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A Robust Ni(II) α-Diimine Catalyst for High Temperature Ethylene Polymerization

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S Supporting Information

ABSTRACT: Sterically demanding Ni^{II} α-diimine precatalysts were synthesized utilizing 2,6-bis(diphenylmethyl)-4-methyl aniline. When activated with methylaluminoxane, the catalyst $NiBr_2(ArN{=}C(Me){-}C(Me){=}NAr)$ (Ar = 2,6 bis(diphenylmethyl)-4-methylbenzene) was highly active, produced well-defined polyethylene at temperatures up to 100 °C (M_w/M_n = 1.09−1.46), and demonstrated remarkable thermal stability at temperatures appropriate for industrially used gas-phase polymerizations (80−100 °C).

Over the past three decades, there has been an explosion of research dedicated to the design and development of homogeneous, single-site olefin polymerization catalysts. Single-site catalysts provide tremendous flexibility in ligand design and have revolutionized the field of polyolefin research by establishing new opportunities for mechanistic understanding, catalyst control, and tailored polyolefin synthesis that were impossible using heterogeneous catalyst systems.[1−6] Perhaps one of the most significant advances during this time period was the development of highly active, late transition-metal-based olefin polymerization catalysts by Brookhart and co-workers.[7,8] These Ni- and Pd-based α-diimine catalysts were capable of producing high molecular weight polyethylenes (PEs), would tolerate and incorporate numerous polar comonomers,[9−12] and could produce multiple polymer topologies ranging from linear to hyperbranched by simply varying ethylene pressure.[13−20]

Despite these advantages, Ni- and Pd-based catalysts generally exhibit poor thermal stability at elevated temperatures that are required for industrially used gas-phase polymerizations (70−110 °C).[13,21] As a result, the commercialization and overall industrial appeal of α-diimine-derived catalyst systems has been greatly hindered. For example, typical Pd^{II}- and Ni^{II}-based α-diimine catalyst systems have been shown to undergo rapid catalyst decomposition at temperatures ≤60 °C. This observation has been attributed to increased *N*-aryl rotations from perpendicular relative to the ligand backbone leading to events such as C−H activation of the ligand itself and increased associative chain transfer, as well as potential decomposition pathways arising from *in situ* generated Ni-hydride species.[13,18,22,23] In addition, ethylene polymerizations that utilize Ni- and Pd-based catalysts often produce PE with decreased molecular weights as reaction temperatures are elevated. This phenomenon, which is attributed to increased rates of chain transfer (via β-hydride elimination) relative to chain propagation and to the decreased solubility of ethylene in toluene at elevated temperatures, further compounds the need for thermally robust catalysts, as extended reaction times are required to produce polymers of sufficient molecular weight.[13] Consequently, the development of late transition-metal-based α-diimine catalysts with enhanced temperature stability is of tremendous importance to the field of olefin polymerization.[13,24,25]

To date, few examples of α-diimine-based catalysts with improved thermal stability have been reported.[22,26−29] To address these temperature sensitivities, researchers have examined the effects that ligand backbone modifications and *N*-aryl moiety substitutions have on the thermal stability of α-diimine-based catalysts. For example, catalysts bearing α-diimine ligands with camphor-derived backbones have displayed modest activity at temperatures as high as 80 °C, yet their turnover frequency (TOF) was shown to decay as a function of time and the polymers produced had broad molecular weight distributions ($M_w/M_n \geq 2.0$) and were highly branched (no T_m was observed).[22] In contrast, Ni^{II}-based catalysts developed by Guan and co-workers, which featured cyclophane-derived *N*-aryl substituents, have demonstrated remarkable activities for ethylene polymerization (TOFs = 1 000 000−1 400 000 h^{-1}), produced well-defined polymers (M_w/M_n = 1.2−1.7), and showed constant TOFs at 70 and 90 °C for 10 min; however, the catalysts did show decomposition upon extended reaction times.[27] In addition, while an elegant example of synthetic chemistry, cyclophane-based ligands require an elaborate multistep synthesis involving three separate transition metal catalyzed reactions to construct the ligand alone.

In an effort to develop a complementary, yet readily accessible alternative to cyclophane-derived catalysts, we sought to design and synthesize α-diimine catalysts featuring sterically demanding *i*Pr* moieties (*i*Pr* = 1,3-bis(2,6-bis(diphenylmethyl)-4-methylphenyl)imidazo-2-ylidene). The *i*Pr* functionality has recently gained popularity in the field of bulky N-heterocyclic carbenes and is structurally related to several reported olefin polymerization catalysts.[30−32] We envisioned that the steric bulk of the *i*Pr* moieties would greatly inhibit *N*-aryl rotations of the α-diimine ligand and thereby dramatically enhance their thermal stability. Herein, we report the successful synthesis and high temperature polymerization of ethylene by a bulky, thermally robust Ni^{II} α-diimine catalyst bearing symmetrical *i*Pr* moieties. To the best of the authors' knowledge,

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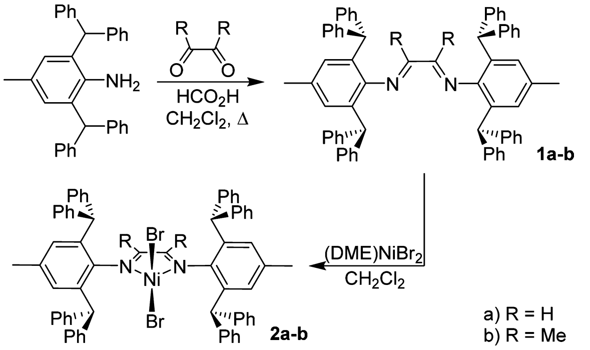
this represents the most thermally stable Ni^{II} α-diimine catalyst reported to date.

The synthesis of Ni^{II} precatalysts **2a** and **2b** (Scheme 1) were completed in three steps from commercially available starting materials. *p*-Toluidine was alkylated using 2 equiv of biphenylmethanol in the presence of stoichiometric HCl and $ZnCl_2$ to yield 2,6-dibenzhydryl-4-methylaniline, which was subsequently condensed onto glyoxal to form ligand **1a**.[32] In an analogous reaction, 2,6-dibenzhydryl-4-methylaniline was condensed onto 2,3-butadione using magnesium sulfate as a desiccant and purified via column chromatography to afford α-diimine ligand **1b**. Ligand **1a** was metalated in methylene chloride at room temperature using the nickel(II) dibromide dimethoxyethane adduct to form precatalyst **2a**. In contrast, ligand **1b** required gentle heating at 30 °C for 5 h to form precatalyst **2b**. Both complexes **2a** and **2b** displayed paramagnetic ^1H NMR spectra, which was indicative of tetrahedral coordination geometries about their Ni^{II} centers.

Scheme 1. Synthesis of α-Diimine Precatalysts 2a and 2b



X-ray quality crystals of precatalyst **2b** were grown by layering a saturated methylene chloride solution with pentane (Figure 1). The observed bond lengths are typical for α-diimine Ni^{II} complexes with N1−Ni = 1.9978(15) Å and N2−Ni = 2.0020(15) Å. The Ni−Br bond lengths were 2.3286(3) and 2.3351(3) Å for Ni−Br1 and Ni−Br2, respectively. Complex **2b** displayed a distorted tetrahedral geometry with a N1−Ni−N2 angle of 80.76(6)° and a Br1−Ni−Br2 angle of 125.767(12)°.

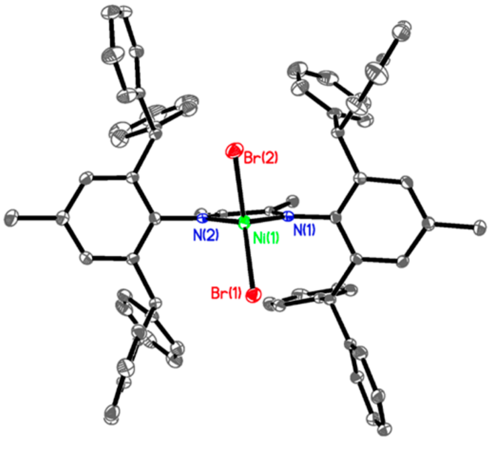


Figure 1. ORTEP drawing of precatalyst **2b** with thermal ellipsoids drawn at 50% probability.

Ethylene polymerizations using precatalysts **2a** and **2b** were evaluated using polymethylaluminoxane-improved performance (PMAO-IP) as an activator.[33] Catalyst **2a** displayed good activity toward ethylene polymerization at 20 °C producing high molecular weight PE (M_n = 165 000 g/mol) with a T_m = 109 °C; however, the polymer displayed broad molecular weight distribution (M_w/M_n = 2.64). In contrast, catalyst **2b** exhibited slightly lower activity at 20 °C, but the molecular weight of the PE produced was in perfect agreement with those theoretically calculated ($M_n^{exp.}$ = 44 000 g/mol, M_n^{theo} = 44 000 g/mol) (Table 1, entry 5), and the resultant PE displayed a remarkably narrow molecular weight distribution (M_w/M_n = 1.09) and a T_m = 60 °C. These observations suggested that catalyst **2b** underwent rapid initiation, could produce branched PE and that little to no chain termination or chain transfer events were detected during the polymerization. Encouraged by this result, all subsequent polymerizations were conducted using catalyst **2b**.

Table 1. Ethylene Polymerization Results for Temperature Screening of Catalyst 2b[a]

entry	T_{rxn} (°C)	time (min)	yield (mg)	TOF[b] (h^{-1})	M_n[c] (kg/mol)	M_w/M_n[c]	T_m[d] (°C)
1	−60	1050	213	277	118	3.25	132
2	−40	110	190	2363	115	2.00	127[e]
3	−20	60	187	4258	102	1.55	111
4	0	45	120	3652	91	1.15	77
5	20	15	69	6297	44	1.09	60
6	40	15	55	4959	47	1.12	39
7	60	15	45	4076	63	1.06	39
8	80	15	22	2029	82	1.22	32
9	100	20	38	2578	94	1.21	30

[a] Polymerization conditions: [**2b**] = 1.57 μmol, 100 mL of toluene, 15 psi, and 100 equiv of methyl aluminiumoxane (PMAO-IP). [b] Turnover frequency (TOF) = mol of ethylene/(mol of cat.*h). [c] Determined using gel permeation chromatography at 145 °C in 1,2,4-trichlorobenzene. [d] Determined by differential scanning calorimetry, second heating. [e] Second heating showed a bimodal melting temperature of 127 and 130 °C.

A temperature-dependent study was performed at 15 psi of ethylene using catalyst **2b** (Table 1). Polymerizations conducted at temperatures ≤ −20 °C (entries 1−3) exhibited low activities (ie. TOFs), broad molecular weight distributions ($M_w/M_n \geq 1.55$), and produced highly linear polymer with T_m = 132, 127, and 111 °C respectively (entries 1−3). In contrast, polymerizations performed at temperatures ≥0 °C (entries 4−7) produced lower molecular weight PEs; however, all PEs were well-defined with narrow molecular weight distributions ($M_w/M_n \leq 1.22$). It should be noted that decreased PE yields and molecular weights were observed at elevated temperatures, which is an observation that is attributed to increased rates of chain transfer (via β-hydride elimination) relative to chain propagation and to the decreased solubility of ethylene in toluene at elevated temperatures.[13,24,25]

To evaluate the thermal stability of catalyst **2b** and to overcome the limitations associated with elevated reaction temperatures, additional polymerizations were performed at 100 psi of ethylene at 80, 90, and 100 °C (Table 2). Polymerizations were run for durations up to 20 min in 5 min intervals, and the polymer obtained was thoroughly characterized. As can be seen in Figure 2, polymerizations conducted at 80 and 90 °C displayed nearly linear growth of molecular weight with time, reached molecular weights of over 600 000 g/mol, and maintained narrow molecular weight distributions

Table 2. Ethylene Polymerization Results at 100 psi for 2b[a]

entry	T_{rxn} (°C)	time (min)	yield (mg)	TOF[b] (× 10^3 h^{-1})	M_n[c] (kg/mol)	M_w/M_n[c]	T_m[d] (°C)
1	80	5	241	66	208	1.13	46
2	80	10	538	74	376	1.18	45
3	80	15	831	76	508	1.25	44
4	80	20	1144	79	625	1.27	43
5	90	5	303	83	260	1.10	43
6	90	10	652	89	377	1.26	42
7	90	15	972	88	516	1.31	40
8	90	20	1273	88	605	1.31	42
9	100	5	346	95	235	1.19	40
10	100	10	746	102	422	1.24	39
11	100	15	1100	100	459	1.42	38
12	100	20	1139	79	564	1.46	37

[a] Polymerization conditions: [**2b**] = 1.57 μmol, 100 mL of toluene, 100 psi of ethylene, and 300 equiv of PMAO-IP. [b] TOF = mol of ethylene/(mol of cat.*h). [c] Determined using gel permeation chromatography at 145 °C in 1,2,4-trichlorobenzene. [d] Determined by differential scanning calorimetry, second heating.

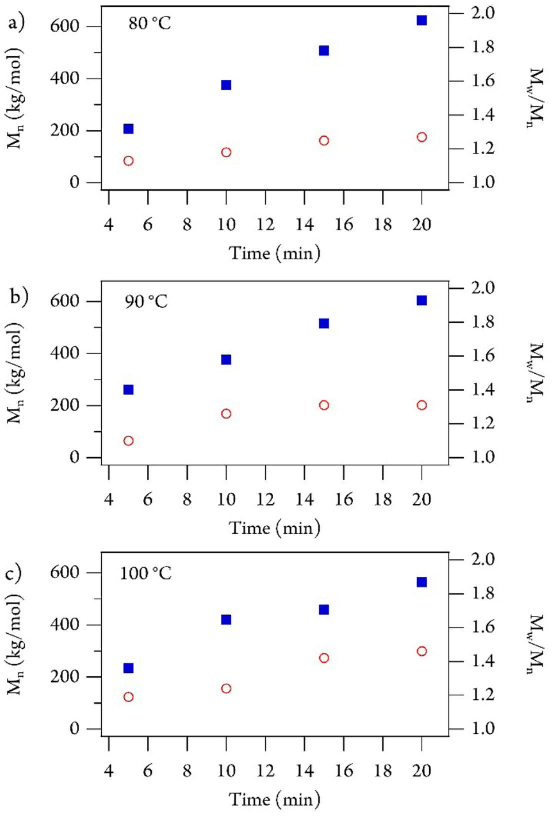


Figure 2. Plot of M_n (blue ■) and M_w/M_n (red ○) versus yield for catalyst **2b** at (a) 80 °C, 100 psi, (b) 90 °C, 100 psi, and (c) 100 °C, 100 psi.

(M_w/M_n ≤ 1.31, Table 2, entries 1−8). In contrast, polymerizations conducted at 100 °C clearly deviate from this behavior displaying nonlinear growth of molecular weight with time and noticeable increases in molecular weight distribution after polymerization times of just 10 min (Table 2, entries 9−12). Each of these PE samples displayed melting transitions just above room temperature (37−46 °C) suggesting that the PE was moderately branched. This was confirmed by NMR spectroscopy in which branching contents of 63−75 branches per 1000 carbons were observed (see Supporting Information) and consisted of both short- and long-chain branches.

Additionally, TOFs and productivities of catalyst **2b** were plotted as a function of polymerization time (Figure 3). At 80 °C, the turnover frequency of catalyst **2b** was found to slightly increase with polymerization time, which could be attributed to the slight exothermicity of the polymerization, and TOFs at 90 °C remained almost perfectly constant for the entire polymerization supporting their stability at these temperatures. At 100 °C, TOFs remained relatively constant up to 15 min; however, a dramatic decrease was observed upon extended polymerization times. An identical trend was also observed in plots of productivity versus time (Figure 3b) in which catalyst **2b** remained highly productive throughout the entire 20 min polymerization at 80 and 90 °C, while productivities at 100 °C do not increase upon polymerization times longer than 15 min, thereby signifying significant catalyst decomposition at this temperature.[34]

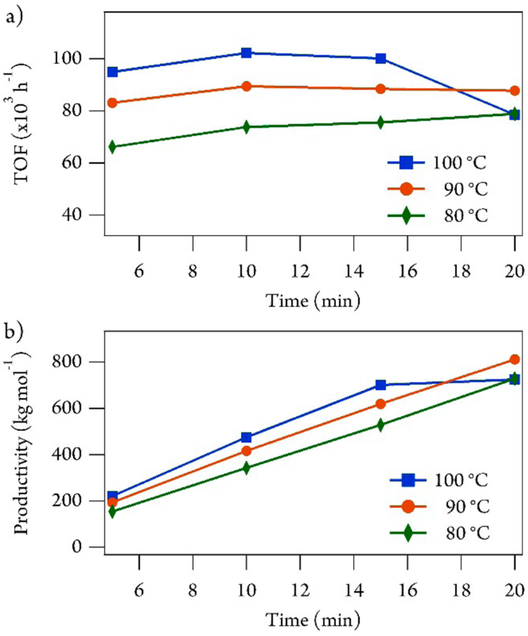


Figure 3. Plots of (a) turnover frequency (TOF) versus time and (b) productivity versus time for catalyst **2b** at 80 °C (blue ■), 90 °C (red ●), and 100 °C (green ♦).

The molecular weight, molecular weight distribution, TOF, and productivity data all strongly support that catalyst **2b** is remarkably stable at both 80 and 90 °C and that it is moderately stable at 100 °C for polymerizations up to 15 min. This enhanced stability represents a dramatic improvement over other reported α-diimine-based systems, and we attribute this behavior to the unique nature of the *i*Pr* *N*-aryl moieties. The steric demand of the *i*Pr* moieties greatly inhibits *N*-aryl rotation preventing premature catalyst decomposition while effectively blocking the axial sites of the active Ni^{II} center, thereby preventing associative chain transfer that can drastically limit polymer molecular weight.

In summary, we report a synthetically simple, Ni^{II} α-diimine precatalyst that demonstrates remarkable thermal stability for ethylene polymerization. Precatalyst **2b** was activated with

PMAO-IP and found to produce moderately branched PE with narrow molecular weight distributions ($M_w/M_n \le 1.22$) at temperatures up to 100 °C at 15 psi of ethylene pressure. To circumvent issues related to elevated polymerization temperatures, the thermal stability of catalyst **2b** was evaluated using increased ethylene pressures (100 psi) and found to exhibit virtually no catalyst decomposition at temperatures as high as 90 °C for polymerization times up to 20 min. The PE produced demonstrated well-defined molecular weight distributions ($M_w/M_n \le 1.31$), was of high molecular weight (Mn > 600 000 g/mol), and was moderately branched (63−75 branches per 1000 carbons). Stable turnover frequencies and a nearly linear increase in productivity were also observed at 100 °C for polymerizations times ≤15 min, though extended reaction times did clearly show that catalyst decomposition could be problematic. The enhanced thermal stability of catalyst **2b**, as well as its ability to make high molecular weight PE with narrow molecular weight distributions, provides a significant advance toward developing Ni- and Pd-based catalysts suitable for industrially used gas-phase polymerizations.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthesis and characterization of **1b**, **2a**, and **2b**, and polymerization data for **2a** and **2b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283.

(2) Zohuri, G. H.; Albahily, K.; Schwerdtfeger, E. D.; Miller, S. A. *Polymer Science: A Comprehensive Reference*; Elsevier: 2012; Vol. 3.

(3) Alt, H. G.; Köppl, A. *Chem. Rev.* **2000**, *100*, 1205.

(4) Chen, E. Y. X.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391.

(5) Coates, G. W. *Chem. Rev.* **2000**, *100*, 1223.

(6) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169.

(7) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414.

(8) Killian, C. M.; Tempel, D. J.; Johnson, L. K.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 11664.

(9) Boffa, L. S.; Novak, B. M. *Chem. Rev.* **2000**, *100*, 1479.

(10) Johnson, L. K.; Mecking, S.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 267.

(11) Mecking, S.; Johnson, L. K.; Wang, L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 888.

(12) Popeney, C. S.; Guan, Z. *J. Am. Chem. Soc.* **2009**, *131*, 12384.

(13) Gates, D. P.; Svejda, S. A.; Oñate, E.; Killian, C. M.; Johnson, L. K.; White, P. S.; Brookhart, M. *Macromolecules* **2000**, *33*, 2320.

(14) Guan, Z.; Cotts, P. M.; McCord, E. F.; McLain, S. J. *Science* **1999**, *283*, 2059.

(15) Anselment, T. M. J.; Vagin, S. I.; Rieger, B. *Dalton Trans.* **2008**, 4537.

(16) Coates, G. W.; Hustad, P. D.; Reinartz, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 2236.

(17) Younkin, T. R.; Connor, E. F.; Henderson, J. I.; Friedrich, S. K.; Grubbs, R. H.; Bansleben, D. A. *Science* **2000**, *288*, 1750.

(18) Tempel, D. J.; Johnson, L. K.; Huff, R. L.; White, P. S.; Brookhart, M. *J. Am. Chem. Soc.* **2000**, *122*, 6686.

(19) Mecking, S. *Coord. Chem. Rev.* **2000**, *203*, 325.

(20) Guan, Z.; Popeney, C. S. *Top. Organometal. Chem.* **2009**, *26*, 179.

(21) Xie, T. Y.; Mcauley, K. B.; Hsu, J. C. C.; Bacon, D. W. *Ind. Eng. Chem. Res.* **1994**, *33*, 449.

(22) Liu, F.-S.; Hu, H.-B.; Xu, Y.; Guo, L.-H.; Zai, S.-B.; Song, K.-M.; Gao, H.-Y.; Zhang, L.; Zhu, F.-M.; Wu, Q. *Macromolecules* **2009**, *42*, 7789.

(23) Berkefeld, A.; Mecking, S. *J. Am. Chem. Soc.* **2009**, *131*, 1565.

(24) Popeney, C. S.; Rheingold, A. L.; Guan, Z. *Organometallics* **2009**, *28*, 4452.

(25) Lee, L. S.; Ou, H. J.; Hsu, H. F. *Fluid Phase Equilib.* **2005**, *231*, 221.

(26) Gao, H. Y.; Hu, H. B.; Zhu, F. M.; Wu, Q. *Chem. Commun.* **2012**, *48*, 3312.

(27) Camacho, D. H.; Salo, E. V.; Ziller, J. W.; Guan, Z. B. *Angew. Chem., Int. Ed.* **2004**, *43*, 1821.

(28) Meinhard, D.; Wegner, M.; Kipiani, G.; Hearley, A.; Reuter, P.; Fischer, S.; Marti, O.; Rieger, B. *J. Am. Chem. Soc.* **2007**, *129*, 9182.

(29) Moody, L. S.; Mackenzie, P. B.; Killian, C. M.; Lavoie, G. G.; Ponasik, J. A., Jr.; Barrett, A. G. M.; Smith, T. W.; Pearson, J. C. Catalysts containing *n*-pyrrolyl substituted nitrogen donors for polymerization of olefins. WO2000050470A2, 2000.

(30) Liu, H.; Zhao, W. Z.; Hao, X. A.; Redshaw, C.; Huang, W.; Sun, W. H. *Organometallics* **2011**, *30*, 2418.

(31) Cherian, A. E.; Lobkovsky, E. B.; Coates, G. W. *Chem. Commun.* **2003**, 2566.

(32) Berthon-Gelloz, G.; Siegler, M. A.; Spek, A. L.; Tinant, B.; Reek, J. N.; Marko, I. E. *Dalton Trans.* **2010**, *39*, 1444.

(33) See Supporting Information for complete ethylene polymerization data for catalysts **2a**.

(34) Polymerization times extending beyond 20 min were performed; however, polymer precipitation from solution became problematic making TOF and productivity calculations unreliable.