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A thermally robust amine–imine nickel catalyst precursor for living polymerization of ethylene above room temperature†

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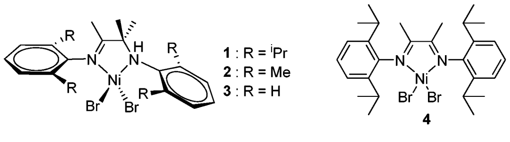
A bulky amine–imine nickel complex containing two 2,6-diisopropyl substituents after activation with MMAO or Et_2AlCl can polymerize ethylene in a living fashion over a period of 120 minutes at room temperature or above.

Living catalytic olefin polymerization is unsurpassed in terms of microstructure control of the polymer, which allows controlled synthesis of polyolefins with precise architectures, such as monodisperse polymers, block copolymers and end-functionalized materials.[1] Currently, living coordination polymerization of olefins is a long-standing scientific challenge because of the processes of chain termination by β-H elimination and polymeryl transfer to the cocatalyst or monomer.[2,3] Besides, short lifetime and rapid deactivation of living metal species at elevated temperature also limit precise tuning of polymer structures. Lowering reaction temperature and reducing/eliminating the use of alkylaluminium cocatalysts have thereby been devised to stabilize the living metal center and decrease the rate of chain termination/transfer such that living systems can be formed.[2] However, lowering reaction temperature generally leads to low catalytic activity and limits molecular weight attainable because of poor dissolution of polyolefins in reaction media.[4] Design of novel thermostable transition metal catalysts for living polymerization of ethylene thus remains a persistent challenge.

Late transition metal catalysts, such as α-diimine nickel and palladium, can produce branched polyethylenes (PEs) with relatively good dissolution,[5] but there are rare examples of living polymerization of ethylene with late transition metal catalysts in the current literature. Despite some successful applications of α-diimine nickel catalysts in living polymerizations of α-olefins such as propylene, hexene, and 4-methyl-1-pentene,[6] to date no living characteristics for ethylene polymerization have been observed.[4b] Two noteworthy examples are α-diimine palladium catalyst that can produce highly branched PE in a living manner at 5 °C[7] and α-keto-β-diimine nickel catalyst that is capable of producing semicrystalline PE under living conditions at −10 °C.[8] An approach of increasing axially steric hindrance of α-diimine nickel and palladium complexes sheds light on this issue, which not only can slow down the growing chain transfer process (associative displacement or chain transfer to bound monomer),[5c,9] but also can suppress deactivation of metal species resulting from a free rotation C–NAr bond.[4b,c,10]

Recently, an amine–pyridine nickel catalyst precursor with 2,4,6-trimethylphenyl on the bridge carbon has been reported to be capable of producing PEs with narrow molecular weight distributions in a living fashion below −10 °C by our group.[11] In view of less axially steric effect of the pyridine moiety in amine–pyridine nickel and the alkyl substituents on the amine moiety in aminoaldimine nickel,[12] we herein design new amine–imine nickel complexes containing two N-aryl substituents for long-lifetime living polymerization of ethylene above room temperature.

Amine–imine ligands were prepared by a reduction reaction of α-diimine with trimethylaluminium (TMA) in high yields,[13] and nickel complexes **1**, **2**, and **3** with different substituents (Scheme 1) were obtained by addition of the ligands to a stirring suspension of $(DME)NiBr_2$ in CH_2Cl_2 (*cf.* ESI†). Single crystals of **1** (Fig. 1), **2**, and **3** (ESI†) suitable for X-ray diffraction analysis were obtained by slow diffusion of hexane into nickel complexes solution in CH_2Cl_2. The molecular connectivity of **1** is consistent with a neutral *N*,*N*-bound amine–imine ligand. The imine moiety of **1** is roughly perpendicular to



Scheme 1 Structures of amine–imine nickel complexes **1–3** and **4**.

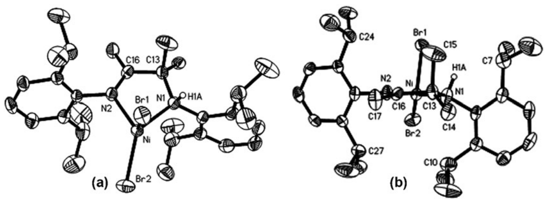


Fig. 1 Crystal structure of amine–imine nickel complex **1**.

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Table 1 Ethylene polymerization results with nickel precursors **1–4**[a]

Entry	Cat.	Al/Ni	T_p/°C	Yield/g	Act.[b]	M_n[c]	PDI[c]	Br[d]	T_g[e]/°C
1	**1**	200	20	0.582	58.2	107	1.02	153	−53
2	**2**	200	20	0.849	84.9	92	1.13	213	−64
3	**3**	200	20	1.085	109	3	1.59	175	—[h]
4[f]	**1**	200	20	0.440	880	339	1.08	119	−41
5	**1**	50	20	0.502	50.2	97	1.03	147	−51
6	**1**	100	20	0.544	54.4	109	1.02	151	−52
7	**1**	500	20	0.524	52.4	114	1.02	155	−53
8	**1**	200	0	0.411	41.1	94	1.05	123	−49
9	**1**	200	35	0.482	48.2	104	1.08	164	−59
10	**1**	200	50	0.392	39.2	70	1.24	175	−61
11	**1**	200	20	0.188	18.8	28	1.03	171	−53
12	**1**	200	35	0.373	37.3	50	1.04	180	−55
13	**1**	200	50	0.358	35.8	48	1.08	185	−56
14	**1**	200	75	0.124	12.4	22	1.65	194	−64
15[g]	**4**	200	20	0.385	770	168	1.73	136	−50

[a] Polymerization conditions: 10 μmol of nickel, 60 min, 3 psig, 28 mL toluene and 2 mL CH_2Cl_2, activators: MMAO for entries 1–10, 15; Et_2AlCl for entries 11–14. [b] Activity: kg PE (mol Ni)$^{-1}$ h^{-1}. [c] M_n (in units of 10^3 g mol^{-1}) and PDI were determined by gel permeation chromatography (GPC) in 1,2,4-trichlorobenzene at 150 °C using a light scattering detector. [d] Branching density, branches per 1000 carbon atoms determined by ^{13}C NMR spectroscopy. [e] Determined by DSC. [f] 2 μmol of nickel, 15 min, 300 psig, 28 mL toluene and 2 mL CH_2Cl_2. [g] 2 μmol of α-diimine nickel, 15 min, 3 psig, 30 mL toluene. [h] Not determined.

the slightly distorted five-membered coordination plane (dihedral angle of 78.5°), while the amine moiety of **1** is almost completely perpendicular (87.6°). Besides, one of the isopropyl groups on the amine moiety is closer to nickel (C(10)–Ni 3.6491 Å) than those on the imine moiety (C(24)–Ni 4.2417 Å) due to the distorted tetrahedral configuration of nitrogen on the amine, which causes a more crowded space on one side of the coordination plane.[12] Two methyl substituents on the backbone carbon ((*Me*)$_2$CNH) are oriented toward the axial space, showing steric effect on the metal center (Fig. 1b). Compared with the "classic" α-diimine nickel analogue,[5] the amine–imine nickel complex exhibits more effective steric blocks at the axial sites, anticipated to suppress chain transfer from the axial direction.

A series of ethylene polymerizations were carried out using catalyst precursors **1**, **2**, and **3** under various conditions (Table 1). With **1** after activation with MMAO, ethylene polymerization can produce extremely narrow-dispersed polyethylene (PDI = 1.02) in a living fashion with moderate activity under atmospheric pressure at 20 °C (entry 1). Reducing the steric hindrance of the amine–imine ligand by substituting *o*-methyl groups for *o*-isopropyl groups results in an increased polymerization activity, but a reduced molecular weight polymer with a slightly broadened polydispersity (precursor **2**). Lack of substituents on the N-aryl moiety leads to a remarkable drop in molecular weight of polyethylene and an obvious increase in the PDI value (precursor **3**). Compared with the previously reported amine–pyridine nickel catalyst,[11] the amine–imine nickel catalyst can more actively polymerize ethylene to produce higher molecular weight PE with narrow polydispersity at higher temperature.

Increasing ethylene pressure from atmospheric pressure to 300 psig (entry 4) for the **1**/MMAO system leads to an increased activity and affords higher molecular weight PE with a PDI value of 1.08. Only a little broader polydispersity of PE is observed under high pressure, suggesting that living polymerization of ethylene catalyzed by **1**/MMAO can be achieved in a wide range of ethylene pressures. The Et_2AlCl compound can also replace MMAO as the activator for living polymerization of ethylene. The **1**/Et_2AlCl system is less active than the **1**/MMAO system, and produces lower molecular weight polymers with narrower distributions (entries 11 and 12). Additionally, **1** can be effectively activated with only a small amount of MMAO or Et_2AlCl (Al/Ni = 50) and exhibits good activity for ethylene polymerization. There is no substantial change in catalytic activity, molecular weight, and polydispersity of the obtained polymers when the Al/Ni ratio varies from 50 to 500 (entries 1, 5–7 for MMAO, Table S2 in ESI† for Et_2AlCl), strongly indicating no occurrence of chain transfer to the aluminium cocatalyst.

Generally, late metal catalysts are highly sensitive to polymerization temperature. High temperature (above room temperature) for Ni and Pd catalysts usually leads to a low molecular weight product due to chain transfer, and causes a decay of polymerization activity because of deactivation of metal species.[4,5] The polymerization results using **1**/MMAO over the temperature range from 0 to 50 °C (entries 1, 8–10) show that the catalytic activity and molecular weight of the PE reach the maximum values at 20 °C and then slightly decrease with elevated temperature. When the stronger Lewis-acid Et_2AlCl is used instead of MMAO (entries 11–14), the highest catalytic activity can be achieved at 35 °C and the obtained polymer still has very narrow molecular weight distribution (PDI = 1.04) (entry 12). Higher temperatures lead to increased PDIs and decreased activities. A long-standing polymerization of ethylene at elevated temperatures was performed to further probe the stability of the active site. Fig. 2 illustrates the time dependence of the rate of ethylene consumption over a period of 120 minutes at 35 °C for the **1**/Et_2AlCl system, and clearly shows a constant rate curve and rapid initiation. This proves that the amine–imine nickel catalyst is highly stable at 35 °C and no catalyst deactivation occurs over a 120 minute period under the adopted conditions. It is distinct from α-diimine nickel catalysts, for which a rapid decay of activity above room temperature could be usually observed.[5,10a] Good thermal stability of amine–imine nickel **1** should exhibit a great potential for precise synthesis of monodisperse PE with different branch topology structures and corresponding block copolymers.

The living feature of ethylene polymerizations with **1** was further investigated at 20 °C using MMAO as the activator and at 35 °C using Et_2AlCl instead of MMAO, respectively. Fig. 3b shows symmetric GPC traces of the polymers obtained at different polymerization times, which shift to the higher molecular weight region with the increasing polymerization time. Plots of absolute number-average molecular weight (M_n) and M_w/M_n (PDI) determined by GPC using a light scattering

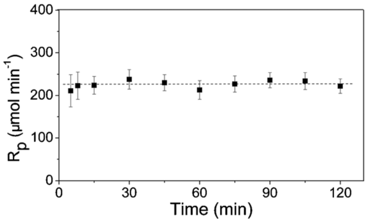

Fig. 2 Plots of polymerization rate *vs.* reaction time in ethylene polymerization using **1**/Et_2AlCl at 35 °C (10 μmol of nickel).

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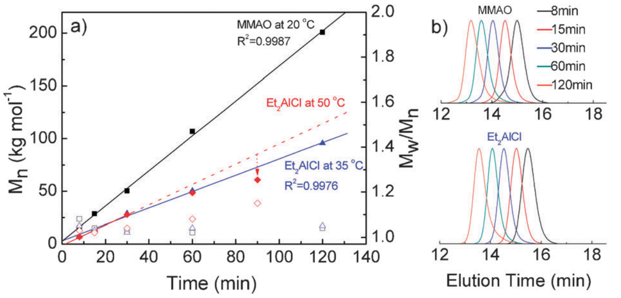

Fig. 3 (a) Plots of M_n (■,▲,◆) and M_w/M_n (PDI) (□,△,◇) as a function of polymerization time using **1**/MMAO at 20 °C or using **1**/Et_2AlCl at 35 and 50 °C (polymerization conditions: 3 psig, 10 μmol Ni, 200 equiv. activator). (b) GPC traces at different times using a light scattering detector.

detector (ESI†) as a function of polymerization time (Fig. 3a) also illustrate that M_n grows linearly with polymerization time, and M_w/M_n values are below 1.10 within 2 hours, proving living polymerizations with long lifetime using **1**/MMAO at 20 °C and **1**/Et_2AlCl at 35 °C. PE with an M_n of 2×10^5 g mol^{-1} is formed after 2 hours using **1**/MMAO, and its molecular weight is still precisely controlled (PDI = 1.04) (ESI†). Polyethylene-block-polyhexene copolymers (PE-*b*-PH) with narrow PDI of ~1.05 are also successfully synthesized under the adopted living polymerization conditions by subsequent copolymerization (ethylene: 0.25 h, hexene: 6 h) (ESI†), further supporting that amine–imine nickel **1** species is long-standing and shows living nature for olefin polymerization. To the best of our knowledge, this is the first report on living polymerization of ethylene above room temperature with a late transition metal catalyst. At the higher temperature (50 °C), M_n grows linearly with time in the early stages of polymerization (~30 min), but then the slope begins to decrease and PDI also becomes broad.

It is informative at this point to compare different behaviors of ethylene polymerization using amine–imine nickel **1** and a classic α-diimine nickel **4** (Scheme 1), which have seemingly similar metal–ligand frameworks. The catalytic system **4**/MMAO has been known to polymerize ethylene in a nonliving fashion[4,5] and herein produces a PE with a PDI value of 1.73 under the same conditions (entry 15). This molecular weight distribution is much broader than that of PE produced by amine–imine nickel **1** (entry 1), although the higher catalytic activity is achieved by **4**. The living catalytic ethylene polymerization behavior of amine–imine nickel **1** not only arises from the effective axially steric block, but also may be attributed to the weak Lewis base of amine with N-aryl (ArNH), which can result in retardation of chain transfer to the ethylene monomer and the alkylaluminium cocatalyst.[5c,d]

Like the PEs produced by α-diimine nickel,[5] the PEs produced by these amine–imine nickel catalysts are also highly branched products with methyl branches predominating as revealed by ^{13}C NMR spectra (*cf.* ESI†).[14] Various branches originate from a chain walking process involving a β-agostic nickel complex.[9,15] The PEs obtained under living polymerization conditions are branched, suggesting that chain termination through β-H elimination of the β-agostic nickel complex cannot occur. This may be explained as a quite low barrier to chain isomerization and an extremely unstable hydride–olefin nickel complex from thermodynamic aspect.[9]

In summary, we successfully developed conveniently accessible novel amine–imine nickel precursors that can catalyze ethylene polymerization to produce highly branched polymers in a living fashion. For complex **1** containing 2,6-diisopropyl substituents on amine and imine moieties, a stationary polymerization kinetics proves no occurrence of catalyst deactivation within 120 minutes at 35 °C, and narrow-dispersed polyethylene (PDI < 1.10) with high molecular weight can be produced at room temperature or above in the presence of MMAO or Et_2AlCl. Living polymerization of ethylene using a thermally robust catalyst provides a viable access to precise synthesis of monodisperse PE with various branch topology structures by changing reaction temperature, corresponding block copolymers, and functionalized PE. Further optimization of variations in amine–imine frameworks will enable improvements in polymerization control.

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Notes and references

1 (*a*) G. J. Domski, J. M. Rose, G. W. Coates, A. D. Bolig and M. Brookhart, *Prog. Polym. Sci.*, 2007, **32**, 30; (*b*) H. Makio, H. Terao, A. Iwashita and T. Fujita, *Chem. Rev.*, 2011, **111**, 2363.

2 G. W. Coates, P. D. Hustad and S. Reinartz, *Angew. Chem., Int. Ed.*, 2002, **41**, 2236.

3 R. Műlhaupt, *Macromol. Chem. Phys.*, 2003, **204**, 289.

4 (*a*) S. M. Yu and S. Mecking, *J. Am. Chem. Soc.*, 2008, **130**, 13204; (*b*) D. H. Camacho, E. V. Salo, J. W. Ziller and Z. Guan, *Angew. Chem., Int. Ed.*, 2004, **43**, 1821; (*c*) D. H. Camacho and Z. Guan, *Macromolecules*, 2005, **38**, 2544.

5 (*a*) S. D. Ittel, L. K. Johnson and M. Brookhart, *Chem. Rev.*, 2000, **100**, 1169; (*b*) S. Mecking, *Coord. Chem. Rev.*, 2000, **203**, 325; (*c*) L. K. Johnson, C. M. Killian and M. Brookhart, *J. Am. Chem. Soc.*, 1995, **117**, 6414; (*d*) L. K. Johnson, S. Mecking and M. Brookhart, *J. Am. Chem. Soc.*, 1996, **118**, 267.

6 (*a*) E. Cherian, J. M. Rose, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 2005, **127**, 13770; (*b*) J. Merna, J. Cihlar, M. Kucera, A. Deffieux and H. Cramail, *Eur. Polym. J.*, 2005, **41**, 303; (*c*) H. Gao, J. Pan, L. Guo, D. Xiao and Q. Wu, *Polymer*, 2011, **52**, 130; (*d*) H. Gao, X. Liu, Y. Tang, J. Pan and Q. Wu, *Polym. Chem.*, 2011, **2**, 1398.

7 (*a*) A. C. Gottfried and M. Brookhart, *Macromolecules*, 2001, **34**, 1140; (*b*) A. C. Gottfried and M. Brookhart, *Macromolecules*, 2003, **36**, 3085; (*c*) K. Zhang, Z. Ye and R. Subramanian, *Macromolecules*, 2008, **41**, 640; (*d*) Y. Zhang and Z. Ye, *Chem. Commun.*, 2008, 1178.

8 (*a*) J. D. Azoulay, R. S. Rojas, A. V. Serrano, H. Ohtaki, G. B. Galland, G. Wu and G. C. Bazan, *Angew. Chem., Int. Ed.*, 2009, **48**, 1089; (*b*) J. D. Azoulay, Y. Schneider, G. B. Galland and G. C. Bazan, *Chem. Commun.*, 2009, 6177.

9 (*a*) L. Deng, P. Margl and T. Ziegler, *J. Am. Chem. Soc.*, 1997, **119**, 1094; (*b*) L. Deng, T. K. Woo, L. Cavallo, P. M. Margl and T. Ziegler, *J. Am. Chem. Soc.*, 1997, **119**, 6177; (*c*) D. J. Tempel, L. K. Johnson, R. L. Huff, P. S. White and M. Brookhart, *J. Am. Chem. Soc.*, 2000, **122**, 6686.

10 (*a*) F. Liu, H. Hu, Y. Xu, L. Guo, S. Zai, K. Song, H. Gao, L. Zhang, F. Zhu and Q. Wu, *Macromolecules*, 2009, **42**, 7789; (*b*) L. Guo, H. Gao, L. Zhang, F. Zhu and Q. Wu, *Organometallics*, 2010, **29**, 2118; (*c*) C. S. Popeney and Z. Guan, *Macromolecules*, 2010, **43**, 4091.

11 S. Zai, F. Liu, H. Gao, C. Li, G. Zhou, S. Cheng, L. Guo, L. Zhang, F. Zhu and Q. Wu, *Chem. Commun.*, 2010, **46**, 4321.

12 F. Yang, Y. Chen, Y. Lin, K. Yu, Y. Liu, Y. Wang, S. Liu and J. Chen, *Dalton Trans.*, 2009, 1243.

13 (*a*) R. E. Murray, *WO* 2003051935, 2003; (*b*) M. Bhadbhade, G. K. B. Clentsmith and L. D. Field, *Organometallics*, 2010, **29**, 6509.

14 (*a*) G. B. Galland, R. F. de Souza, R. S. Mauler and F. F. Nunes, *Macromolecules*, 1999, **32**, 1620; (*b*) F. A. Kunrath, E. F. Monta, O. L. Casagrande, R. S. Mauler and R. F. de Souza, *Macromol. Chem. Phys.*, 2002, **203**, 2407.

15 V. M. Möhring and G. Fink, *Angew. Chem., Int. Ed.*, 1985, **24**, 1001.

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