# Ethene/Norbornene Copolymerization with Palladium(II) $\alpha$-Diimine Catalysts: From Ligand Screening to Discrete Catalyst Species

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**Abstract:** Sixteen palladium(II) $\alpha$-diimine catalysts were investigated in a screening-like procedure for the copolymerization of ethene with norbornene. The resulting copolymers were characterized by $^{13}$C NMR spectroscopy, differential scanning calorimetry, gel permeation chromatography, and viscosimetry. The degree of incorporation of norbornene in the polymer chain is very high for most of the catalysts. To validate the results achieved in the screening, two catalysts, $[\{ArN{=}CHCH{=}NAr\}Pd(Me)(CH_3CN)]BAr^f_4$ (**1b′**; Ar = 2,6-$Me_2C_6H_3$, $BAr^f_4 = B[3,5\text{-}C_6H_3(CF_3)_2]_4$) and $[\{ArN{=}C(CH_3)C(CH_3){=}NAr\}Pd(Me)(CH_3CN)]BAr^f_4$ (**2c′**; Ar = 2,6-$i$$Pr_2C_6H_3$), were synthesized as discrete catalytically active species, and their copolymerization behavior was investigated in detail. In agreement with the screening results, **1b′** incorporates norbornene much better in the polymer chain than ethene, a property that has no analogue in metallocene catalysts.

**Keywords:** homogeneous catalysis · N ligands · palladium · polymerization · polyolefins

## Introduction

The discovery of the metallocene/methylaluminoxane-(MAO)-catalyzed copolymerization of ethene with norbornene in 1991 opened a new field of interest in polyolefin chemistry.[1] Since then, these cyclic olefin copolymers (COCs) have been the focus of academic and industrial research. Due to the rigidity of the bicyclic norbornene units, ethene/norbornene copolymers are usually amorphous and show excellent transparency and high refractive index, which make them suitable for optical applications. In addition, their glass transition temperatures $T_g$ are high, and their densities low. In many applications, they have better mechanical properties than comparable amorphous thermoplastics, and they are processible by all conventional methods. Ethene/norbornene copolymers are proving valuable as materials for high-capacity CDs and DVDs, lenses, blister foils, medical equipment, capacitors, and packaging.[2]

The copolymer properties depend on different parameters, such as comonomer content and distribution in the polymer chain, as well as the conformational orientation of the comonomer units. The microstructure of the copolymer can be controlled by appropriate choice of the reaction conditions and the catalyst structure. The most powerful method to determine the copolymer microstructure is $^{13}$C NMR spectroscopy. In the past few years, much progress has been achieved in peak assignment for COCs.[3]

The major disadvantage of metallocene/MAO-based catalyst systems is their high sensitivity to polar impurities. The incorporation of norbornene in the polymer chain is generally low, and high molar fractions of norbornene in the feed are required to cover all technically interesting degrees of incorporation. Since Brookhart et al. discovered that cationic nickel and palladium complexes with bulky $\alpha$-diimine ligands can produce high molar mass polymers,[4] catalysts based on late transition metals became an interesting alternative.[5] In 1998, Goodall et al. reported on ethene/norbornene copolymerization with a variety of late transition metal catalysts.[6] In contrast to their nickel analogues, $\alpha$-diimine/palladium(II) systems can copolymerize ethene with norbornene. These catalysts are relatively insensitive to polar impurities.[7]

Another interesting feature of these catalyst systems is that they generate highly branched or even hyperbranched (i.e., branches on branches) products when applied in ethene polymerization.[8] Ethene/norbornene copolymers with low norbornene contents also show these hyperbranches. The mechanical properties of these branched polymers are assumed to differ from those of the metallocene/MAO-based COCs.

The synthesis of palladium(II) $\alpha$-diimine catalysts is comparatively easy and fast. This makes them a candidate for combinatorial chemistry. Symyx Technologies recently reported combinatorial syntheses of large libraries of $Ni^{II}$ and $Pd^{II}$ $\alpha$-diimine complexes and investigated their polymerization behavior towards ethene by high-throughput screening.[9]

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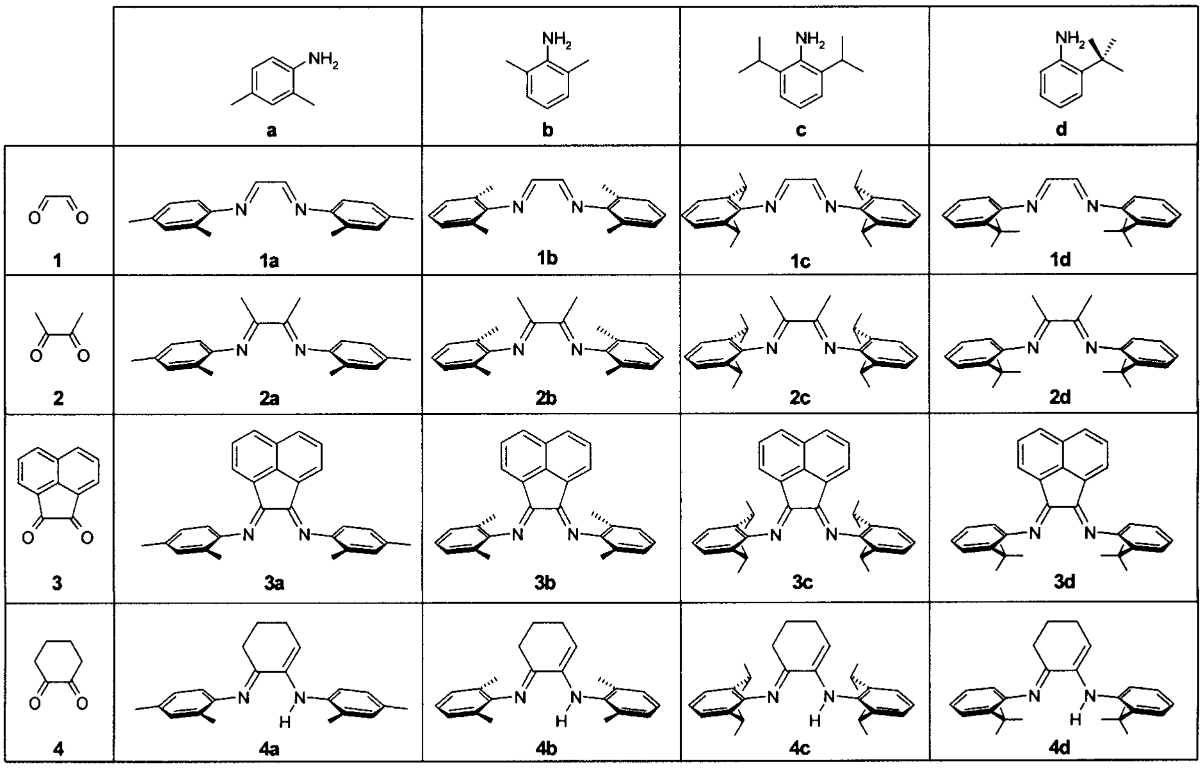


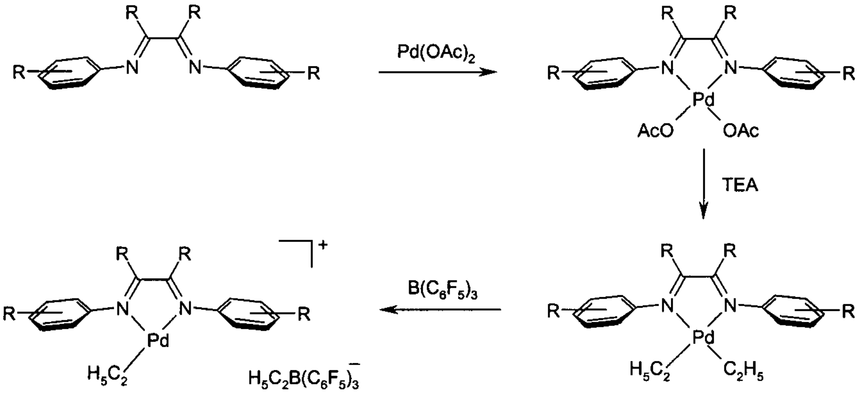
Scheme 1. Ligand library investigated for the copolymerization of ethene with norbornene.

Here we present the results of ethene/norbornene copolymerizations performed by catalysts based on a library of 16 $\alpha$-diimine ligands. To obtain representative results, the screening conditions were optimized and standardized. Two catalysts with interesting performance were synthesized as discrete cationic species, and their properties with regard to the copolymerization of ethene with norbornene were investigated in detail. The results of screening and discrete-species polymerizations are compared in order to check the reliability of the screening results under the chosen reaction conditions.

## Results and Discussion

**Ligand screening**: The investigated ligand library (Scheme 1) for the copolymerization of ethene with norbornene contains 16 symmetric $\alpha$-diimines, which represent the possible combinations of four $\alpha$-diketones (glyoxal (**1**), 2,3-butanedione (**2**), acenaphthenequinone (**3**), and 1,2-cyclohexanedione (**4**)) and four anilines with different substitution patterns (2,4-dimethylaniline (**a**), 2,6-dimethylaniline (**b**), 2,6-diisopropylaniline (**c**), and 2-*tert*-butylaniline (**d**)).

The ligands were synthesized serially by acid-catalyzed condensation of an $\alpha$-diketone with two equivalents of an aniline. Metalation and activation were performed directly in the polymerization reactor just before the polymerization. Palladium(II) acetate was used as Pd precursor, and the resulting complex was alkylated with triethylaluminum (TEA). To generate the cationic active catalysts species, the alkylated complex was treated with of tris(pentafluorophenyl)borane (Scheme 2).[6]



Scheme 2. Generation of the catalytically active species by alkylation with triethylaluminum (TEA) and alkyl group abstraction with tris(pentafluorophenyl)borane.

The conditions of the screening experiments are presented in Table 1 and are based on previous results of our group.[10] To ensure complete turnover of the metal precursor, a sixfold excess of the ligand, a threefold excess of TEA, and a 1.8-fold excess of tris(pentafluorophenyl)borane were required.

Table 1. Polymerization conditions in screening experiments.

| Condition | Screening | Excess rel. to [Pd] |
|---|---|---|
| [Pd] | $(1.8-2.1)\times10^{-4}$ mol L$^{-1}$ | 1 |
| [diimine] | $(1.12-1.17)\times10^{-3}$ mol L$^{-1}$ | 5.5–6.0 |
| [TEA] | $5.71\times10^{-4}$ mol L$^{-1}$ | 2.9–3.2 |
| [borane] | $(3.48-3.52)\times10^{-4}$ mol L$^{-1}$ | 1.7–1.9 |
| pressure (ethene) | 6 bar | |
| [ethene] | 0.7 mol L$^{-1}$ | |
| [norbornene] | 0.35 mol L$^{-1}$ | |
| polymerization temp. | 30 °C | |
| solvent | toluene | |
| reaction volume | 200 mL | |
| reaction time | 30 min | |

Table 2. Results of ligand screening. Polymerization of ethene with norbornene at 30 °C in toluene.

| Ligand | $A$[a] | $X_N$[b] | $T_g$[c] [°C] | $M_\eta$[d] [g mol$^{-1}$] | $M_w/M_n$[e] |
|---|---|---|---|---|---|
| **1a** | 8 | –[f] | 215 | 6000 | 2.4[g] |
| **1b** | 73 | 0.65 | 168 | 48000 | 1.8 |
| **1c** | 9 | 0.37 | 145 | 25000 | 1.7 |
| **1d** | 29 | –[f] | 194 | 9000 | 2.3[g] |
| **2a** | 30 | 0.42 | 156 | 16000 | 1.5 |
| **2b** | 49 | 0.48 | 112 | 209000 | 1.3 |
| **2c** | 94 | 0.25 | 51 | 293000 | 1.7 |
| **2d** | 105 | 0.42 | 93 | 146000 | 1.6 |
| **3a** | 43 | 0.69 | 168 | 37000 | 1.7 |
| **3b** | 71 | 0.46 | 129 | 181000 | 1.4 |
| **3c** | 70 | 0.36 | 67 | 195000 | 1.3 |
| **3d** | 100 | 0.47 | 133 | 128000 | 1.5 |
| **4a** | 25 | 0.48 | 141 | 12000 | 1.3 |
| **4b** | 39 | 0.39 | 101 | 93000 | 1.3 |
| **4c** | 52 | 0.21 | 41 | 158000 | 1.6 |
| **4d** | 30 | 0.41 | 107 | 65000 | 1.3 |

[a] Activity ($A$): kg(Pol) mol(Pd)$^{-1}$ h$^{-1}$. [b] Molar fraction of norbornene in the polymer determined by $^{13}$C NMR spectroscopy. [c] Determined by differential scanning calorimetry. [d] Determined by viscosimetry. [e] Determined by gel permeation chromatography, relative to polystyrene standards. [f] Not evaluable by $^{13}$C NMR spectroscopy. [g] Polymer is bi- or multimodal.

The polymerization sequence was optimized and standardized to guarantee identical conditions for each polymerization run (Figure 1). The polymerization sequence of the screening experiments is described in the Experimental Section. The results of the screening experiments are summarized in Table 2.

The activities range from 8 kg(Pol) mol(Pd)$^{-1}$ h$^{-1}$ for **1a** to 105 kg(Pol) mol(Pd)$^{-1}$ h$^{-1}$ for **2d**. Considering the high degrees of incorporation of norbornene, the activities are about one order of magnitude lower than for typical metallocene/MAO catalyst systems. Bulky and rigid bridges, as well as bulky substituents in the *ortho* positions of the *N*-aryl rings, yield higher activities. An exception is catalyst **1b**, which has higher activity than expected.

The norbornene contents were calculated from the $^{13}$C NMR spectra of the ethene/norbornene copolymers. For the calculation, the $^{13}$C NMR spectra were separated into four peak areas (Figure 2, Scheme 3, Table 3).

In the case of the metallocene/MAO-catalyzed copolymerization of ethene with norbornene, the norbornene content can be calculated by Equation (1).

$$X_N = \frac{[I(\mathrm{C2,C3}) + I(\mathrm{C1,C4})]/5}{[I(\mathrm{C5,C6}) + I(\mathrm{C}_\alpha,\mathrm{C}_\beta,\mathrm{C}_\gamma,\mathrm{C}_\delta)]/2} = \frac{I(\mathrm{A}) + I(\mathrm{B}) + I(\mathrm{C})}{2.5\, I(\mathrm{D})} \quad (1)$$

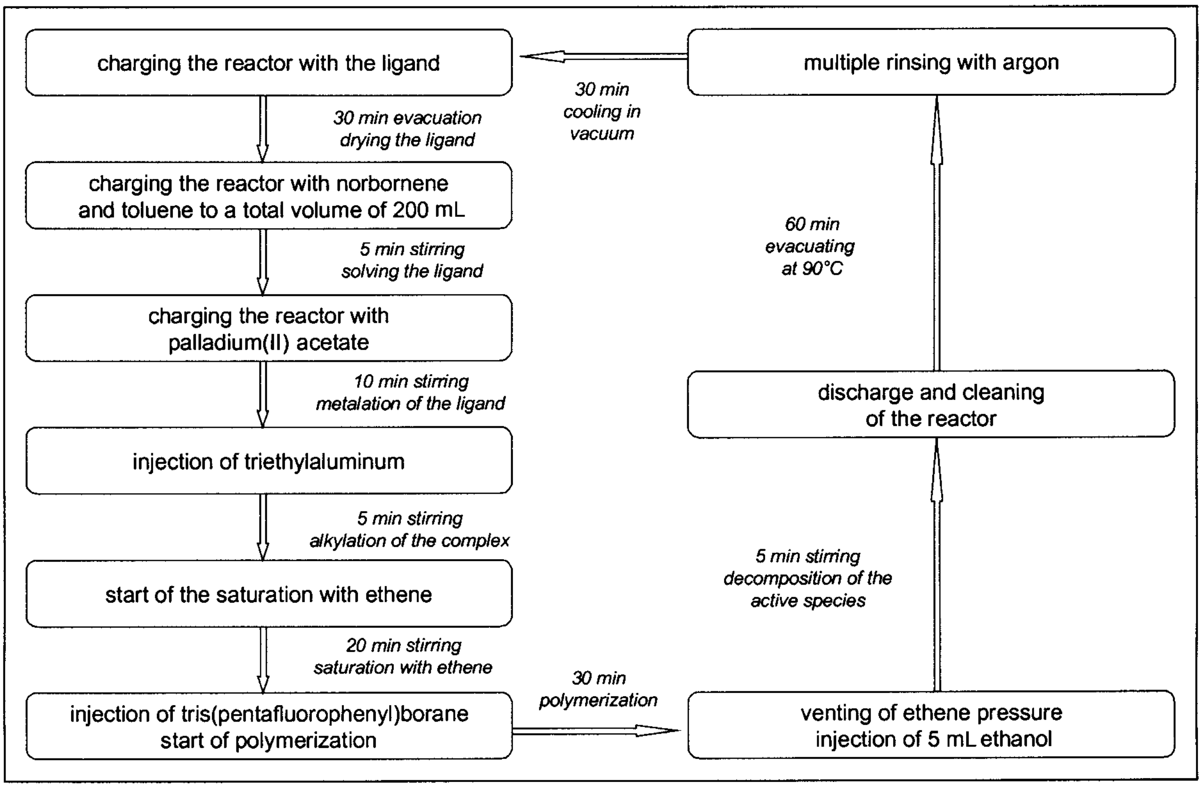


Figure 1. Standardized polymerization sequence applied in screening experiments.

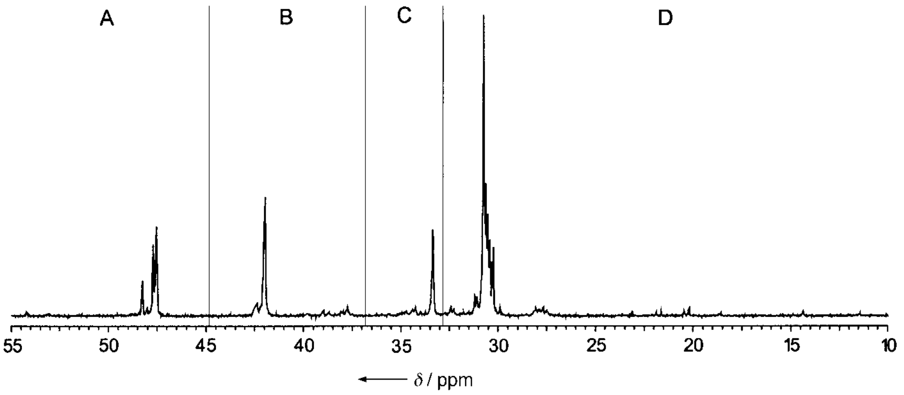
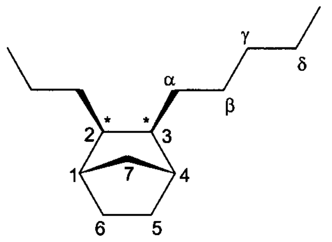


Figure 2. $^{13}C$ NMR spectrum of an ethene/norbornene copolymer with a content of norbornene of $X_N = 0.25$, produced by **2c** at 30 °C in toluene. Separation into the peak regions A to D for calculating the norbornene content of the polymer.



Scheme 3. Denomination of a 2,3-*cis-exo*-orientated norbornene unit and the neighboring methylene carbon atoms in an ethene/norbornene polymer chain.

Table 3. $^{13}C$ NMR assignments of ethene/norbornene copolymers in four seperate peak regions.

| Signal area | $\delta(^{13}C)$ [ppm] | Assignments |
|---|---|---|
| A | 56–44.8 | C2, C3 |
| B | 44.8–36.8 | C1, C4 |
| C | 36.8–32.8 | C7 |
| D | 32.8–10 | C5, C6, Cα, Cβ, Cγ, Cδ |

The presence of branches and hyperbranches in the methylene chain in the case of Pd-based catalysts impedes calculation by Equation (1), since signals of branching points (33–40 ppm), methylene groups adjacent to branching points (31–38 ppm), other methylene groups in branches (20–37 ppm), and of methyl groups in branches (10–20 ppm) also appear in signal areas B, C, and D. Therefore, the norbornene content was calculated from signals above 46 ppm (area A in Figure 2), which can be assigned exclusively to norbornene [Eq. (2)].[10]

$$X_N = \frac{I(A)}{I(B) + I(C) + I(D) - 1.5\,I(A)} \tag{2}$$

The molar fractions of norbornene in the polymer chain $X_N$ (see Table 2) are very high. They range from $X_N = 0.21$ for **4c** to $X_N = 0.69$ for **3a**. Most catalysts incorporate norbornene better in the polymer chain than ethene. This result has no counterpart in the case of catalysts based on early transition metals. Bulky substituents in the *ortho* positions of the *N*-aryl rings, such as isopropyl, favor the coordination of the sterically less hindered ethene, which leads to lower degrees of incorporation of norbornene. The bulk and rigidity of the bridging unit intensifies this trend. Ligands with small or no substituents in the *ortho* position of the *N*-aryl rings, such as methyl, show very high values of $X_N$ since norbornene can easily be coordinated. For the ethanediimine-bridged catalysts **1a** and **1d**, both of which bear only one *ortho* substituent, partial displacement of the ligand by norbornene is assumed. The resulting copolymers were bi- or multimodal, and the formation of polynorbornene is likely, which indicates the presence of "naked", ligand-free palladium. The determination of the norbornene content by $^{13}C$ NMR spectroscopy is aggravated by the presence of polynorbornene, since it leads to a strong increase of signal linewidth due to the heterogeneous nature of the NMR sample. Nevertheless, some polynorbornenes produced by late transition metal catalysts have good solubility.

Generally, the degree of incorporation of norbornene corresponds to the activity. Catalysts that incorporate norbornene well are less active. Again a significant exception is **1b**, which is highly active and produces copolymers with a high norbornene content.

The microstructure of the copolymers is closely related to the molar fraction of norbornene in the polymer. Figure 3 shows a series of $^{13}C$ NMR spectra of copolymers with increasing norbornene contents. At low degrees of incorporation, the copolymer shows signals of isolated norbornene units together with the typical signals of branches and hyperbranches in the methylene chain. At higher $X_N$, signals of smaller norbornene blocks coexist with signals of alternating sequences and branching. Copolymers with a norbornene content of greater than $X_N = 0.5$ show signals of longer norbornene blocks, and no branching signals are observed. Copolymers containing more than 70 mol% of norbornene are not evaluable, probably due to the presence of polynorbornene.

The molar masses $M_\eta$, determined by viscosimetry, are summarized in Table 2. They range from oligomeric to high molar mass products. Most of the molar masses are in a technically interesting range and are comparable to those of polymers produced by metallocene/MAO catalysts. The molar masses are directly influenced by the ligand structure. To obtain high molar mass polymers, the rate of chain transfer reactions must be slowed relative to chain propagation. This is the case when the ligand bears bulky substituents in the *ortho* position of the *N*-aryl ring and when a rigid and bulky bridge is present. The bulky substituents and the rigid bridge force the *N*-aryl rings into an axial position of the square-planar complex. Brookhart et al. assumed that the chain termination proceeds by a β-hydride elimination to yield an olefin hydride complex, followed by an associative displacement of the

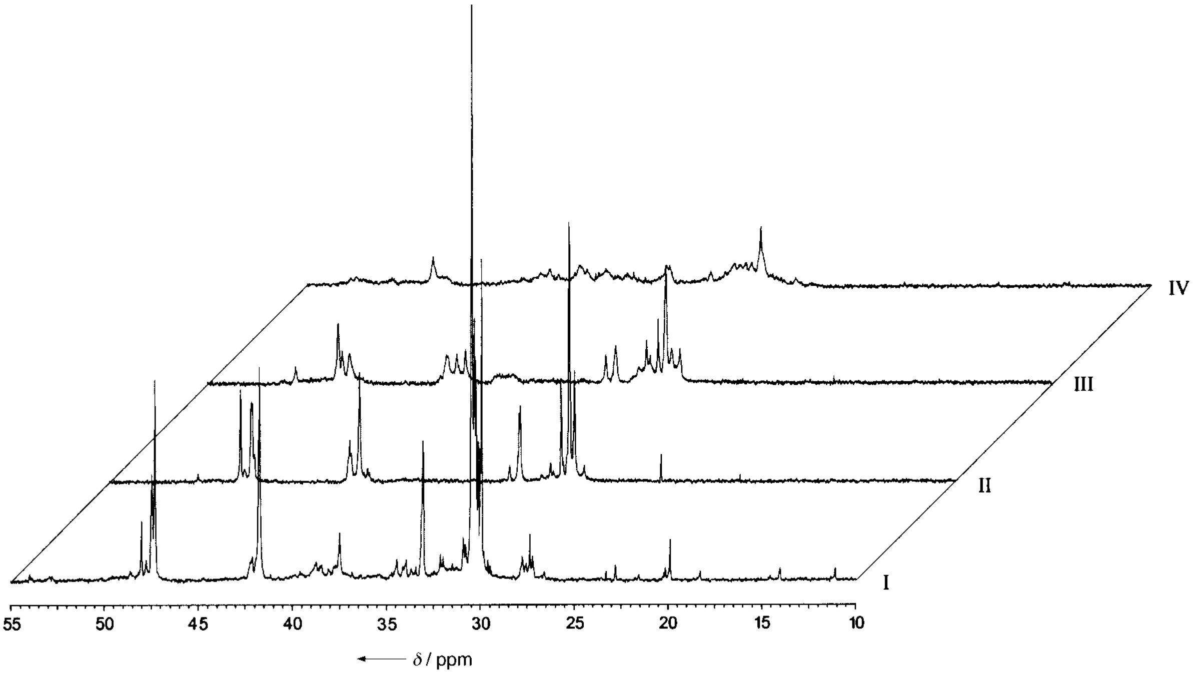


Figure 3. $^{13}$C NMR spectra of ethene/norbornene copolymers produced with the catalysts **4c** (I, $X_N = 0.21$), **3d** (II, $X_N = 0.47$), **1b** (III, $X_N = 0.65$), and **1d** (IV, $X_N$ = not evaluable).

olefin.[4] The latter process is disfavored, since the bulky substituents block the axial approach of olefins. According to DFT calculations by Ziegler et al. on ethene polymerization with Ni$^{II}$ $\alpha$-diimines,[11] chain transfer does not involve an olefin hydride complex but occurs by a concerted process involving direct $\beta$-hydrogen transfer to the coordinated monomer. Despite the different mechanism, this reaction is also slowed by bulky substituents in the axial position. In conformity with these results, **1a** produces the copolymer with the lowest molar mass, and **2c** that with the highest. Again catalyst **1b** does not follow this trend. The molar mass of the produced copolymer is higher than expected.

Molar mass distributions (Table 2) were determined by gel permeation chromatography (GPC). Most of the catalysts produce monomodal polymers with polydispersities $M_w/M_n$ of less than 2, which indicates that the polymerization is likely to show "living" character. This behavior is consistent with results recently published by Brookhart et al. on the living polymerization of ethene with Pd$^{II}$ $\alpha$-diimine catalysts.[12] Under appropriate polymerization conditions (low temperature, low concentration of active centers), it should be possible to produce copolymers with even smaller polydispersities. Catalysts **1a** and **1d** produce bi- or even multimodal polymers, probably due to partial ligand displacement by norbornene during polymerization. For catalysts bearing only one *ortho* substituent, the formation of $C_2$ and $C_s$ symmetric isomers due to the relative orientation of the aryl rings might lead to bimodal polymers, though bimodality is exclusively observed for **1a** and **1d**.

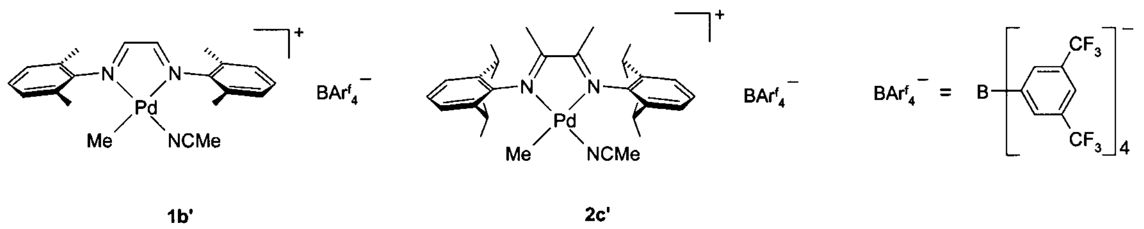
Glass transition temperatures $T_g$ were determined by differential scanning calorimetry (DSC). The $T_g$ values of the copolymers are correlated with the norbornene contents $X_N$. The bicyclic nature of norbornene leads to higher rigidity of the polymer chain and therefore higher $T_g$. Catalysts with bulky substituents produce copolymers with high norbornene contents and high $T_g$. In accordance with the norbornene content, **4c** produces the polymer with the lowest $T_g$ of 41 °C, while **1b** and **3a** produce those with the highest $T_g$ of 168 °C. The polymers synthesized with **1a** and **1d** have $T_g$ values of 194 and 215 °C, respectively. Since the polymers are multimodal and the presence of polynorbornene is assumed, these data are not reliable. None of the copolymers showed crystallinity, although in the literature semicrystalline, stereoregular, alternating ethene/norbornene copolymers were described for metallocene/MAO and constrained-geometry catalysts.[13]

**Discrete cationic catalysts**. Based on the results of the ligand screening, two catalysts showing interesting performance were synthesized as discrete cationic species and investigated in detail (Scheme 4).

Catalyst **1b′** was selected since its behavior deviates from the general trends. Catalyst **2c′** showed a balanced performance, that is, high activity and high molar mass polymer together with moderate degrees of norbornene incorporation. The results of the polymerizations with the two catalysts are summarized in Table 4.

The copolymerization diagrams are presented in Figure 4. It shows the molar fraction of norbornene in the polymer $X_N$ as a function of the molar fraction of norbornene in the feed $x_N$.

The two catalysts show a notably different polymerization behavior. As predicted in the ligand screening, **1b′** incorporates norbornene much better in the polymer chain than ethene. Even at very low molar fractions of norbornene in the feed (e.g., $x_N = 0.05$), the incorporation of norbornene is about $X_N = 0.44$. When metallocene/MAO catalyst systems are applied, it is necessary to polymerize at feed compositions of up to $x_N = 0.90$ to incorporate norbornene to the same



Scheme 4. Discrete cationic catalysts investigated for the copolymerization of ethene with norbornene.

Table 4. Ethene/norbornene copolymerization with the catalysts **1b′** and **2c′**. Results of polymerizations at 30 °C in toluene.

| | Reaction conditions | | | | Results | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Cat. | $x_N$[a] | $c_E$ [mol L$^{-1}$] | $c_N$ [mol L$^{-1}$] | $n_{cat}$ [µmol] | $A$[b] | $X_N$[c] | $T_g$[d] [°C] | $M_\eta$[e] [g mol$^{-1}$] | $M_w/M_n$[f] |
| **1b′** | 0.00 | 0.70 | – | 16.76 | 36 | 0.00 | – 75 | 1500[g] | 1.4 |
| **1b′** | 0.05 | 0.72 | 0.04 | 4.19 | 161 | 0.44 | 98 | 13000 | 1.4 |
| **1b′** | 0.10 | 0.72 | 0.08 | 4.19 | 243 | 0.48 | 126 | 36000 | 1.5 |
| **1b′** | 0.20 | 0.57 | 0.14 | 4.19 | 120 | 0.54 | 146 | 40000 | 1.7 |
| **1b′** | 0.34 | 0.47 | 0.24 | 8.38 | 67 | 0.59 | 169 | 55000 | 1.9 |
| **1b′** | 0.40 | 0.42 | 0.28 | 16.76 | 57 | 0.60 | 177 | 54000 | 1.8 |
| **1b′** | 0.50 | 0.35 | 0.35 | 16.76 | 50 | 0.62 | 189 | 36000 | 1.7 |
| **1b′** | 0.59 | 0.29 | 0.41 | 16.76 | 34 | 0.62 | 216 | 18000 | 1.7 |
| **1b′** | 0.80 | 0.14 | 0.56 | 16.76 | 11 | –[h] | –[i] | 12000 | 1.7 |
| **1b′** | 0.90 | 0.07 | 0.63 | 33.54 | 10 | –[h] | –[i] | 7000 | 2.7[j] |
| **1b′** | 1.00 | – | 0.88 | 33.54 | < 1 | 1.00 | –[i] | –[k] | –[k] |
| **2c′** | 0.00 | 0.69 | – | 7.77 | 185 | 0.00 | – 67 | 73000 | 1.1 |
| **2c′** | 0.10 | 0.63 | 0.07 | 7.77 | 75 | 0.09 | – 28 | 502000 | 1.7 |
| **2c′** | 0.20 | 0.55 | 0.14 | 7.77 | 63 | 0.16 | 10 | 358000 | 1.7 |
| **2c′** | 0.34 | 0.47 | 0.24 | 7.77 | 53 | 0.26 | 48 | 287000 | 1.7 |
| **2c′** | 0.40 | 0.42 | 0.28 | 7.77 | 57 | 0.29 | 63 | 248000 | 1.6 |
| **2c′** | 0.49 | 0.36 | 0.35 | 7.82 | 48 | 0.34 | 83 | 231000 | 1.5 |
| **2c′** | 0.59 | 0.29 | 0.42 | 7.82 | 37 | 0.40 | 97 | 157000 | 2.7 |
| **2c′** | 0.81 | 0.17 | 0.70 | 7.82 | 8 | 0.40 | 120 | 22000 | 6.3 |
| **2c′** | 0.90 | 0.17 | 1.52 | 15.65 | 4 | –[h] | –[i] | –[k] | –[k] |
| **2c′** | 1.00 | – | 0.79 | 26.22 | < 1 | 1.00 | –[i] | –[k] | –[k] |

[a] Molar fraction of norbornene in the feed. [b] Activity ($A$): kg(Pol) mol(Pd)$^{-1}$ h$^{-1}$. [c] Molar fraction of norbornene in the polymer determined by $^{13}$C NMR spectroscopy. [d] Determined by differential scanning calorimetry. [e] Determined by viscosimetry. [f] Determined by gel permeation chromatography, relative to polystyrene standards. [g] $M_w$ determined by GPC. [h] Not evaluable by $^{13}$C NMR spectroscopy. [i] Polymer decomposes. [j] Polymer is bi- or multimodal. [k] Polymer not soluble in decahydronaphthalene and 1,2,4-trichlorobenzene.

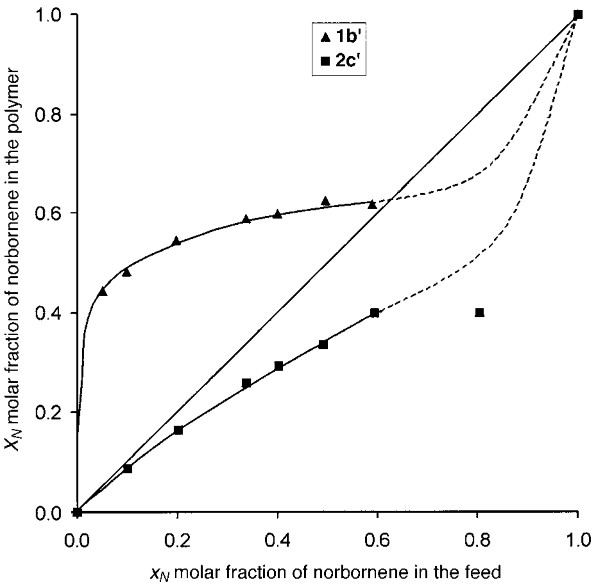


Figure 4. Copolymerization diagrams. Copolymerizations of ethene with norbornene performed by the catalysts **1b′** and **2c′**.

extent. At higher molar fractions of norbornene in the feed, the incorporation is nearly independent of $x_N$ and reaches a plateau of about $X_N = 0.60$. Polymerizations carried out at $x_N$ of more than 0.70 yielded partially insoluble polymers. Again the formation of polynorbornene is assumed, and indicates that to some extent the ligand is displaced by norbornene. The $^{13}$C NMR spectra of these polymers were not evaluable.

In contrast, **2c′** shows almost ideal copolymerization behavior at low to moderate values of $x_N$, that is, the norbornene content of the polymer reflects the feed composition. The degree of incorporation is low compared to **1b′**, but still higher than for most metallocene/MAO catalysts. The norbornene content does not surpass $X_N = 0.40$. No norbornene block structures could be observed in the $^{13}$C NMR spectra, and even at higher $x_N$ sequences with isolated norbornene units are formed exclusively. The coordination site is blocked by the isopropyl substituents, and the ligand is inflexible because of the 2,3-butanediimine bridge. The steric bulk of the growing polymer chain when norbornene is the last inserted unit aggravates the coordination of norbornene. The formation of norbornene block sequences is therefore improbable. The coordination of ethene and hence the formation of copolymers with isolated norbornene units, is much more likely. The steric bulk of the methyl groups in **1b′** is much lower, and the 1,2-ethanediimine bridge is more flexible than 2,3-butanediimine. The coordination site is therefore less blocked in **1b′**, and norbornene block sequences are more likely. At molar fractions of norbornene in the feed of less than 10 %, alternating structures are dominant.

The molar fractions of norbornene in the polymer at $x_N = 0.33$ are interesting for comparison with the values achieved in ligand screening. For **2c′** the value of $X_N = 0.26$ fully confirms the screening value of $X_N = 0.25$. For **1b′**, the screening value of $X_N = 0.65$ is higher than the degree of incorporation of $X_N = 0.59$ achieved with the discrete catalyst, although it is of the right magnitude. Therefore, the screening can be said to give representative results for the degree of incorporation of norbornene.

The copolymerization behavior also influences the activity. Figure 5 shows the activity as a function of the molar fraction of norbornene in the feed.

As could be predicted from the copolymerization diagram, **1b′** shows the course of a distinct comonomer effect, that is an increase in the polymerization rate in the presence of a comonomer. The activity in the homopolymerization of ethene is comparatively low, but even small amounts of

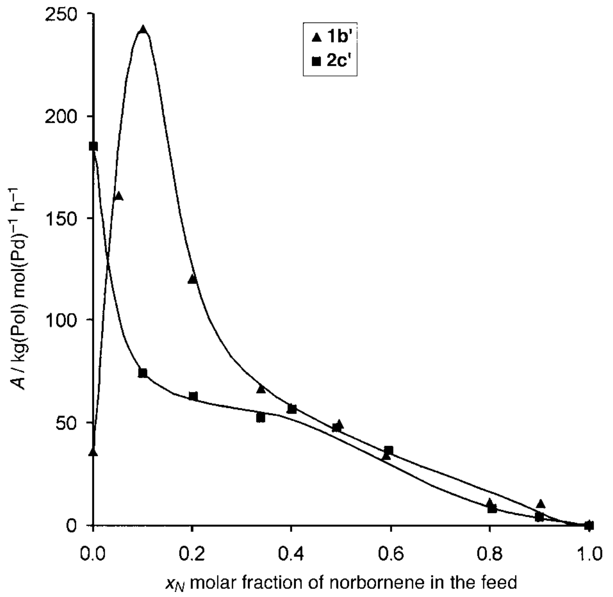


Figure 5. Copolymerization of ethene with norbornene performed with **1b′** and **2c′**. Dependence of the catalyst activity on the molar fraction of norbornene in the feed. $A$ = activity.

norbornene in the polymerization mixture lead to a massive increase. The maximum of 243 kg(Pol) mol(Pd)$^{-1}$ h$^{-1}$ is reached at $x_N = 0.10$. Considering the very high norbornene content of the resulting polymers, this catalyst can compete with the activity of metallocenes. At higher molar fractions of norbornene in the feed, the activity decreases rapidly. The activity in the homopolymerization of norbornene is low.

In contrast, **2c′** shows the highest activity of 185 kg(Pol) mol(Pd)$^{-1}$ h$^{-1}$ for the homopolymerization of ethene. The activity decreases with increasing molar fraction of norbornene. The activities in polymerizations with a high molar fraction of norbornene in the feed and for the homopolymerization of norbornene are very low. At $x_N =$ 0.33, the activity of **1b′** (67 kg(Pol) mol(Pd)$^{-1}$ h$^{-1}$) is consistent with the screening results (73 kg(Pol) mol(Pd)$^{-1}$ h$^{-1}$). The activity of **2c′** of 53 kg(Pol) mol(Pd)$^{-1}$ h$^{-1}$ is lower than the screening activity of 94 kg(Pol) mol(Pd)$^{-1}$ h$^{-1}$. Nevertheless, the activities are of the right order of magnitude, and hence the screening values are reliable.

The molar masses presented in Tables 2 and 4 show a general problem. Mark–Houwink constants of statistical ethene/norbornene copolymers with branches in the methylene chain and of block copolymers are not described in the literature. All values for copolymers were calculated by using constants for strictly alternating ethene/norbornene copolymers. In the case of polymers produced with **2c′**, the vast increase in the molar mass on going from polyethene ($M_\eta = 73000$ g mol$^{-1}$) to an ethene/norbornene copolymer produced at a monomer composition of $X_N = 0.10$ ($M_\eta =$ 502000 g mol$^{-1}$) is mainly caused by the change in the Mark–Houwink constants. Polymers for which the applied Mark–Houwink constants should be suitable nonetheless give molar masses greater than 200000 g mol$^{-1}$, indicating that **2c′** usually produces high molar masses products. Catalyst **1b′** shows a different behavior. The molar mass is generally lower than for **2c′**. The polyethene produced is oligomeric, and the molar mass increases with increasing $x_N$. A maximum of $M_\eta =$ 55000 g mol$^{-1}$ is attained at $x_N = 0.33$. At higher molar ratios of norbornene molar masses decrease rapidly. The conformity with the screening results is excellent for both catalysts.

The polydispersities are generally lower than 2, which indicates that the polymerization mechanism has a "living-like" character. Polymers produced at high molar fractions of norbornene in the feed are bi- or multimodal.

As seen in the screening, the degrees of incorporation of norbornene also influence the glass transition temperatures $T_g$. The $T_g$ of copolymers produced with **1b′** are very high and range from 98 to 217 °C. Copolymers produced at $x_N = 0.80$ and above, as well as polynorbornene, show no glass transition or melting points below 350 °C, and decompose at higher temperatures. The $T_g$ values of copolymers produced by **2c′** range from −28 to 120 °C due to the lower norbornene contents. Figure 6 shows $T_g$ as a function of the molar fraction of norbornene in the polymer $X_N$.

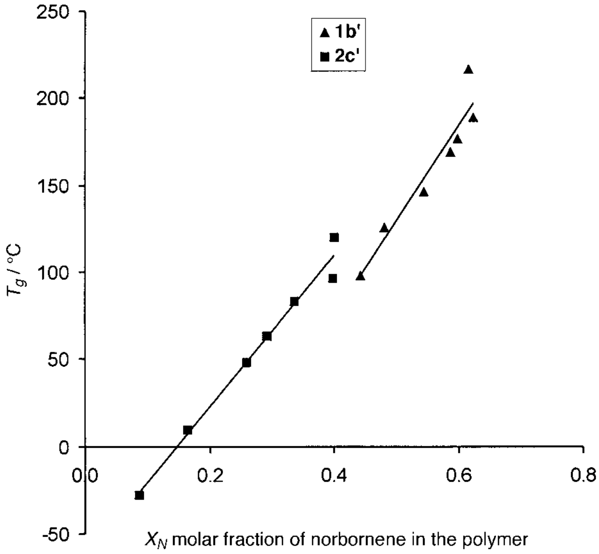


Figure 6. Copolymerization of ethene with norbornene performed by **1b′** and **2c′**. Glass transition temperatures as a function of the molar fraction of norbornene in the polymer.

The linear relationship observed for **2c′** indicates that the Fox correlation[14] is valid in this case. For **1b′** a linear relationship could also be identified, but the deviation is greater. Generally, deviation from a linear correlation is due to the presence of branches in the methylene chain[15] and of norbornene block structures.[16] The much higher molar masses of the copolymers produced by **2c′** compared to those produced by **1b′** leads to a higher $T_g$, as can be seen in the linear fits in Figure 6. The $T_g$ of copolymers produced at $x_N =$ 0.33 align with the screening results. The deviation for both catalysts is within the accuracy of the measurement.

Despite the different microstructures, the relationship between norbornene content and glass transition temperature for copolymers produced by Group 4 metallocene/MAO systems is comparable with the relationship obtained for palladium catalysts. Deviations are mainly due to differences in the molar masses of the polymers.

**Summary**: The copolymerization of ethene with norbornene is possible with all catalysts tested in the ligand screening. The performance is strongly dependent on the catalyst structure. Catalysts bearing bulky substituents in the *ortho* positions of the *N*-aryl rings and rigid $\alpha$-diimine bridges produce high molar mass polymers with comparatively high activities. Degrees of incorporation of norbornene are generally high, and in most cases norbornene is incorporated better in the polymer chain than ethene. The generally low polydispersities indicate that the polymerization mechanism has a "living-like" character.

Two catalysts were synthesized as discrete cationic species and investigated in detail. Within the limit of error, the results achieved in the ligand screening are consistent with those of the discrete catalysts. Catalyst **1b′** is highly active and incorporates norbornene very well in the polymer chain, whereas the molar masses of the polymers are quite low. In accordance with the high molar fractions of norbornene, **1b′** mainly produces blocky copolymers. In contrast, **2c′** produces high molar mass polymers with discrete norbornene units. No block sequences occur, even with norbornene-rich feed compositions.

For further validation of the screening results, other discrete catalysts will be synthesized. The screening itself should be expanded to different substitution patterns and bridges. Based on the screening results, predictions can be made of which substitution patterns are promising and which are redundant. The mechanical properties of the copolymers are to be investigated in the near future.

## Experimental Section

**General**: All manipulations were performed by using standard Schlenk, syringe, and drybox techniques unless otherwise noted. Argon was purchased from Linde and purified by passage through a Messer-Griesheim Oxisorp cartridge. Solid organometallic compounds were stored and transferred in an argon-filled drybox. $^{13}$C NMR spectra of polymer samples were recorded on a Bruker Ultrashield 400 spectrometer at 100.62 MHz (pulse program: waltz-16, pulse angle: 60°, delay time: 5 s, number of scans: 1000–4000) and 100 °C using 200–300 mg of polymer in 1,2,4-trichoro-benzene (2.7 mL) and 1,1,2,2-tetrachloro[D$_2$]ethane (0.3 mL). Chemical shifts are reported relative to $C_2D_2Cl_4$ ($\delta = 74.24$ ppm for $^{13}$C). High-temperature gel-permeation chromatography (GPC) was performed in 1,2,4-trichlorobenzene at 135 °C using a Waters GPCV 2000 instrument with Ultrastyragel columns. Calibration was against polystyrene standards. Differential scanning calorimetry curves were recorded on a Mettler Toledo DSC 821$^e$ instrument calibrated with *n*-heptane ($T_m = -90.6$ °C), mercury ($T_m = -38.9$ °C), gallium ($T_m = 29.8$ °C), indium ($T_m = 156.6$ °C), and zinc ($T_m = 419.5$ °C). Results of the second thermal cycle are presented exclusively. Viscosimetric measurements were performed in decahydronaphthalene at 135 °C with an Ubbelohde viscosimeter (0a capillary, $K = 0.005\ mm^2 s^{-2}$). In case of copolymers with an degree of incorporation of norbornene of less than 5%, Mark–Houwink constants of polyethene ($K = 4.34 \times 10^{-2}\ mL\,g^{-1}$, $a = 0.724$) were applied. For all other copolymers, molar masses were calculated with Mark–Houwink constants of a highly alternating ethene/norbornene copolymer ($K = 4.93 \times 10^{-2}\ mL\,g^{-1}$, $a = 0.589$).

**Materials**: Ethene (Linde) and toluene were purified by passage through columns of BASF R3-11 catalyst and 3 Å molecular sieves. Norbornene (Acros) was stirred for 48 h with triisobutylaluminum at 50 °C and distilled off. A 6–7 mol L$^{-1}$ solution in toluene was used for polymerizations. Ligand syntheses were performed according to literature procedures.[17] Palladium(II) acetate, triethylaluminum, and tris(pentafluorophenyl)borane were purchased from Aldrich, Schering, and Lancaster, respectively. sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (Na[BAr$^f_4$]),[18] [{ArN=CHCH=NAr}Pd(Me)(CH$_3$CN)]BAr$^f_4$ (**1b′**; Ar = 2,6-Me$_2$C$_6$H$_3$),[19] and [{ArN=C(CH$_3$)C(CH$_3$)=NAr}Pd(Me)(CH$_3$CN)]BAr$^f_4$ (**2c′**; Ar = 2,6-*i*Pr$_2$C$_6$H$_3$)[19] were synthesized by literature procedures.

**General polymerization procedure**: Norbornene homopolymerizations were performed in a 200 mL glass reactor equipped with a heat jacket and a magnetic stirrer. All other polymerizations were performed in a Büchi BEP 280 laboratory autoclave with a Type I glass pressure vessel. Temperature was adjusted with a heat jacket connected to a thermostat, which allowed adjustment of the polymerization temperature with an accuracy of ±0.5 °C. During polymerization runs, the ethene pressure was kept constant using a pressure controller. The ethene consumption was monitored with a Brooks 5850 TR mass flow meter and a Westphal WMR 4000 control unit. A standardized ligand screening experiment is described in detail in the results and discussion section. For a typical screening experiment, the reactor was evacuated at 90 °C for 60 min. It was then flushed with argon several times while the temperature was equilibrated to 30 °C within 30 min. The ligand was filled into the reactor and evacuated for 30 min. Subsequently, the reactor was charged with a solution of norbornene in toluene, toluene, palladium(II) acetate, a solution of triethylaluminum in toluene, and ethene up to a total volume of 200 mL. The polymerization was started by injection of tris(pentafluorophenyl)borane in toluene. After 30 min, the reaction was quenched by addition of ethanol (5 mL). After discharge and cleaning, the reactor was evacuated at 90 °C for the next polymerization cycle.

For a typical discrete-catalyst experiment, the reactor was evacuated at 90 °C for 60 min and then cooled to 30 °C. Subsequently, the reactor was charged with norbornene in toluene, toluene, and ethene up to a total volume of 200 mL at the desired feed composition. The polymerization was started by injection of the catalyst dissolved in fluorobenzene. The reaction was quenched by addition of ethanol (5 mL).

All polymer solutions were stirred overnight with 100 mL of dilute hydrochloric acid. After phase separation, the organic phase was washed three times with water and reduced to 50–70 mL on a rotary evaporator. The polymer was precipitated with a tenfold excess of ethanol, filtered off with a fritted glass filter, and dried in vacuo at 60 °C until the weight remained constant.

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[1] a) W. Kaminsky, A. Bark, M. Arndt, *Makromol. Chem. Macromol. Symp.* **1991**, *47*, 83–93; b) W. Kaminsky, A. Bark, R. Steiger, *J. Mol. Catal.* **1992**, *74*, 109; c) W. Kaminsky, A. Noll, *Polym. Bull.* **1993**, *31*, 175.

[2] R. R. Lamonte, D. McNally, *Adv. Mater. Process.* **2001**, *3*, 1–4.

[3] a) H. Cherdron, M.-J. Brekner, F. Osan, *Angew. Makromol. Chem.* **1994**, *223*, 121–133; b) T. Rische, A. J. Waddon, L. C. Dickinson, W. J. MacKnight, *Macromolecules* **1998**, *31*, 1871–1874; c) C. H. Bergström, B. R. Sperlich, J. Ruotoistenmäki, J. V. Seppälä, *J. Polym. Sci. Part A: Polym. Chem.* **1998**, *36*, 1633–1638; d) D. Ruchatz, G. Fink, *Macromolecules* **1998**, *31*, 4674–4680. e) M. Arndt-Rosenau, I. Beulich, *Macromolecules* **1999**, *32*, 7335–7343; f) I. Tritto, C. Marestin, L. Boggioni, L. Zetta, A. Provasoli, D. R. Ferro, *Macromolecules* **2000**, *33*, 8931–8944; g) I. Tritto, C. Marestin, L. Boggioni, M. C. Sacchi, H.-H. Brintzinger, D. R. Ferro, *Macromolecules* **2001**, *34*, 5770–5777; h) I. Tritto, L. Boggioni, J. C. Jansen, K. Thorshaug, M. C. Sacchi, D. R. Ferro, *Macromolecules* **2002**, *35*, 616–623; i) R. A. Wendt, R. Mynott, K. Hauschild, D. Ruchatz, G. Fink, *Macromol. Chem. Phys.* **1999**, *200*, 1340–1350; j) R. A. Wendt, G. Fink, *Macromol. Chem. Phys.* **2001**, *202*, 3490–3501.

[4] a) L. K. Johnson, C. M. Killian, M. Brookhart, *J. Am. Chem. Soc.* **1995**, *117*, 6141–6142; b) L. K. Johnson, C. M. Killian, S. D. Arthur, J. Feldman, E. McCord, S. J. McLain, K. A. Kreutzer, M. A. Bennett, E. B. Coughlin, S. D. Ittel, A. Parthasarathy, D. Tempel, M. Brookhart (University of North Carolina, Chapel Hill/DuPont), WO 96/23010, **1996**; [*Chem. Abstr.* **1996**, *125*, 222773t].

[5] a) G. J. P. Britovsek, V. C. Gibson, D. F. Wass, *Angew. Chem.* **1999**, *111*, 448–468; *Angew. Chem. Int. Ed.* **1999**, *38*, 428–447; b) S. D. Ittel, L. K. Johnson, M. Brookhart, *Chem. Rev.* **2000**, *100*, 1169–1204; c) S. Mecking, *Angew. Chem.* **2001**, *113*, 550–557; *Angew. Chem. Int. Ed.* **2001**, *40*, 534–540.

[6] a) K. L. Makovetsky, E. S. Finkelstein, V. I. Bykov, A. K. Bagdasaryan, B. L. Goodall, L. F. Rhodes (The B.F. Goodrich Company) WO Patent No. 9856837, **1998**; [*Chem. Abstr.* **1998**, *130*, 66910f]; b) B. L. Goodall, L. H. McIntosh (The B.F. Goodrich Company), WO Patent No. 9856839, **1998**; [*Chem. Abstr.* **1998**, *130*, 66911f].

[7] a) L. K. Johnson, S. Mecking, M. Brookhart, *J. Am. Chem. Soc.* **1996**, *118*, 267–268; b) S. Mecking, L. K. Johnson, L. Wang, M. Brookhart, *J. Am. Chem. Soc.* **1998**, *120*, 888–889; c) S. Mecking, A. Held, F. M. Bauers, *Angew. Chem.* **2002**, *114*, 564–582; *Angew. Chem. Int. Ed.* **2002**, *41*, 544–561.

[8] a) Z. B. Guan, P. M. Cotts, E. F. McCord, S. J. McLain, *Science* **1999**, *283*, 2059–2062; b) D. J. Tempel, L. K. Johnson, R. L. Huff, P. S. White, M. Brookhart, *J. Am. Chem. Soc.* **2000**, *122*, 6686–6700; c) L. H. Shultz, D. J. Tempel, M. Brookhart, *J. Am. Chem. Soc.* **2001**, *123*, 11539–11555; d) L. H. Shultz, M. Brookhart, *Organometallics* **2001**, *20*, 3975–3982.

[9] a) T. R. Boussie, C. Coutard, H. Turner, V. Murphy, T. S. Powers, *Angew. Chem.* **1998**, *110*, 3472–3475; *Angew. Chem. Int. Ed.* **1998**, *37*, 3272–3275; b) W. Weinberg, E. McFarland, I. Goldwasser, T. Boussie, H. Turner, J. A. M. Van Beek, V. Murphy, T. S. Powers (Symyx), WO Patent Application 9803521, **1998**; [*Chem. Abstr. 128*, 141181h].

[10] a) M. Gosmann, PhD Thesis, University of Hamburg (Germany), **2000**; b) M. Arndt-Rosenau, Habilitation Thesis, University of Hamburg (Germany), **2001**.

[11] a) L. Deng, T. K. Woo, T. Ziegler, *J. Am. Chem. Soc.* **1997**, *119*, 1094–1100; b) L. Deng, T. K. Woo, L. Cavallo, P. M. Margl, T. Ziegler, *J. Am. Chem. Soc.* **1997**, *119*, 6177–6186.

[12] A. C. Gottfried, M. Brookhart, *Macromolecules* **2001**, *34*, 1140–1142.

[13] a) M. Arndt, I. Beulich, W. Kaminsky, World-wide Metallocene Conference, Houston, TX, **1996**; b) B. A. Harrington, D. J. Crowther, *J. Mol. Catal. A: Chem.* **1998**, *128*, 79–84.

[14] L. H. Sperling, *Introduction to Physical Polymer Science*, Wiley, New York, **1992**.

[15] D. Mäder, J. Heinemann, P. Walter, R. Mülhaupt, *Macromolecules* **2000**, *33*, 1254–1261.

[16] J. Forsyth, J. M. Pereña, R. Benavente, E. Peréz, I. Tritto, L. Boggioni, H.-H. Brintzinger, *Macromol. Chem. Phys.* **2001**, *202*, 614–620.

[17] a) M. Svoboda, H. tom Dieck, *J. Organomet. Chem.* **1980**, *191*, 321–328; b) H. tom Dieck, M. Svoboda, T. Greiser, *Z. Naturforsch. B* **1981**, *36*, 823–832; c) G. van Koten, K. Vrieze, *Adv. Organomet. Chem.* **1982**, *21*, 151–239; d) R. van Asselt, C. J. Elsevier, W. J. J. Smeets, A. L. Spek, R. Benedix, *Recl. Trav. Chim. Pays-Bas* **1994**, *113*, 88–98.

[18] a) H. Nishida, N. Takada, M. Yoshimura, T. Sonoda, H. Kobayashi, *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2600–2604; b) M. Brookhart, B. Grant, A. F. Volpe, Jr., *Organometallics* **1992**, *11*, 3920–3922.

[19] M. S. Brookhart, L. K. Johnson, S. D. Arthur, J. Feldman, K. A. Kreutzer, A. M. A. Bennett, E. B. Coughlin, S. D. Ittel, A. Parthasarathy, D. J. Tempel, (University of North Carolina, Chapel Hill/DuPont), US Patent 5886224, **1999**; [*Chem. Abstr.* **1996**, *125*, 222773t].

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