Formation and Evolution of Chain-Propagating Species Upon Ethylene Polymerization with Neutral Salicylaldiminato Nickel(II) Catalysts

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Abstract: Formation of Ni–polymeryl propagating species upon the interaction of three salicylaldiminato nickel(II) complexes of the type [(N,O)Ni(CH₃)(Py)] (where (N,O)=salicylaldimine ligands, Py=pyridine) with ethylene (C₂H₄/Ni=10:30) has been studied by ¹H and ¹³C NMR spectroscopy. Typically, the ethylene/catalyst mixtures in [D₈]toluene were stored for short periods of time at +60°C to generate the [(N,O)Ni(polymeryl)] species, then quickly cooled, and the NMR measurements were conducted at –20°C. At that temperature, the [(N,O)Ni(polymeryl)] species are stable for days; dif-

fusion ¹H NMR measurements provide an estimate of the average length of polymeryl chain (polymeryl = (C₂H₄)_nH, *n*=6–18). At high ethylene consumptions, the [(N,O)Ni(polymeryl)] intermediates decline, releasing free polymer chains and yielding [(N,O)Ni(Et)(Py)] species, which also further decompose to form the ultimate catalyst degradation product, a

paramagnetic [(N,O)₂Ni(Py)] complex. In [(N,O)₂Ni(Py)], the pyridine ligand is labile (with activation energy for its dissociation of (12.3±0.5) kcal mol^{–1}, Δ*H*[‡]₂₉₈=(11.7±0.5) kcal mol^{–1}, Δ*S*[‡]₂₉₈=(–7±1) cal K^{–1} mol^{–1}). Upon the addition of nonpolar solvent (pentane), the pyridine ligand is lost completely to yield the crystals of diamagnetic [(N,O)₂Ni] complex. NMR spectroscopic analysis of the polyethylenes formed suggests that the evolution of chain-propagating species ends up with formation of polyethylene with predominately internal and terminal vinylene groups rather than vinyl groups.

Introduction

Since the discovery of α-diimine nickel(II) catalysts,^[1] neutral nickel(II) polymerization catalysts have attracted undiminished interest due to their tolerance toward polar reagents, as well as the controllable degree of polymer branching and α-olefin enchainment.^[2] Some single-component nickel(II) catalysts exhibit polymerization activity without any co-catalyst (i.e., without methylalumoxane or boron compounds),^[3] which is of particular value when designing polymerizations of polar monomers or for the synthesis of latexes by direct olefin polymerization in aqueous media.^[4]

Mechanistic studies of neutral Ni^{II} polymerization catalysts have so far been rather rare. Jenkins and Brookhart reported a ¹H NMR spectroscopic investigation of a Ni^{II} anilinetropone system. In their study the kinetic parameters of the first insertion of ethylene into the Ni–aryl bond of [(N,O)Ni(Ph)(PPh₃)] and of the second insertion of ethylene into the Ni–alkyl bond of [(N,O)Ni(CH₂CH₂Ph)(PPh₃)] were evaluated from the NMR data.^[3b] Grubbs with co-workers studied the interaction of a [(N,O)Ni(Ph)(PPh₃)] type catalyst with methyl acrylate.^[4j] Mecking and co-workers studied the dimerization of ethylene to butenes over Ni^{II} salicylaldiminato complex of the type [(N,O)Ni(CH₃)(DMSO)] in dimethylsulfoxide and documented the formation of [(N,O)Ni(CH₂CH₃)(DMSO)] intermediate upon the interaction of the starting catalyst with ethylene, accompanied by the formation of propene.^[3i] In a subsequent publication, the insertion of polar vinyl monomers into the [(N,O)Ni(CH₂CH₃)(DMSO)] and [(N,O)Ni(H)(PMe₃)] precatalysts was investigated.^[3kl] More recently, Delferro and Marks with co-workers have reported a bimetallic Ni^{II} catalyst and discussed its deactivation pathways.^[2q] In none of those mechanistic studies, however, were the true catalytically active sites (Ni–polymeryl chain-propagating species) detected spectroscopically and nor has their evolution in the course of polymerization been traced.

This work focused on direct spectroscopic monitoring of the interaction of three Ni^{II} pre-catalysts of the type

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[(N,O)Ni(CH₃)(Py)] with ethylene, in an effort to better understand the processes occurring during the chain propagation and termination (and also catalyst deactivation), and to assess the nature of chain-carrying intermediates. Differences in the behavior of active species, caused by different salicylaldimine ligand substituents, are discussed. The size of the Ni–polymeryl intermediates has been estimated by diffusion NMR spectroscopic techniques. Furthermore, the major chain termination pathway has been ascertained, and the catalyst deactivation has been scrutinized. The ultimate product of catalyst degradation [(N,O)₂Ni] has been isolated from the reaction media and identified by X-ray crystallography.

Results and Discussion

All starting catalysts **1–3** (Scheme 1) exhibit ¹H and ¹³C NMR spectra typical for diamagnetic Ni^{II} complexes (see the Supporting Information). The Ni–CH₃ NMR signals are found in the range of $\delta = -0.6$ to -1.0 ppm (in

Scheme 1. Catalysts **1–3** considered in this study. Anth = 9-anthryl.

[D₈]toluene), depending on the catalyst and on the temperature. In [D₈]toluene solution, all catalysts are stable at room temperature. However, the injection of ethylene into the catalyst solutions at room and higher temperatures caused rapid chemical reactions that complicated NMR-based characterization. Therefore, the following experimental technique was used. Ethylene was injected into the NMR tube containing the catalyst solution at reduced temperature (cooled in acetone/liquid N₂), and the sample was placed in a thermostated bath at +60°C for short periods of time (2 or 3 min) to trigger the formation of [(N,O)Ni(polymeryl)] species. The sample was then quickly cooled with liquid N₂, and placed into the NMR probe maintained at -20°C , and the measurements were conducted at that temperature.

After storing for 2 min at +60°C, formation of new nickel-alkyl species **1a** was detected by the appearance of new resonances in the range of $\delta = +0.8$ to -1.0 ppm (Figure 1). The most upfield resonance of **1a** ($\delta = -0.19$ ppm) is close to the Ni–CH₃ peak in **1** and, based on literature data,^[1c,2r,3i] can be assigned to the protons of the Ni–CH₂–CH₂– methylene group of the Ni–polymeryl species formed through ethylene insertion into the nickel–methyl bond of catalyst **1a**. ¹H COSY spectrum (see Figure S1 in

Figure 1. ¹H NMR spectra ([D₈]toluene, -20°C) of a 0.012 M solution of catalyst **1** after the injection of 30 equiv of C₂H₄: A) full spectrum and B) regions of $\delta = 8.4$ to 7.6 and 1.5 to -1.2 ppm; the same sample after storing for C) 2 min, D) 22 min, and E) 51 min at $+60^{\circ}\text{C}$. The admixture (grease, pentane) in [D₈]toluene is marked by an asterisk.

the Supporting Information) reveals direct spin-spin coupling between the Ni–CH₂–CH₂– protons at $\delta = -0.19$ ppm and those at $\delta = 0.73$ ppm, which could be assigned to the adjacent Ni–CH₂–CH₂– methylene group of intermediate **1a**. At the same time, a ¹H TOCSY spectrum shows that protons of the nickel-bound methylene group Ni–CH₂–CH₂– correlate with protons of at least three remote methylene groups of the same molecule (see Figure S2 in the Supporting Information), thus confirming that **1a** is indeed a “Ni–polymeryl” species rather than Ni–propyl or Ni–ethyl products resulting from either a single ethylene insertion or from a single insertion followed by propene elimination and ethylene reinsertion into the resulting nickel hydride species.^[5]

In the ¹³C NMR spectrum, resonances of the corresponding Ni–CH₂–CH₂– and Ni–CH₂–CH₂– carbon atoms were found at $\delta = 15.34$ and 31.94 ppm, respectively (Figure 2, Table 1; to facilitate the ¹³C NMR measurements, [¹³C₂]ethylene was used as the monomer). At the early

Figure 2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra ($[\text{D}_8]\text{toluene}$, -20°C) of a 0.012 M solution of catalyst **1A** after the injection of 30 equiv of $^{13}\text{C}_2\text{H}_4$ and B) the same sample after storing for 3 min at $+60^\circ\text{C}$. Minor impurities originally present in $^{13}\text{C}_2\text{H}_4$, that is, ^{13}C -enriched ethane, 1-butene, *cis*-2-butene, and *trans*-2-butene, are marked as $^{13}\text{C}_2\text{H}_6$, 1-B, Z-2-B, and E-2-B, respectively.^[7]

stages of interaction (2–5 min at $+60^\circ\text{C}$), only very small NMR signals assignable to unsaturated products of ethylene oligomerization were observed in the ^1H and ^{13}C NMR spectra, so the spectrum in Figure 2B mostly represents the alkyl part of the $\text{Ni}-(^{13}\text{CH}_2^{13}\text{CH}_2)_n-^{12}\text{CH}_3$ chain-carrying species **1a**.^[6]

The assignment of ^{13}C and ^1H NMR peaks was confirmed by 2D heteronuclear correlation spectra (see Figure S3 in the Supporting Information). We note that even at this early stage of polymerization, the existence of chain walking is evidenced by the presence of Me branches (marked as B1 in Figure 2).^[7]

Further storage of the chain propagating species **1a** in the presence of ethylene at $+60^\circ\text{C}$ results in the appearance of

intense PE signals at $\delta=1.3$ ($-\text{CH}_2-$) and 0.9 ($-\text{CH}_3$) ppm (see Figure 1D and E). At the same time, peaks of **1a** decline, whereas those of a new complex **1b** increase (Figure 1D and E). ^1H and ^{13}C NMR parameters of **1b** (Table 1) as well as the fact that **1b** prevails when most ethylene is consumed (Scheme 2), allows its assignment to a Ni–Et complex. Compound **1b** is relatively stable and partially survives in solution even after storing the sample for days at room temperature or for hours at $+60^\circ\text{C}$. One possible reason for this high stability is the presence of equatorially coordinated pyridine in the coordination sphere of Ni, which hampers β -hydride elimination, so that **1b** could be reasonably formulated as $[(\text{N},\text{O})\text{Ni}(\text{Et})(\text{Py})]$. Although rather stable, the latter nevertheless gradually declines upon prolonged storage for hours at $+60^\circ\text{C}$ or for days at room temperature, yielding new paramagnetic nickel species (see below).

Complex **2** reacts with ethylene in a similar way, yielding species $[(\text{N},\text{O})\text{Ni}(\text{polymeryl})]$ (**2a**) and $[(\text{N},\text{O})\text{Ni}(\text{Et})(\text{Py})]$ (**2b**) (Table 1). Their NMR spectra are reported in the Supporting Information (Figure S4–S6).

In contrast, the $[(\text{N},\text{O})\text{Ni}(\text{polymeryl})]$ intermediate has not been detected for catalyst **3**. Apparently, **3** is more prone to β -hydride elimination, so that after storing the sample **3**/ C_2H_4 for 3 min at 60°C , the majority of **3** undergoes ethylene insertion with subsequent fast formation of polymer and $[(\text{N},\text{O})\text{Ni}(\text{Et})(\text{Py})]$ (**3b**); some residual **3** can also be detected. At the same time, intense NMR signals of olefinic groups (*cis*- and *trans*-vinylene groups) of free polymer chains are observed (Figure S7). This result is in qualitative agreement with the report that catalyst **3** yields a much shorter (and more densely branched) PE than with **1** and **2**.^[21] The most likely reason for the different catalytic behavior of complexes **1** and **2**, on the one hand, and **3** on the other hand, is the presence of trifluoromethyl groups near the active center in the chain-propagating species **1a**

Table 1. Selected NMR parameters (-20°C , $[\text{D}_8]\text{toluene}$) of Ni^{II} -alkyl species considered in this study.

Species	Ni-CH ₂ - $\delta^1\text{H}$ ($^1J(\text{C,H})$)	$\delta^{13}\text{C}$ ($^1J(\text{C,C})$)	Ni-CH ₂ -CH ₂ - $\delta^1\text{H}$ ($^1J(\text{C,C})$)	Ni-CH ₂ -CH ₃ $\delta^1\text{H}$ ($^1J(\text{C,H})$)	$\delta^{13}\text{C}$ ($^1J(\text{C,C})$)	Ar-H ₄ $\delta^1\text{H}$	Other $\delta^1\text{H}$	$\delta^{13}\text{C}$
1	—	—	—	—	—	8.13	—0.86 (Ni-CH ₃)	—6.99 (Ni-CH ₃)
1a	—0.19 (126 Hz)	15.34 (d, 32.3 Hz)	0.73 (t, 32 Hz)	—	—	8.07	1.21, 1.47 (-CH ₂ -)	30.6 (-CH ₂ -)
1b	—0.25 (126 Hz)	7.53 (d, 33.5 Hz)	—	0.13 (124.5 Hz)	15.85 (d, 33.5 Hz)	8.02	—	—
2	—	—	—	—	—	8.28	—1.08 (Ni-CH ₃)	—7.47 (Ni-CH ₃)
2a	—0.44	14.40 (d, 32.8 Hz)	0.48 (t, 33 Hz)	—	—	8.23	1.00, 1.22 (-CH ₂ -)	30.5 (-CH ₂ -)
2b	—0.48	6.69 (d, 33.3 Hz)	—	0.01	15.85 (d, 33.3 Hz)	8.22	—	—
3	—	—	—	—	—	7.37	—0.59 (Ni-CH ₃) 2.26 (Ar-(CH ₃) ₄)	—7.18 (Ni-CH ₃)
3b	0.06	7.08 (d, 33.2 Hz)	—	0.33	16.67 (d, 33.2 Hz)	7.31	2.26 (Ar-(CH ₃) ₄)	—

Scheme 2. Proposed pathways for the formation of nickel intermediates **1a** and **1b** and of branched polyethylenes. Compounds detected by NMR spectroscopic analysis are boxed.

and **2a**, and their absence in **3a**, however, the nature of their influence is not yet entirely clear.^[21, p. 5]

Catalyst deactivation: In the absence of ethylene, complexes **1–3** are stable in toluene solution at +60 °C. In the course of ethylene polymerization at +60 °C, however, these catalysts gradually decomposed (particularly when all injected ethylene was consumed), which led to a decrease in the ¹H NMR peaks of the diamagnetic Ni–Me, Ni–polymeryl, and Ni–Et complexes. At the same time, a new species exhibiting highly paramagnetically shifted ¹H NMR peaks appeared. The ¹H NMR spectrum of a new species **1c** in the catalyst system **1**/¹³C₂H₄ is shown in Figure 3 A. The latter exhibits a set of relatively sharp paramagnetically shifted peaks; most of them having integral intensities of 2H, except the resonance at $\delta = 16.4$ ppm, which has an integral intensity of 1H (see Experimental Section). The shifts and line widths are characteristic of a high-spin nickel(II) complex^[8] (apparently, nonplanar,^[8d] in contrast to diamagnetic square-planar complexes **1**, **1b**, and **1c**).

The temperature dependence of paramagnetic shifts obeyed the conventional Curie law^[9a] (see Figure S9 and S10 in the Supporting Information), thus confirming the absence of antiferromagnetic interactions in the presumably mononuclear species **1c**. The picture shown in Figure 1 A did not change when ¹²C₂H₄ or ¹²C₂D₄ was used instead of ¹³C₂H₄, thus indicating that ethylene was not incorporated into the structure of **1c**.

Reliable identification of the catalyst degradation product **1c** is crucial because it can assist in unraveling the major deactivation pathways of salicylaldiminato nickel(II) catalysts. Fortunately, it was found that **1c** was poorly soluble in non-polar hydrocarbons, which allowed its isolation in crystalline

form by layering its toluene solution with pentane (see the Experimental Section). X-ray analysis indicated that the crystals had a mononuclear bis-ligated structure [(N,O)₂Ni]. The quality of crystals of **1c** obtained from the reaction mixture was insufficient for publication; for the latter purpose, the bis-ligated complex (**1c'**) was prepared independently by reaction of deprotonated ligand with anhydrous NiCl₂ (see the Experimental Section) and was characterized by X-ray crystallography (Figure 4). NMR spectroscopic analysis indicated that **1c** and **1c'** had identical ¹H NMR spectra under similar conditions; furthermore, all their resonances were located within the diamagnetic region (see the Supporting Informa-

tion, Figure S8). The origin of this behavior became clear when [D₅]pyridine was added to samples of **1c** (Figure 3 B) or **1c'** (Figure 3 C). In effect, formation of paramagnetic species was detected (Figure 3 B and C). Intriguingly, the spectra presented in Figure 3 B and C, as compared with that in Figure 3 A, lack three ¹H peaks (due to [D₅]pyridine). This is indicative of the presence of one pyridine molecule in the structure of **1c**·Py (in Figure 3 A, pyridine peaks are marked as Py). Additional [D₅]pyridine caused formation of another paramagnetic species (presumably **1c**·2Py, see Figure 3 C), which, under high pyridine/Ni ratios (ca. 100:1), became the major species in solution.

Taking the above observations together, our idea of the major deactivation pathway of catalyst **1** is the following (Scheme 3 and Scheme S1 of the Supporting Information). Apparently, under our experimental conditions, the deactivation is kinetically limited by the formation of the elusive [(N,O)Ni(H)] hydride species from the relatively stable [(N,O)Ni(Et)(Py)], followed by reductive elimination of the chelating ligand (N,O)H. The resulting (N,O)H ligand can accumulate in solution and further react with the abundant [(N,O)Ni(Et)(Py)], releasing ethane and bis-ligated [(N,O)₂Ni] **1c**.^[10a] Similar deactivation pathways involving the reductive elimination of the chelating ligand were previously considered for nickel and palladium based catalyst systems.^[3h, j, l, 4j] We note that no precipitation of nickel black was observed.^[10b]

Variable temperature experiments revealed an abnormal temperature dependence of the paramagnetic line widths^[9b] of ¹H NMR resonances of **1c**·Py; unexpectedly, above 249 K, the line widths *increased* with increasing temperature. Close inspection revealed that such behavior is caused by the dissociation of a coordinated pyridine molecule

Figure 3. ^1H NMR spectra ($[\text{D}_8]\text{toluene}$, 0°C). A) A 0.012 M solution of catalyst **1** after the injection of 30 equiv of $^{13}\text{C}_2\text{H}_4$ and storing for 82 min at $+60^\circ\text{C}$. B) ^1H NMR spectrum of crystals of **1c**+ $[\text{D}_5]\text{pyridine}$ (Py/Ni ca. 1.5:1). C) ^1H NMR spectrum of independently prepared bis-ligated complex **1c'** ($[(\text{N},\text{O})_2\text{Ni}]+[\text{D}_5]\text{pyridine}$ (Py/Ni of 5:1)). Peaks of coordinated pyridine are marked as Py. Small peaks of another paramagnetic complex (**1c2Py**) are marked with asterisks.

(Scheme 3, bottom), with activation energy for its dissociation of $(12.3 \pm 0.5) \text{ kcal mol}^{-1}$, $\Delta H^\ddagger_{298} = (11.7 \pm 0.5) \text{ kcal mol}^{-1}$, $\Delta S^\ddagger_{298} = (-7 \pm 1) \text{ cal K}^{-1} \text{ mol}^{-1}$ (see the Supporting Information, Figure S9–S11). On the other hand, upon the addition of pentane, the pyridine ligand is lost completely to form crystals of nearly planar diamagnetic $[(\text{N},\text{O})_2\text{Ni}]$ complex **1c** (see above).

Chain termination—inspection of the polymer end groups:

To evaluate the structure of polymeric products and ascertain the major processes responsible for chain termination in catalyst systems based on complexes **1–3**, ^{13}C -labeled pol-

Scheme 3. Hypothetical pathways for catalyst deactivation in the system **1**/ C_2H_4 and dynamic equilibrium involving **1c**. S=pyridine, solvent molecule, or vacancy.

Figure 4. Molecular structure of complex **1c'** with 25% probability ellipsoids.

ymers formed in the corresponding NMR samples after storing at $+60^\circ\text{C}$ for at least 2 h and then 2 days at room temperature were isolated (Experimental section) and characterized by NMR spectroscopic analysis. Extensive chain-walking was evidenced by the presence of methyl and ethyl branches (Table 2). Signals from longer branches were

Table 2. Properties of ^{13}C -PE isolated from the catalyst systems studied.^[a]

Sample	M_n	Branches/1000C		Double bonds, per molecule		
		Methyl	Ethyl	Terminal vinyl	Terminal vinylenes (<i>cis/trans</i>)	Internal vinylenes
1 / $^{13}\text{C}_2\text{H}_4$	633	22	<2	0.14	0.53 (46:54)	0.33
2 / $^{13}\text{C}_2\text{H}_4$	1008	21	3	–	0.29 (57:43)	0.61
3 / $^{13}\text{C}_2\text{H}_4$	476	67	23	–	0.35 (52:48)	0.65

[a] According to ^{13}C and ^1H NMR data.

below the NMR detection limit. The resulting polymers were found to have one olefinic group per polymer molecule. Interestingly, vinylenes (terminal and internal, *cis+trans*, see Figure 5) groups predominated over terminal vinyl groups. Apparently, fast chain walking facilitates the formation of more thermodynamically favored internal double bonds rather than terminal double bonds (Scheme 4). None of the three catalysts studied exhibited *cis*- or *trans*-selectivity for double bond formation. As could be expected,^[21] catalyst **3** yielded the shortest and the most highly branched polymeric product, whereas polyethylenes formed in samples containing **1** and **2** featured lower amounts of branches per 1000C (Table 2). A more detailed NMR characterization of polymers formed can be found

Figure 5. A) $^1\text{H}\{^{13}\text{C}\}$ and B) $^{13}\text{C}\{^1\text{H}\}$ inverse-gated NMR spectra of ^{13}C -polyethylene ($\text{CDCl}_3/\text{C}_6\text{D}_6$, 60°C) isolated from the sample containing species **2b**.

1, **2**, **1b**, and **2b**, and of **1a** and **2a** at various ethylene consumptions were estimated (Table 3).

It appears that even at this rather approximate level (the technique does not take into account the presence of branches in the polymeryl chain, or conformation of the latter), PFG NMR provides a reasonably plausible direct size-estimate of the chain-propagating inter-

Scheme 4. Proposed scheme for chain termination. Branches are not shown for simplicity.

in the Supporting information (Figure S12–S14). For resonance assignments, we used conventional Randall–Carman nomenclature,^[11a] and consulted some relevant literature.^[11]

Evaluation of the size of Ni–polymeryl species by pulsed-field-gradient (PFG) NMR spectroscopy: Evaluation of the size of active species operating in coordination polymerization of olefins is a challenging task; this knowledge is of particular value for a detailed understanding of their nature and solution behavior. In recent years, ^1H PFG NMR^[12] has been successfully applied for the determination of translational diffusion coefficients and size estimates of cationic precursors of propagating species in various single-site olefin polymerization catalysts.^[13] In this work, we report the first PFG NMR based determination of the size of chain-propagating species **1a** and **2a** formed upon the interaction of catalysts **1** and **2** with ethylene in $[\text{D}_8]\text{toluene}$. Using the dstegp3s1d pulse sequence, taking advantage of convection compensation,^[12c] the diffusion-average radii of

Table 3. Radii, volumes, and estimated lengths of various nickel species ($[\text{D}_8]\text{toluene}$, -20°C).^[a]

Entry	Species	t [min] ^[b]	r_{H} [Å] ^[c]	Polymeryl, $n-(\text{C}_2\text{H}_4)$ ^[d]
1	1 $[(\text{N},\text{O})\text{Ni}(\text{CH}_3)(\text{Py})]^{[\text{e}]}$	–	5.96	–
2	1a $[(\text{N},\text{O})\text{Ni}(\text{polymeryl})]^{[\text{f}]}$	2	6.80	11
3	1a $[(\text{N},\text{O})\text{Ni}(\text{polymeryl})]^{[\text{f}]}$	5	7.07	14–15
4	1a $[(\text{N},\text{O})\text{Ni}(\text{polymeryl})]^{[\text{f}]}$	10	7.00	14
5	1a $[(\text{N},\text{O})\text{Ni}(\text{polymeryl})]^{[\text{f}]}$	20	6.73	10–11
6	1a $[(\text{N},\text{O})\text{Ni}(\text{polymeryl})]^{[\text{f}]}$	32	6.37	6–7
7	1b $[(\text{N},\text{O})\text{Ni}(\text{Et})(\text{Py})]^{[\text{e}]}$	60	5.96	–
8	2 $[(\text{N},\text{O})\text{Ni}(\text{CH}_3)(\text{Py})]^{[\text{e}]}$	–	6.34	–
9	2a $[(\text{N},\text{O})\text{Ni}(\text{polymeryl})]^{[\text{g}]}$	2	7.40	16
10	2a $[(\text{N},\text{O})\text{Ni}(\text{polymeryl})]^{[\text{g}]}$	5	7.48	17
11	2a $[(\text{N},\text{O})\text{Ni}(\text{polymeryl})]^{[\text{g}]}$	20	7.56	18
12	2a $[(\text{N},\text{O})\text{Ni}(\text{polymeryl})]^{[\text{g}]}$	40	7.33	15
13	2b $[(\text{N},\text{O})\text{Ni}(\text{Et})(\text{Py})]^{[\text{e}]}$	60	6.34	–

[a] For measurement details see the Supporting Information. [b] Time of interaction at $+60^\circ\text{C}$. [c] Hydrodynamic radius. [d] For the evaluation of the polymeryl chain lengths see the Supporting Information. [e] at 303 K. [f] $\text{C}_2\text{H}_4/\mathbf{1} = 30$. [g] $\text{C}_2\text{H}_4/\mathbf{2} = 30$.

mediates. The estimated average hydrodynamic radii of the chain-propagating intermediates demonstrated a nonmonotonic behavior; they increased in intensity at the early stages of the interaction (2–5 min for catalyst **1** and 2–20 min for catalyst **2**), and decreased at high ethylene consumption, thus reflecting the nonstationary character of the polymerization process in the NMR tube in which no continuous ethylene inflow could be arranged. The highest observed radii corresponded to polymeryl chain lengths of 15–18 C_2H_4 units.

Upon prolonged storage at $+60^\circ\text{C}$ (40–60 min), the amount of $[(\text{N},\text{O})\text{Ni}(\text{polymeryl})]$ intermediate decreased, whereas the concentrations of relatively stable $(\text{N},\text{O})\text{Ni}-\text{Et}$ intermediates increased and became sufficient for the PFG measurements. Significantly, the estimated radii of Ni–Et intermediates **1b** and **2b** were very close to those of the parent catalysts **1** and **2**, respectively (Table 3, entries 1, 7 and 8, 13), in line with our suggestion that a pyridine molecule is likely to remain in the structures of **1b** and **2b** $[(\text{N},\text{O})\text{Ni}(\text{C}_2\text{H}_5)(\text{Py})]$ (see above). More data are reported in the Supporting Information.

Conclusion

The polymer chain growth on salicylaldiminato nickel(II) catalysts [(N,O)Ni(CH₃)(Py)] (where (N,O)=salicylaldimine ligand) has been observed directly by NMR spectroscopy. Storing solutions containing [¹³C₂]ethylene and catalysts **1** or **2** (ethylene/Ni=10:30) at +60 °C for controlled (short) periods of time results in the generation of [(N,O)Ni(polymeryl)] propagating species **1a** or **2a**. At –20 °C, the latter are stable and can be characterized by ¹H and ¹³C NMR spectroscopy. At +60 °C, the amounts of [(N,O)Ni(polymeryl)] intermediates **1a** and **2a** decrease at high ethylene consumptions, yielding free polymer molecules and [(N,O)Ni(C₂H₅)(Py)] species. The latter are stable for hours at +60 °C. For catalyst **3** (without CF₃ substituents), Ni–polymeryl intermediates are not detected under identical experimental conditions {only [(N,O)Ni(C₂H₅)(Py)] (**3b**)}, which is in accordance with the higher propensity of **3** to chain termination through β-hydride elimination. NMR spectroscopic analysis of polyethylenes formed indicates the presence of one olefinic group (predominately *cis*- and *trans*-vinylene groups rather than terminal vinyl groups) per PE molecule. The behavior of the Ni catalysts under these conditions resembles their behavior under typical preparative polymerization conditions in a pressure reactor, in that **3** affords shorter and more densely branched PE than **1** and **2**.

Our data agree with earlier predictions that the major catalyst deactivation pathway, at least at high ethylene conversions, may be associated with reductive elimination of the free salicylaldimine ligand (N,O)H from the elusive nickel hydride intermediate [(N,O)Ni(H)(S)] (S=solvent, pyridine, or vacancy). The free ligand is likely to further react with the abundant nickel compound [(N,O)Ni(Et)(Py)] to yield the ultimate catalyst degradation product, a paramagnetic [(N,O)₂Ni(Py)] complex, in which the pyridine ligand is labile (with activation energy for its dissociation of 12.3 kcal mol^{–1}). Upon addition of a nonpolar solvent, the pyridine ligand is lost completely to yield the nearly square-planar [(N,O)₂Ni] diamagnetic complex in a crystalline form.

Using PFG ¹H NMR measurements, the hydrodynamic radii of [(N,O)Ni(polymeryl)] chain propagating intermediates **1a** and **2a** and average polymeryl chain lengths (polymeryl=(CH₂)_nH, *n*=6–18) were estimated at various stages of catalysts interaction with C₂H₄. In the course of the reaction, the average radii initially increased, then decreased at high ethylene consumption. Although of approximate nature, owing to the neglect of chain branches and conformational effects, these data still provide the first plausible NMR-based size-estimate of chain-propagating intermediates at the early stages of ethylene polymerization in a practical post-metallocene catalyst system.

Experimental Section

General remarks: Complexes **1–3**, were prepared as described.^[21] [¹³C₂]Ethene (99% ¹³C) was purchased from Aldrich, [D₈]toluene was

dried over molecular sieves (4 Å) and degassed prior to use. All operations were carried out under dry argon (99.999%) by using standard Schlenk techniques. Solids were stored in a glove box.

¹H and ¹³C NMR spectra were recorded in standard 5 mm NMR tubes with a Bruker Avance III 600 MHz spectrometer by using a 5 mm TXI probe, at 600.24 and 150.94 MHz, respectively. Typical operating conditions for ¹³C NMR measurements: spectral width 40 kHz; spectrum accumulation frequency 0.1–0.05 Hz; 500–5000 transients, 90° pulse at 13.0 μs. Operating conditions for ¹H NMR measurements: spectral width 15 kHz; spectrum accumulation frequency 0.2–0.25 Hz; number of transients 32–64, 90° pulse at 8.8 μs. ¹H and ¹³C chemical shifts are referenced internally to the CHD₂-group of toluene, δ=2.12 ppm (¹H) and CD₃-group of toluene, δ=20.40 ppm (¹³C), respectively. Sample temperature measurements uncertainty and temperature reproducibility did not exceed ±1 °C.

Sample preparation: An appropriate amount of nickel complex (typically, 6 μmol) was placed in a 5 mm NMR tube in a glove box, [D₈]toluene (0.6 mL) was added, and the tube was capped with a rubber septum. The tube was taken out of the glovebox, cooled in acetone/liquid N₂ mixture, and ethylene (or [¹³C₂]ethylene) was injected by using a gas-tight syringe. Polymers for ¹³C analysis were prepared by storing the samples in [D₈]toluene solutions of **1**/¹³C₂H₄, **2**/¹³C₂H₄, or **3**/¹³C₂H₄ (ethylene/Ni=30:1) for 2 h at +60 °C, and precipitated by opening the samples to air and diluting them with water/methanol solutions. The supernatant was removed and the solids were washed several times with methanol and dried in a vacuum.

Diffusion measurements were performed with a Bruker Avance III 600 MHz NMR spectrometer, equipped with a TXI probe with Z-gradient. Sample solutions were prepared by dissolving weighed amounts of catalyst **1** or **2** in a 5 mm NMR tube in [D₈]toluene and closing the tube with a septum stopper, followed by the injection of ethylene by using a gas-tight microsyringe upon cooling the sample outside the glovebox. The PFG NMR measurements were performed at 253 and 303 K using the pulse sequence *dstepp3s1d*,^[12a] 10–14 different gradient strengths (from 0.5 to 50 G/cm), gradient pulse durations 1.6–4.0 ms, diffusion time of 100 ms, longitudinal eddy current delay of 5 ms, relaxation delays of 60 s, 8 or 16 transients, 64 K points. For further details see the Supporting Information.

Formation of 1c-Py in the course of polymerization of ethylene by catalyst 1: To a solution of catalyst **1** (0.012 M in [D₈]toluene, 0.6 mL) in an NMR tube, ¹³C₂H₄ (30 equiv) was injected at reduced temperature (below –20 °C). The sample was stored in a thermostated bath at +60 °C for 82 min (when [¹³C₂]ethylene was consumed). ¹H NMR (600.24 MHz, [D₈]toluene, 0 °C, TMS): δ (data for paramagnetic species **1c**-Py)=372.8 (2H; imine H),^[8a] 162.5 (2H; Py), 48.2 (2H; Py), 34.9 (2H), 17.8 (2H), 16.4 (1H; Py), 15.3 (2H), 10.7 (2H), 4.4 (2H), 3.7 (2H), –2.1 ppm (2H). Some signals were not found due to overlapping with peaks of PE and with those of residual **1** and **1b**. The sample was stored at RT overnight, then the precipitate of polyethylene was filtered off under inert atmosphere. The solute was placed in a 5 mm NMR tube, and pentane (ca. 1 mL) was layered upon. Dark-brown crystals formed in a few days, which were separated and dried in a glovebox atmosphere. ¹H NMR (600.24 MHz, [D₈]toluene, 0 °C, TMS): δ (data for **1c**)=7.98 (s, 4H; H_b), 7.73 (d, ³J(H,H)=2 Hz, 2H; H_c), 7.35 (s, 8H; H_a), 6.86 (t, ³J(H,H)=7.8 Hz, 2H; H_d), 6.62 (d, ³J(H,H)=7.8 Hz, 4H; H_d), 6.59 (d, ³J(H,H)=2 Hz, 2H; H_i), 5.90 (s, 2H; H_e).

Independent synthesis of 1c': Bis-ligated complex **1c'** was prepared as follows. (N,O)H (100.6 mg, 0.12 mmol, 2 equiv), NaH (12 mg, 0.50 mmol, 4 equiv), and anhydrous NiCl₂ (7.6 mg, 0.06 mmol, 1 equiv) were suspended in absolute THF (6 mL) and stirred for 72 h at RT. The solvent was removed in vacuo and the brown residue was suspended in anhydrous toluene (2 mL), filtered, and the filtrate was covered with anhydrous pentane (5 mL). Storage at 4 °C yielded brown crystals of **1c'** (69 mg, 0.04 mmol, 67%) that were suitable for X-ray analysis. ¹H NMR (600.24 MHz, [D₈]toluene, –20 °C, TMS): δ (for **1c'**)=7.98 (s, 4H; H_b), 7.73 (d, ³J(H,H)=2 Hz, 2H; H_c), 7.34 (s, 8H; H_a), 6.83 (t, ³J(H,H)=7.8 Hz, 2H; H_d), 6.57 (d, ³J(H,H)=2 Hz, 2H; H_i), 6.55 (d, ³J(H,H)=7.8 Hz, 4H; H_d), 5.80 ppm (s, 2H; H_e).

X-ray measurements: X-Ray diffraction analysis was performed at 100 K with a STOE IPDS-II diffractometer equipped with a graphite-monochromated radiation source ($\lambda = 0.71073 \text{ \AA}$) and an image plate detection system. Crystals were mounted on a fine glass fiber with silicon grease. The selection, integration, and averaging procedure of the measured reflex intensities, the determination of the unit cell dimensions, and a least-squares fit of the 2θ values as well as data reduction are described in the Electronic Supporting Information. CCDC-910995 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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- [7] Commercial $^{13}\text{C}_2\text{H}_4$ was found to contain minor impurities of ^{13}C -enriched ethane, butene-1, Z-butene-2, and E-butene-2 (1–2% each impurity). However, under our NMR polymerization conditions, the presence of 1- or 2-butenes did not contribute to the formation of polymers with B2 or B1 branches: even at virtually complete ethylene consumption, no changes of the concentrations of butenes were detected by ^{13}C NMR spectroscopic analysis.
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