolymer).

Table G.31: Comparison of experimental versus calculated T_g s of as-synthesized Dow CGC/MAO E-1-hexene elastomers.

Ethylene weight fraction W_E	Glass transition temperature T_g (°C)	Polymerization trials	Polymerization temperature (K)	^{13}C NMR W_E	T_g calculated** for as-synthesized elastomers (°C)	T_g experimental (°C)
0.00	-50.00*	YR-024	313.15	0.45	-75.58	-64.82
0.25	-64.97**	YR-023	323.15	0.49	-77.50	-64.04
0.5	-78.09**	YR-025	333.15	0.49	-77.67	-63.78
0.75	-89.68**	YR-026	343.15	0.57	-81.51	-63.46
1.00	-100.00*		Average		-78.06	-64.03

T_{g1} (Polyethylene) (K) = 173.15; T_{g2} [Poly(1-hexene)] (K) = 223.15; K_{12} = 173.15/223.15 = 0.78. *Literature value. **Gordon's relation (applicable to random copolymer).

Table G.32: Comparison of experimental versus calculated T_g s of as-synthesized Dow CGC/(TTB + TIBA) E-1-hexene elastomers.

Ethylene weight fraction W_E	Glass transition temperature T_g (°C)	Polymerization trials	Polymerization temperature (K)	^{13}C NMR W_E	T_g calculated** for as-synthesized elastomers (°C)	T_g experimental (°C)
0.00	-50.00*	YR-032	313.15	0.49	-77.51	-65.14
0.25	-64.97**	YR-033	323.15	0.52	-79.05	-65.58
0.5	-78.09**	YR-030	333.15	0.53	-79.49	-62.92
0.75	-89.68**	YR-034	343.15	0.56	-80.93	-63.63
1.00	-100.00*		Average		-79.25	-64.32

T_{g1} (Polyethylene) (K) = 173.15; T_{g2} [Poly(1-hexene)] (K) = 223.15; K_{12} = 173.15/223.15 = 0.78. *Literature value. **Gordon's relation (applicable to random copolymer).

Table G.33: As-synthesized Spaleck/MAO E-1-octene elastomers peak melting and peak crystalline temperatures and Crystaf results.

Polymerization trials	Polymerization temperature (K)	Peak melting temperature T_m (°C)	Peak crystalline temperature T_c (°C)	% crystallinity	As-synthesized elastomer Crystaf results*
YR-039	313.15	122.64	96.81	3.99	Elastomer precipitation at $25 \leq T(^{\circ}\text{C}) \leq 30$
YR-036	323.15	123.93	103.73	5.44	
YR-037	333.15	123.65	109.25	6.76	
YR-040	343.15	124.76	113.18	10.03	

*Cooling rate = 0.2 °C/min. Indicates liquid-solid phase separation.

Table G.34: As-synthesized Spaleck/(TTB + TIBA) E-1-octene elastomers peak melting and peak crystalline temperatures and Crystaf results.

Polymerization trials	Polymerization temperature (K)	Peak melting temperature T_m (°C)	Peak crystalline temperature T_c (°C)	% crystallinity	As-synthesized elastomer Crystaf results*
YR-055	313.15	None	None	None	Elastomer precipitation at $25 \leq T(^{\circ}\text{C}) \leq 30$
YR-054	323.15	120.82	106.22	1.68	
YR-053	333.15	122.28	100.77	1.53	
YR-052	343.15	124.07	111.67	5.71	

*Cooling rate = 0.2 °C/min. Indicates liquid-solid phase separation.

Table G.35: As-synthesized Dow CGC/MAO E-1-octene elastomers peak melting and peak crystalline temperatures and Crystaf results.

Polymerization trials	Polymerization temperature (K)	Peak melting temperature T_m (°C)	Peak crystalline temperature T_c (°C)	% crystallinity	As-synthesized elastomer Crystaf results*
YR-041	313.15	None	None	0.19	Elastomer precipitation at $25 \leq T(^{\circ}\text{C}) \leq 30$
YR-042	323.15	None	None	0.00	
YR-043	333.15	None	None	0.00	
YR-044	343.15	96.62	75.71	1.93	

*Cooling rate = 0.2 °C/min. Indicates liquid-solid phase separation.

Table G.36: As-synthesized Dow CGC/(TTB+TIBA) E-1-octene elastomers peak melting and peak crystalline temperatures and Crystaf results.

Polymerization trials	Polymerization temperature (K)	Peak melting temperature T_m (°C)	Peak crystalline temperature T_c (°C)	% crystallinity	As-synthesized elastomer Crystaf results*
YR-056	313.15	124.71	98.13	1.07	Elastomer precipitation at $25 \leq T(^{\circ}\text{C}) \leq 30$
YR-049	323.15	123.89	112.88	1.13	
YR-050	333.15	None	None	0.28	
YR-051	343.15	None	None	0.00	

*Cooling rate = 0.2 °C/min. Indicates liquid-solid phase separation.

Table G.37: Comparison of experimental versus calculated T_g s of as-synthesized Spaleck/MAO E-1-octene elastomers.

Ethylene weight fraction W_E	Glass transition temperature T_g (°C)	Polymerization trials	Polymerization temperature (K)	^{13}C NMR W_E	T_g calculated** for as-synthesized elastomers (°C)	T_g experimental (°C)
0.00	-65.00*	YR-039	313.15	0.38	-79.85	-69.51
0.25	-75.01**	YR-036	323.15	0.48	-83.26	-69.70
0.5	-84.11**	YR-037	333.15	0.44	-82.00	-69.90
0.75	-92.40**	YR-040	343.15	0.42	-81.20	-69.53
1.00	-100.00*		Average		-81.58	-69.66

T_{g1} (Polyethylene) (K) = 173.15; T_{g2} [Poly(1-octene)] (K) = 208.15; $K_{12} = 173.15/208.15 = 0.83$. *Literature value. **Gordon's relation (applicable to random copolymer).

Table G.38: Comparison of experimental versus calculated T_g s of as-synthesized Spaleck/(TTB + TIBA) E-1-octene elastomers.

Ethylene weight fraction W_E	Glass transition temperature T_g (°C)	Polymerization trials	Polymerization temperature (K)	^{13}C NMR W_E	T_g calculated** for as-synthesized elastomers (°C)	T_g experimental (°C)
0.00	-65.00*	YR-055	313.15	0.30	-77.05	-69.12
0.25	-75.01**	YR-054	323.15	0.35	-78.87	-68.68
0.5	-84.11**	YR-053	333.15	0.34	-78.50	-68.71
0.75	-92.40**	YR-052	343.15	0.40	-80.66	-70.54
1.00	-100.00*		Average		-78.77	-69.26

T_{g1} (Polyethylene) (K) = 173.15; T_{g2} [Poly(1-octene)] (K) = 208.15; $K_{12} = 173.15/208.15 = 0.83$. *Literature value. **Gordon's relation (applicable to random copolymer).

Table G.39: Comparison of experimental versus calculated T_g s of as-synthesized Dow CGC/MAO E-1-octene elastomers.

Ethylene weight fraction W_E	Glass transition temperature T_g (°C)	Polymerization trials	Polymerization temperature (K)	^{13}C NMR W_E	T_g calculated** for as-synthesized elastomers (°C)	T_g experimental (°C)
0.00	-65.00*	YR-041	313.15	0.47	-82.90	-68.29
0.25	-75.01**	YR-042	323.15	0.47	-83.01	-68.76
0.5	-84.11**	YR-043	333.15	0.45	-82.42	-67.00
0.75	-92.40**	YR-044	343.15	0.50	-84.01	-67.43
1.00	-100.00*		Average		-83.09	-67.87

T_{g1} (Polyethylene) (K) = 173.15; T_{g2} [Poly(1-octene)] (K) = 208.15; $K_{12} = 173.15/208.15 = 0.83$. *Literature value. **Gordon's relation (applicable to random copolymer).

Table G.40: Comparison of experimental versus calculated T_g s of as-synthesized Dow CGC/(TTB + TIBA) E-1-octene elastomers.

Ethylene weight fraction W_E	Glass transition temperature T_g (°C)	Polymerization trials	Polymerization temperature (K)	^{13}C NMR W_E	T_g calculated** for as-synthesized elastomers (°C)	T_g experimental (°C)
0.00	-65.00*	YR-056	313.15	0.50	-83.99	-69.07
0.25	-75.01**	YR-049	323.15	0.50	-84.07	-68.45
0.5	-84.11**	YR-050	333.15	0.52	-84.92	-68.76
0.75	-92.40**	YR-051	343.15	0.49	-83.85	-67.94
1.00	-100.00*		Average		-84.21	-68.56

T_{g1} (Polyethylene) (K) = 173.15; T_{g2} [Poly(1-octene)] (K) = 208.15; $K_{12} = 173.15/208.15 = 0.83$. *Literature value. **Gordon's relation (applicable to random copolymer).

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