Synthesis and Structural Characterization of a Nickel(II) Precatalyst Bearing a β -Triketimine Ligand and Study of Its Ethylene Polymerization Performance Using Response Surface Methods

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ABSTRACT: The reaction of *N*-(4-(mesitylamino)pent-3-en-2-ylidene)-2,4,6-trimethylbenzenamine (1) with *n*-butyl lithium and then with *N*-(2,4,6-trimethyl-phenyl)-acetimidoyl chloride yields a new β -triketimine ligand, *N*-(4-(mesitylamino)-3-(1-(mesitylimino)ethyl)pent-3-en-2-ylidene)-2,4,6-trimethylbenzenamine, **2**. The addition of **2** to nickel (II) dibromide 1,2-dimethoxyethane (NiBr₂(DME)) in the presence of [Na]⁺[3,5-(CF₃)₄C₆H₃]₄B]⁻ (NaBAr'₄) gives a five-coordinate dimeric complex [(**2**.NiBr)₂].2 [(BAr'₄)], **3**. The structure of **3** has been determined by single crystal X-ray diffraction. This complex generates catalytically active species for the homopolymerization of ethylene in combination with methylaluminoxane to produce elastomeric, branched polyethylene. The effect of factors (temperature, pressure, and cocatalyst to catalyst molar ratio (CC)) on the polymerization process has been investigated using regression models

INTRODUCTION Polyolefins are a range of commodity materials with major economic implications. The range of polyolefin products will grow steadily to meet the increasingly sophisticated needs of consumers.¹ Therefore, the requirement of designing new catalysts for tailoring of bulk polyolefin properties is a major focus of many industrial and academic research groups. The design of new catalysts initially focused on early transition metal systems. Recently, however there has been a shift to an increased emphasis on the development of late transition metal complexes. This shift is based largely on reduced oxophilicity, high polar functional group tolerance, and also the ease with which large ligand libraries and catalyst of late transition metal systems can be generated.² With the late transition metal system, it was not only feasible to prepare known polyolefinic materials under gentle conditions (i.e., low pressure and temperature) but also new materials with well-defined molecular characteristics, including a variety of functionalities.³⁻⁹ Due to the influence

of responses (catalyst activity, crystallinity, and weight-average molecular weight of polymer (M_w)) and visualized via the response surface method (RSM). Activity and M_w responses show a second-order variation with temperature and vary linearly with pressure. Conversely, crystallinity follows a secondorder model while varying temperature, pressure, and CC. Furthermore, a set of polymerization conditions for reaching desirable responses was predicted and then experimentally verified. The activities achieved challenge the best reported activities for Ni(II) catalysts with β -connected imine ligand supports, but fall short of those for α -diimines. © 2013 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 000: 000–000, 2013

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of the ligand framework on the reactivity of the metal center, the design of the ligand is a key step in the development of new catalyst systems. A large number and range of ligands (bi, tri, and tetra dentate organic molecules) for use in late transition metal complexes have been reported.¹⁰ But the field of designing ligand structure was revitalized by the seminal work reported by Brookhart and Gibson on these systems. Brookhart and coworkers'¹¹ ortho-bulky α -diimine nickel catalysts offer a relatively unconfined five-membered ring structure, 4 (Scheme 1). Gibson's iron-based catalysts used a tridentate ligand, sharing the bis-imino structure of the Brookhart systems but containing an additional interaction through a backbone integrated pyridine, 5 (Scheme 1). This led to a more planar and rigid ligand geometry in addition to substantial changes to the electronics of the metal center; the N,N,N ligand set was presented to the metal in a meridional arrangement.¹² The simplicity and symmetry of these structures was striking and led to great flexibility in

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SCHEME 1 Related ligand and complex structures.

ligand design, with much work focused on introducing new ligand families that share some structural similarities to the Brookhart and Gibson systems. More recent attention has focused on provision of additional locations from which to incorporate steric and electronic modifications.¹³

The β -diketiminate class of ligands, generally denoted as "nacnac," or $\{ArNC(R)\}_2CH$ (where Ar = aryl and R=CH₃ or bulkier group) was originally introduced in the 1968,¹⁴ but attracted sustained interest only with the introduction of diaryl diketiminates possessing extreme ortho-bulk,15 a requirement of applications in polymerization, as it hinders chain-transfer and β -hydride elimination processes, while still allowing the β -hydride transfer and readdition sequences that result in chain walking. The first demonstration of their use as N,N bidentate, neutral ligands for NiBr₂ was accompanied by reports of very modest polymerization activity, of less than 1 kg [(mol Ni)⁻¹ h⁻¹ bar⁻¹].¹⁵ The same ligand, but in deprotonated, monoanionic form, was almost contemporaneously reported, in an article which highlighted the remarkable degree of steric control the ligands offered.¹⁶ They subsequently generated wide employment through their ability to stabilize unique coordination environments and to support reactive organometallic reagents, especially those in low oxidation states and with low co-ordination numbers, as is required for polymerization catalysis.^{17,18} When ligands such as 1 were used in anionic form as diketiminates, modest improvement in activity, to 18 kg [(mol Ni)⁻¹ h⁻¹ bar⁻¹], was found.¹⁹ Fluorination of the backbone produced further improvement, to 38.6 kg $[(mol Ni)^{-1} h^{-1} bar^{-1}]$ ²⁰ Only most recently, through the incorporation of further functional groups which confer the ability to remotely modify the electronic properties of the metal center without significantly altering the steric environment, have activities competitive with α -diimine complexes such as 4 been achieved. In the case of **6**, usage of an α -keto- β -diketimine ligand framework makes it susceptible to *O*-coordination by Lewis acids, which can be used to activate the metal center through remote locations.^{21,22} This generated catalysts with much-improved activities of several hundred kg [(mol Ni)⁻¹ h⁻¹ bar⁻¹],²¹ associated with much greater catalyst stability, including claims of living character at high temperatures.²² In a similar vein, nickel precatalysts bearing (*N*-imidoylamidine) ligands have recently been reported.²³ The variation of the electron withdrawing/donating capacity of the substituted phenyl ring on the central nitrogen of the ligand was found to influence polymerization activity of the complexes, with optimal values reaching over 100 kg [(mol Ni)⁻¹ h⁻¹ bar⁻¹].²³

We recently reported on a new class of ligands, derived from Nacnac **1**, termed the β -triketimines, **2** (Scheme 1), neutral and tridentate, as for the *mer* ligand in **5**, but *fac* capping, as shown in the products of their reaction with M(CO)₃ [M = Cr, Mo, W].²⁴ This family of ligands with finely tunable bulk have wide potential in coordination chemistry; a number of their nickel complexes have been prepared, as neutral complexes and as cations, such as **3a** (Scheme 1), which when paired with large anions and activated with methylaluminoxane (MAO), show activity as catalysts for polyethylene (PE) polymerization.²⁵

The systems share the tendency of other nickel catalysts to show complex behavior in polymerization, with short-chain branching accompanying linear chain propagation,¹⁷ in ratios dependent on temperature, cocatalyst to catalyst ratio, and pressure. This complex interdependent behavior is appropriate for study by experimental design methods such as response surface method (RSM). This method identifies any synergistic effect of the reaction parameters on polymerization performance and polymer properties; it provides the best information regarding the effects of independent variables (termed "factors," e.g., temperature, pressure, etc.) and their interactions on observable outputs (termed "model parameters," e.g., activity, $M_{\rm wo}$ etc.) with the minimal number of experimental runs.²⁶ Although there has been use of RSM to evaluate the effects of polymerization controlling factors in Ziegler Natta and metallocene systems,^{26–29} the work reported herein represents its first application to the field of late transition metal polymerizations.

The main objective of this work is to demonstrate the usage of RSM in charting the complex behavior of nickel-catalyzed polymerizations, while investigating the effect of three critical factors [temperature, pressure, and cocatalyst to catalyst molar ratio (CC)] on polymerization behavior of one representative example of an MAO-activated nickel(II) β -triketimine complex, **3**. This is the first report in the open literature of nickel β -triketimine complexes and their potential as polymerization catalysts. Furthermore, we report the development of catalyst activity, polymer molecular weight, and polymer crystallinity regression models using RSM.

RSM

RSM is a collection of mathematical and statistical techniques that can be used for studying the effect of independent variables (factors) and their influence on each other. Furthermore, it models a relationship between the factors and the "response" (the measurable outputs). The models can be used to generate surface and contour plots that provide efficient visualization of the parameter interaction. The objective of RSM is to allow a user to find the optimum values of the input "factors," which will deliver the desired outputs ("response").³⁰ In this experiment, the response surface design developed was based on Box–Behnken design; accordingly, a quadratic regression model was used to develop second-order response surface models. The general form is as shown in eq 1:

$$R = b_0 + \sum_{i=1}^n b_i x_i + \sum_{i=1}^n b_{ii} x_i^2 + \sum_{i< j}^n b_{ij} x_i x_j$$
(1)

where *R* denotes the predicted response of the process, x_i refers to the coded factors (temperature, $x_{\rm D}$ pressure, $x_{\rm B}$ and cocatalyst to catalyst ratio, $x_{\rm C}$) and b_0 , b_i , b_{ii} , b_{ij} are regression coefficients. From this general form, three different equations were derived, one for each of the three observable responses, $R_{\rm A}$ (activity), R_{MW} (weight-average Molar mass), and $R_{\rm Xtl}$ (percent crystallinity). After performing the experimental test runs and determining the coefficients of the models, insignificant coefficients for terms which did not influence the response variation were removed from each of the fitted models. Such reduction simplified the regression model while maintaining its high accuracy. The statistical basis for this process is detailed in Supporting Information.

EXPERIMENTAL

Materials

All manipulations involving air or water sensitive compounds were performed under an inert atmosphere using standard high vacuum Schlenk line techniques and glovebox. All reagents were used as received from Aldrich and Merck unless otherwise specified. Hexane was distilled immediately before use from Na/K alloy, Tetrahydrofuran (THF) and Et₂O from sodium/benzophenone and dichloromethane (DCM) from calcium hydride. Triethylamine and 2, 4, 6-trimethylaniline was dried over calcium hydride. Polymerization grade ethylene with high purity was obtained from Arak Petrochemical Co. (Arak, Iran) and was further purified by passage through an oxygen/moisture trap. Industrial toluene for polymerization was obtained from Arak Petrochemical Co. (Arak, Iran) and was further purified by passage through an oxygen/moisture trap. Industrial toluene for polymerization was obtained from Arak Petrochemical Co. (Arak, Iran) and was distilled over sodium wire. The starting compounds N-(2, 4, 6-trimethyl phenyl acetimidoyl chloride and NaBAr'₄ ([Na]⁺[3,5-(CF₃)₄C₆H₃]₄B]⁻) were prepared according to literature procedures.^{24,31}

Synthesis

2,4,6-Trimethyl-N-[4-(2,4,6-trimethylphenyl) iminopent-2-en-2-yl]aniline, 1

1 was produced by a modification of a literature method:³² 2,4,6-trimethylaniline(30 mL,0.21 mol) and acetyl acetone (10 mL, 0.1 mol) were stirred in toluene (100 mL) and *p*-toluene sulfonic acid (~ 0.05 g) was added. The solution was refluxed for 5 h using a Dean-Stark azeotropic distillation trap to remove the fractions of amine and toluene (55–61 °C) and yellow oil (enamineone) at 103–126 °C. The dark brown solid obtained was recrystallized with methanol and DCM. The Product **1** was isolated as white crystals. Yield: 30.74%, mp: 60 °C, ¹H NMR (400 MHz, CDCl₃, δ , ppm): 1.88 (s, 12H), 2.10 (s, 6H), 2.20 (s, 6H), 4.76 (s, 1H); 6.85(s, 2H), 7.40 (s, 2H), 12.05 (br s, 1H). Anal. calcd for C₂₃H₃₀N₂: C, 82.58; H, 9.05; N, 8.37. Found: C, 82.41; H, 8.80; N, 8.38. Data concurred with those reported.³²

N-(4-(Mesitylamino)-3-(1-(mesitylimino)ethyl) pent-3-en-2-ylidene)-2,4,6-rimethylbenzenamine, 2

To a stirred solution of 1 (3.42 g, 0.0102 mol) in hexane (20 mL) in a Schlenk tube was added N-butyl lithium (6.4 mL of a 1.6 M solution in hexanes, 0.0102 mol) under a nitrogen atmosphere. The solution was stirred at 50 °C for 5 min and then N-(2,4,6-trimethyl phenyl acetimidoyl chloride (2 g, 0.0102 mol) was added, and the reaction stirred at room temperature for 48 h. The solution was washed three times with deionized water, and the organic layer was separated, dried over MgSO₄, and the solvent removed. The residue was recrystallized from methanol and DCM, and the final product was isolated as pale yellow crystals of 2. Yield: 34%, mp: 132 °C. ¹H NMR (400 MHz, CDCl₃, δ , ppm): (solution composition immediately after dissolution: enamine-diimine tautomer (*E*-isomer) 87%, β -triketimine tautomer 13%; solution composition \sim 24 h after dissolution: enamine-diimine tautomer (*E*-isomer) 66%, β -triketimine tautomer 34%; peaks due to both isomers (unless otherwise specified): 1.61, 1.85 (2 s, 18H), 1.91, 2.15 (2 s, 9H), 2.18 (s, 9H), 6.80, 7.20 (2 s, 6H), 4.70, 13.20 (2s, 1H, α -CH of β -triketimine tautomer, NH of enamine-diimine tautomer). ¹³C NMR (100 MHz, CDCl₃, δ , ppm) (peaks due to both isomers, unless otherwise specified): 18.47, 18.51, 20.72, 20.81, 20.87, 24.91 (CH_3CN, 4 \times Ar-CH₃), 72.18 (α -CH, β -triketimine tautomer), 108.42 (alkenyl α-C, enamine-diimine tautomer), 125.63, 128.56, 128.66,



129.12, 131.78, 132.10, 146.17, (7 × aromatic carbon), 159.74 (conjugated C=N, enamine diimine tautomer), 169.20 (C=N, β-triketimine tautomer), 172.19 (C=N, enamine diimine tautomer). IR (KBr, powder, cm⁻¹): 1640, 1662 (C=N), 1537 ((C=C) aromatic). HRMS (m/z): calcd for C₃₄H₄₃N₃, 493.72; Found, 494.4[M+H]⁺. Anal. calcd for C₃₄H₄₃N₃: C, 82.71; H, 8.77; N, 8.52. Found: C, 82.79; H, 8.63; N, 8.18.

Nickle(II) β -Triketimine Complex, 3

NaBAr'₄ (0.89 g, 0.001 mol), 2 (0.49 g, 0.001 mol), and NiBr₂(DME) (0.309 g, 0.001 mol) were added to a Schlenk tube under a nitrogen atmosphere. THF (10 mL) was added and the reaction stirred for 24 h. The solvent was removed in vacuo and DCM (20 mL) was added to the reaction mixture. The dark obtained solution was filtered through celite under a nitrogen atmosphere. The celite plug was washed twice with DCM (10 mL). The combined DCM extracts were then concentrated by 40% of their volume in vacuo, and then layered with distilled hexane (60 mL) and left to precipitate for 72 h. Dark green crystals formed which were isolated by filtration, washed with hexane, and dried in vacuo. Yield: 47%. IR (KBr, powder, cm⁻¹): 1630, 1658 (C=N), 1610 ((C=C) aromatic). Anal. calcd for C₁₃₂H₁₁₀N₆ Ni₂Br₂F₄₈B₂ : C, 53.02; H, 3.67; N, 2.80; Br, 5.34. Found: C, 52.82; H, 3.63; N, 2.80; Br, 5.31.

Ethylene Polymerization Procedure

Ethylene polymerization was performed in a 300-mL stainless steel reactor containing systems for full control of temperature and reaction pressure. Before starting, the reactor was warmed up to 100 °C, purged with argon and vacuumed sequentially. It was repeated several times to remove oxygen and humidity. For start-up, the reactor was cooled down while kept purging with argon. The reactor was then charged with toluene (150 mL) and saturated with ethylene. The cocatalyst was added (in an amount as recorded in Table 1), and the ethylene pressure increased to 1 bar. The appropriate amount of catalyst was suspended in 3 mL of toluene and rapidly added to the stirring solution in the reactor. It was then sealed and pressurized to the software suggested ethylene pressure, and the solution was stirred for 1 h. The polymerization was terminated by venting the reactor followed by quenching the mixture with 100 mL of acidified methanol (HCl, 1 vol %). The precipitated polymer was filtered, washed twice with 100 mL of methanol, and dried in vacuo at 40 °C for several hours. If the polymer did not precipitate from the quenched reaction mixture, it was isolated by solvent evaporation on a rotary evaporator, followed by washing with acidified methanol and drying *in vacuo*.

Response Surface Experimental Design

To create a response surface design, the type of design, the number of independent variables (or "factors"), the name of the factors, their upper and lower levels, and replication points must be entered into the software. In this Box-Behnken design, the three factors were temperature (x_T : lower level 10, midpoint 30, higher level 50 °C), pressure (x_P : levels 3, 5, and 7 Bar), and cocatalyst to catalyst ratio, CC (x_C : levels 1000, 2000, and 3000). The levels of these fac-

TABLE 1 Experimental Design of Polymerization Process

Run Number	Temperature (°C)	Pressure (bar)	Co-catalyst to Catalyst Molar Ratio (CC)
1	10	1	2000
2	50	1	2000
3	10	5	2000
4	50	5	2000
5	10	3	1000
6	50	3	1000
7	10	3	3000
8	50	3	3000
9	30	1	1000
10	30	5	1000
11	30	1	3000
12	30	5	3000
13 ^a	30	3	2000
14 ^a	30	3	2000
15 ^a	30	3	2000

^a Replication of center point-related run in Box–Behnken design space.

tors were chosen based on preliminary results with this catalyst.²⁵ The experimental plan generated using the Minitab® 15 software involved 13 runs. Also, to provide an estimate of the experimental error in the process and achieve more precise estimates of the factor effects, the center point, that is, the midpoint between the high and low levels, was replicated twice. Therefore, in total, the software suggested 15 test runs which are shown in Table 1.

The responses measured (i.e., the model parameters) were R_A (catalyst activity), R_{Mw} (weight-average Molar mass), and R_{Xtl} (percent crystallinity).

Characterization

¹H NMR and ¹³C NMR spectra were recorded on a Bruker Avance III 400 MHz or Bruker Avance II 500 MHz spectrometer. IR spectra were recorded on a Perkin-Elmer Spectrum RX1 Fourier transform infrared (FTIR) spectrometer using Nujol mulls between KBr plates or on a Perkin-Elmer Spectrum BX FTIR spectrometer using neat solids. Elemental analysis measurements were performed by CHNSO Elementar Analyzer (Vario EL ???). Melting points of molecular compounds was determined using an Electrothermal melting point apparatus in open capillary tubes. Differential scanning calorimetry (DSC) of polymers was performed using a Mettler-Toledo model 822^e instrument, interfaced to a digital computer equipped with Star E 9.01 software (Sencor FRS5). Samples were heated from room temperature to 170 $^\circ\mathrm{C}$ at a rate of 10 °C min⁻¹ and held there for 2 min, followed by cooling to -120 °C at a rate of 10 °C min⁻¹. Finally, the samples were reheated to 170 °C using the same heating rate. The melting point and crystallinity were determined according to the results obtained from the final step. Crystallinity was calculated by integration of the second heat



SCHEME 2 Synthesis of 2.

melting endotherm and reported as a percentage based on the value 293 J g^{-1} for 100% crystalline PE. High temperature gel permeation chromatography (GPC) was performed by Varian (PL-GPC220) at 145 °C in trichlorobenzene with polystyrene standards. Crystals suitable for X-ray diffraction were obtained by careful layering of hexane onto a saturated DCM solution of complex. Single crystals were mounted in perfluoropolyether oil into an Oxford Instruments Cryostream 700. Diffraction measurements were performed on an Oxford Diffraction X-Calibur 2 diffractometer using graphite-monochromated Mo-K α radiation, and the data were collected and processed by the programs CrysAlis PRO and CrysAlis RED.33 The structure was solved using SHELXS34 and refined with SHELXL.³⁴ Full experimental details, bond lengths and angles, and atomic co-ordinates are available as Supporting Information.

RESULTS AND DISCUSSION

Synthesis and Structure of the Catalyst

The β -triketimine ligand **2** was synthesized by reaction of β diketimine **1** with *n*-BuLi giving a lithium diketiminate which was then reacted with acetimidoyl chloride, giving pale yellow crystals of **2** in good yield after recrystallization from methanol and DCM (Scheme 2).²⁴ This reaction appears to proceed with good chemoselectivity for C—C bond formation as was previously found for other electrophiles.³⁵ The ligand was fully characterized by ¹H and ¹³C NMR spectroscopy as well as elemental analysis. The solution-phase behavior of β triketimines is complicated by the presence of equilibria between numerous isomeric species, as a result of tautomerism between the true β -triketimine and enamine-diimine forms, as well as E/Z-isomerism in the pendant imine of the enamine-diimine tautomer.²⁴ The substituent pattern on three aryl groups has a significant effect on the position of the equilibria: for **2** the major component in solution immediately after dissolution was found to be the *E*-isomer of the enamine-diimine tautomer, with the relative amount of the β -triketimine tautomer increasing over time. Due to steric repulsion, the *Z*-isomer is very unlikely to occur.²⁴ This fluxional behavior of compounds in solution has also been observed for some α -diimine and β -diimine ligands.^{15,36}

The synthesis of **3** by addition of **2** to $NiBr_2(DME)$ in the presence of NaBAr'₄ in THF is depicted in Scheme 3. Crystallization from DCM and hexane allowed isolation of the product as dark green crystals in 47% yield. Single crystals of 3 suitable for X-ray diffraction studies were obtained by vapor diffusion of hexane into a DCM solution under nonanhydrous conditions. The resulting molecular structure (cation only) is shown in Figure 1. The crystallographic parameters and crystal data and refinement are summarized in Tables 2 and 3, respectively. The molecular structure features a centrosymmetric dimeric bromide bridged dication, in which the nickel centers are in a slightly distorted square-pyramidal geometry. The bond distances in the X-ray structure of 3 reveal that the Ni-N bond distances are noticeably longer than corresponding distances seen in other four-coordinate nickel complexes of tridentate β -triketimines which is simply as a result of the increased coordination number at nickel.²⁵ The increase in coordination number is also responsible for the fact that the N–N separation of 2.887(4) Å is somewhat larger than the corresponding distances seen in the fourcoordinate nickel complexes. The basal Ni(1)-N(1) and Ni(1)-



SCHEME 3 Synthesis of 3.

Materials



FIGURE 1 ORTEP representation of the crystal and molecular structure of the dicationic unit in **3** at 60% probability. Hydrogen atoms are omitted.

N(2) distances of 2.083(3) Å and 2.126(3) Å, respectively, are somewhat longer than the axial Ni(1)-N(3) distance (2.038(3) Å), which is likely due to the *trans*-influence of the two bridging bromide ligands. Additionally, The C=N–CAr bond angles all lie close to the sp² ideal of 120°, as would be expected for an all-methyl backbone substituted ligand.¹⁷ The structure of **3** reported here represents the first structurally characterized dicationic $[{LNi(\mu-X)}_2]^{2+}$ complex for any halide X and any tridentate neutral ligand L.

TABLE 2 Crystallographic Data Collection and Refinement

Details in 3	
Formula	$C_{132}H_{110}Br_2N_6Ni_2B_2F_{48}$
Formula weight	2991.06
Crystal system	Triclinic
Space group	P-1
<i>a</i> [Å]	14.5663(5)
b [Å]	14.8071(6)
<i>c</i> [Å]	16.3965(6)
α [°]	82.985(3)
β [°]	85.599(3)
γ [°]	69.118(4)
Volume [Å ³]	3277.4(2)
Ζ	1
$D_{\text{calc}} [\text{g cm}^{-3}]$	1.515
μ [mm ⁻¹]	1.017
Т[К]	100
θ Range [°]	2.9–26.4
Reflections measured	19,471
Unique reflections (R _{int})	13,225 (0.033)
Obs. data [l $>$ 2.0 $\sigma(\text{l})]$	7889
R (observed)	0.0408
wR2 ^a	0.0859
S	0.86

analogs.¹⁹ This is even more probable after reaction with MAO, during which the bromides are replaced with the less-effectively bridging ligand, methyl. Whether the active form of the complex remains tridentate on co-ordination by ethylene is not known. There are reports of tridentate scorpionate complexes of nickel with some polymerization activity;³⁶ however, in our case, we suspect that there may be decomplexation of one imine arm, to provide sufficient space for attachment of ethylene; the detached arm then becomes a point for reaction with or co-ordination by MAO, in a manner analogous to **6**. We will present further evidence in support of this hypothesis in a following article. For the moment, we will focus on the use of RSM for studying the catalyst performance on ethylene polymerization. Specific operational conditions can either favor

The color in solutions of 3 is not the same as that of the crystal. It is likely that the dimeric structure is broken down to monomers in solution, as has been observed for diketiminate

TABLE 3 Selected Bond Distances (Å) and Angles (°) for the Dicationic Units in ${\bf 3}$

Bond Distances	
Br(1)-Ni(1)	2.4969(6)
Br(1)'-Ni(1)	2.5072(5)
Ni(1)-N(1)	2.083(3)
Ni(1)-N(2)	2.126(3)
Ni(1)-N(3)	2.038(3)
N(1)-C(2)	1.283(4)
N(2)-C(13)	1.276(4)
N(3)-C(24)	1.282(4)
N(1)-C(4)	1.455(4)
N(2)-C(15)	1.454(4)
N(3)-C(26)	1.451(4)
C(1)-C(2)	1.536(4)
Bond Angles	
Ni(1)-Br(1)-Ni(1)'	98.70(2)
Br(1)-Ni(1)-Br(1)'	81.30(2)
Br(1)-Ni(1)-N(1)	159.16(7)
Br(1)-Ni(1)-N(2)	93.69(8)
Br(1)-Ni(1)-N(3)	113.59(8)
Br(1)'-Ni(1)-N(1)	94.64(7)
Br(1)'-Ni(1)-N(2)	166.39(7)
Br(1)'-Ni(1)-N(3)	103.00(7)
N(1)-Ni(1)-N(2)	85.55(10)
N(1)-Ni(1)-N(3)	87.25(11)
N(2)-Ni(1)-N(3)	90.61(10)
Ni(1)-N(1)-C(4)	121.70(19)
Ni(1)-N(2)-C(15)	123.90(19)
Ni(1)-N(3)-C(26)	123.69(19)
C(2)-N(1)-C(4)	121.1(3)
C(13)-N(2)-C(15)	119.3(3)
C(24)-N(3)-C(26)	118.8(3)

^a $wR2 = \{\sigma[w(Fo2 - Fc2)2]/\sigma[w(Fo2)2]\}1/2.$

	Independent Variables (Factors)		tors)	A			0
Experimental Run	<i>х</i> т (°С)	x _P (bar)	X _C	$[(mol Ni)^{-1} h^{-1}])$	$M_{ m w}$ (g mol ⁻¹)	PDI	(%)
1	10	1	2000	40	1,20,000	1.58	28.24
2	50	1	2000	30	1,92,815	2.18	1.90
3	10	5	2000	100	2,71,600	1.68	29.79
4	50	5	2000	137	5,78,984	2.60	7.60
5	10	3	1000	65	2,30,823	1.70	31.1
6	50	3	1000	50	4,49,778	2.39	5.07
7	10	3	3000	70	1,57,870	1.77	32.08
8	50	3	3000	50	4,11,656	2.75	5.61
9	30	1	1000	130	3,56,399	2.55	9.84
10	30	5	1000	250	4,54,516	2.98	13.05
11	30	1	3000	50	4,24,259	2.16	12.70
12	30	5	3000	370	5,87,144	2.79	13.60
13	30	3	2000	240	4,50,861	2.25	12
14	30	3	2000	220	4,53,689	2.29	11.07
15	30	3	2000	212.5	4,07,616	2.27	10.55

TABLE 4 Experimental Values for Activity, *M*_w, and Crystallinity

propagation over chain-branching, leading to moderately crystalline plastomeric PE, or vice versa, giving more highly branched, low-crystallinity elastomer.³⁷ The prospect of having sufficient knowledge of the dependence of polymer properties on experimental factors to be able to select desired values of branching, hence crystallinity, is attractive.

Estimated Regression Models

The performance of the nickel (II) β -triketimine complex **3** was evaluated in the ethylene polymerization using MAO as cocatalyst. Table 4 indicates the experimental values of responses namely, activity, weight-average molecular weight (M_w), and crystallinity, according to the experimental plan. Stepwise regression was applied using backward elimination methods to exclude insignificant coefficients from the initial response surface models.

By reducing eq 1, three partial quadratic models with adequate goodness-of-fit were obtained for the responses of activity (R_A), weight-average molecular weight (R_{Mw}), and crystallinity (%) (R_{Xtl}) as shown in eqs 2–4, respectively.

$$R_{\rm A} = 222.3 - x_{\rm T} + 75.9x_{\rm P} + 5.6x_{\rm C} - 144.1x_{\rm T}^2 - 20.8x_{\rm P}^2 + 50x_{\rm P}x_{\rm C}$$
(2)

$$R_{MW} = 447783 + 106618x_{T} + 99846x_{P} + 11177x_{C} - 146093x_{T}^{2} + 58642x_{T}x_{P}$$
(3)

$$R_{\rm xtl} = 11.2 - 12.6x_{\rm T} + 1.4x_{\rm P} + 0.6x_{\rm C} + 5.9x_{\rm T}^2 - 0.2x_{\rm P}^2 + 1.3x_{\rm C}^2 + x_{\rm T}x_{\rm p} - 0.5x_{\rm P}x_{\rm C}$$
(4)

Details of the parameter reduction, goodness of fit, analysis of variance (ANOVA table), and probability plot of residuals are appended in Supporting Information. The response contour and surface plots were generated using Minitab[®] 15 software to reveal the effect of temperature, pressure and CC on the activity, M_{wv} , and crystallinity.

Figure 2 depicts the relations of activity with pressure, temperature and CC. In Figure 2(a), the cocatalyst ratio is held constant at 3000. The U-shaped curve indicates two competing processes. From 10 °C to \sim 25 °C, there is normal Arrhenius behavior, the rate of propagation steeply increasing with temperature. However, activity passes through a maximum at 30 °C. Figure 2(a) shows that this maximum is independent of pressure, so that the maximum activity {291.86 kg [(mol Ni)⁻¹ h⁻¹]} appears at 30 °C after raising pressure and CC to 5 bar and 3000, respectively [Fig. 2(a,b)]. The reason for the drop in activity beyond 30 °C must be catalyst de-activation through a thermally activated process which is zero-order in monomer. This reaction must have a higher activation energy than propagation. Decreasing ethylene solubility due to the rising temperature could also play a role, but catalyst decay clearly has the major effect on decreasing the activity. In this respect, Catalyst 3 is similar to previously reported nickel-based catalysts, though the particular value of temperature which is optimum must be determined for each catalyst.37

Figure 2(b) also shows the U-shaped dependence of activity on temperature versus CC, with no effect of CC on the optimum temperature. This does not mean that co-catalyst is not involved in the de-activation; it is most-probably an MAOmediated reductive process, but over the short range of CC studied, the pre-equilibrium is saturated, that is, MAO is in such large excess that the process will appear pseudo-first order in catalyst. It is also apparent from this figure that the activity showed a rigorously linear increase with reaction pressure. This is also clear in Figure 2(c). This shows that propagation is first-order in monomer, at all pressures. This



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FIGURE 2 Contour and surface plots of activity-related regression model at constant level of: (a) CC; (b) pressure; (c) temperature.

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FIGURE 3 Contour and surface plots of M_w -related regression model at constant level of: (a) CC; (b) pressure; (c) temperature.

Matrials



SCHEME 4 Possible chain-transfer processes limiting $M_{\rm w}$.

is in contrast to kinetic studies on catalysts similar to 4, with bidentate α -diimine ligands, which found first-order behavior only at low pressures. At higher pressures, rate was inhibited, a fact ascribed to co-ordination of a further monomer molecule.³⁸ It is possible that the better encapsulation of the active site offered by the β -connected imines (see Scheme 1), or perhaps the additional co-ordinating imine of the tridentate ligand in 3, is responsible for this difference. Given that this is the first quantitative kinetic study of any β -connected diimine-supported nickel-centered catalyst with pressure as a variable, it is not yet possible to distinguish these two hypotheses. Given the linear pressure-dependence of activity found here, for effective comparisons of activities across other catalysts, it is instructive to consider values corrected for such effects by reporting in units of activity per unit pressure (vide infra). To conclude discussion of activity response, it is important to note that CC has only a minor effect on activity so that increasing this ratio leads to a small increase in catalyst activity, over the limited range studied. A wider range may well produce more significant variation.

Figure 3 shows the contour and response plots of the $M_{\rm w}$ regression model. Like activity, $M_{\rm w}$ increases with temperature to a maximum, then decreases, but unlike activity, the optimum M_w depends on both temperature and pressure. The most surprising aspect of the data is in the range from 10 °C to 30 °C, where the molecular weight increases with temperature. We have previously seen that catalyst de-activation is not important in this temperature range. If there was fast initiation, very slow chain transfer, and constant active site concentration, then the M_w would indeed be expected to scale with temperature, according to Arrhenius, as seen. In this region, then, the polymerization seems to have some "living" character. Consistent with this, the lowest polydispersity index (PDI) values recorded (1.6-1.8) are in the low temperature region. However, these values are not low enough to justify a claim of fully "living" behavior. As temperature rises beyond 30 °C, a greater proportion of active sites may overcome the higher activation energy of chain transfer, thus explaining the dip in $M_{\rm w}$ beyond approximately 30 °C.³⁷

Interestingly, careful examination of Figure 3(a-c) allows us to comment on the three main types of chain transfer, as shown in Scheme 4: The $M_{\rm w}$ varies linearly with the pressure at all temperatures. This suggests that transfer to monomer, either by hydride transfer in a Ni-polymeryl-ethylene-co-ordinated resting state, or by associative exchange of ethene on a Ni-hydride-alkene-terminated-polymeryl intermediate, are both slow; either route should be accelerated at higher pressure, leading to drops in M_{w} . The opposite is seen. For example, $M_{\rm w}$ changes from less than 4,00,000 to above 5,00,000 g mol⁻¹ when the pressure increases from 1 to 5 bar at 30 °C [Fig. 3(c)]. Thus, chain transfer is predominantly to aluminum, and not to monomer. No attempt was made to remove residual Me₃Al from the MAO used, and it is known that chain transfer to Al is favored in the presence of Me₃Al.^{21,22} Yet. the pressure effect dominates; molecular weight is not yet fully limited by chain transfer; the higher propagation rate at higher pressures contributes to longer chains. It may be that this effect is enhanced by high pressures distorting the equilibrium at the head of Scheme 4 to the right, hence suppressing chain transfer to aluminum. Moreover, the increase in $M_{\rm w}$ with pressure is greater at higher temperature than at lower temperature. It is suspected that at the higher temperatures, catalyst de-activation reduces the number of active centers, hence increases $M_{\rm w}$ by that mechanism. The fact that ¹³C NMR evidence shows very little alkene end groups also suggests that chain transfer to aluminum is the main mediator of $M_{\rm w}$ above 30 °C, whereas below this level, the polymerization time and number of active centers dominate in a pseudo-living way.

Similarly, there is a linear variation of M_w with CC, but it is negligibly small over the short range studied. Maximum M_w (i.e., 5,57,000) is achieved at 5 bar, 30 °C and CC equal to 3000. Reducing the amount of Me₃Al in the MAO may have a



FIGURE 4 Contour and surface plots of crystallinity-related regression model at constant level of: (a) CC; (b) pressure; (c) temperature.

TABLE 5 A	Typical	Polymerization	Condition	and	its I	Predicted
Responses						

Polymerization C	Condition	Predicted Response		
Factor	Amounts	Response	Amounts	
Temperature (°C)	15.65	Activity (kg [(mol Ni) ⁻¹ h ⁻¹])	211	
Pressure (bar)	5	<i>M</i> _w (g/mol)	3,58,901	
СС	3000	Crystallinity (%)	25	

more significant effect on $M_{\rm w}$ than its variation over a three-fold range.²¹

Figure 4 depicts crystallinity responses to variation in temperature, pressure, and CC. It is clear that a higher level of crystallinity is obtained at lower temperatures. This mirrors behavior in other nickel-catalyzed polymerizations; the chain-walking process which results in short-chain branches, which reduce crystallite size and increase amorphous content is suppressed relative to linear propagation at lower temperatures because it has a higher activation energy, that is, polymer with greater branching numbers (and hence lower crystallinity) is produced by increasing the temperature.³⁹ Although the crystallinity increases with increasing the pressure, as linear propagation is first-order in ethylene, but branching is zero order, the temperature is the most effective factor in controlling the crystallinity of the polymer. Therefore, the maximum crystallinity level (above 30%) would be achieved at 5 bar, 10 °C and CC equal to 1000 or 3000 [Fig. 4(b)]. We have no explanation for the minor dip in crystallinity at intermediate levels of CC.

In addition to visualization of the variation of the responses, Minitab® 15 provides the means to determine a set of process conditions to meet a polymer user's desired specifications. For this purpose, the desirable range of responses must be introduced to the software; in return, it provides the experimental conditions which give the most optimal compromise, along with predicted values for the responses.⁴⁰ In this investigation, the desired range of the responses were defined as activity higher than 200 kg [(mol Ni)⁻¹ h⁻¹], $M_{\rm w}$ between 3,00,000 and 5,00,000, and crystallinity higher than 20%. Accordingly, the software suggested a set of polymerization conditions as shown in Table 5. This set of conditions was experimentally checked to evaluate the predicted responses. The experimental values from the input factors shown in Table 5 were 200 kg [(mol Ni)⁻¹ h⁻¹] activity (5.2% error), 3,94,791 g mol⁻¹ $M_{\rm w}$ (10% error), and 22.3% crystallinity (10.3% error). This indicates that all three regression models have predicted the experimental responses from set input factors reasonably well. The largest error relates to crystallinity, which, given the broad melting endotherms of these branched PEs, is the least-precisely known parameter. It would be equally valid to define a crystallinity of 0% as a desirable outcome for a highly flexible elastomer. Such a value would correspond to a branching rate of 50-60 or more methyl-terminated branches per thousand carbon atoms.⁴¹ At 22% crystallinity, as in the tested response, a PE would be likely to have a branching rate closer to 30 branches per 1000 carbons.⁴¹ Hence, with the help of the models, operating conditions can be chosen to deliver the polymer properties required.

Given the linear pressure-dependence of activity shown in Figure 2, for effective comparisons of activities across other catalysts, it is instructive to consider values corrected for such effects by reporting in units of activity per unit pressure. The predicted value for activity, when reported in pressure-corrected units, of 42.2 kg [(mol Ni)⁻¹ bar⁻¹ h⁻¹] related to the defined desirable values of high $M_{\rm w}$ and moderate crystallinity. If an elastomer with lower crystallinity is desired, and a lower $M_{\rm w}$ could be tolerated, then the highest activity was obtained during Run 9, which achieved 130 kg $[(mol Ni)^{-1} bar^{-1} h^{-1}]$. This value compares with values of 0.7^{12} to 38.6^{20} kg [(mol Ni)⁻¹ bar⁻¹ h⁻¹] for diketiminate complexes, and 255 kg $[(mol Ni)^{-1} bar^{-1} h^{-1}]$ for keto-diimine complex 6 when activated, as here, with MAO. However, that value was extrapolated from a 10-min run and is therefore not directly compatible with the full 1-h run data reported here. The values reported here may in fact be comparable with those obtained with 6; indeed, the active site may be similar, in a putative bidentate active form of Cation 3a, with a pendant, unco-ordinated enamine taking the role of the keto function in **6**. All these systems derived from β connected imines fall well-short of the activities achievable with the best α -diimine nickel complexes (3000 kg [(mol Ni)⁻¹ bar⁻¹ h⁻¹], 15 min run).⁴² Notwithstanding these details, it is clear that activity alone cannot be optimized with no effect on M_w and crystallinity, both of which are critical to the ultimate usefulness of the polymer produced. Further studies on nickel-catalyzed polymerizations may benefit from similar treatment of all relevant variables using RSMs.

CONCLUSIONS

In summary, the synthesis and characterization of a bulky nickel (II) β -triketimine complex **3** through reaction of **2** and NiBr₂(DME) was demonstrated. In the solid state, 3 exists as a dimeric bromide bridged dication, in which the nickel centers are in a slightly distorted square-pyramidal geometry. It was used as catalyst precursor for ethylene polymerization in the presence of MAO; under these conditions, it is assumed that the active form is monomeric nickel alkyl. Forthcoming papers will report evidence that this active form may contain a bidentate form of the triketimine ligand. RSM was applied to study the effect of polymerization conditions (temperature, pressure, and CC) on catalyst performance. This provided predictive models for activity, weight-average molecular weight (M_w) , and crystallinity with adequate goodness-of-fit. The activity, M_{w} and crystallinity regression models illustrated that temperature and pressure played an important role in controlling the measured outputs (activity, M_{w} and crystallinity): activity showed first-order dependence on pressure at all pressures but was mediated by a pressure-independent thermally activated catalyst decay process, while CC had only minor effects over the limited

threefold range studied. Additionally, the software accurately predicted a set of polymerization conditions in which the desirable responses (i.e., activity > 200 kg [(mol Ni)⁻¹ h⁻¹], $M_{\rm w} = 3,00,000-5,00,000$, crystallinity > 20 percent) were obtained.

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