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Articles

Polymeryl Exchange between *ansa*-Zirconocene Catalysts for Norbornene−Ethene Copolymerization and Aluminum or Zinc Alkyls

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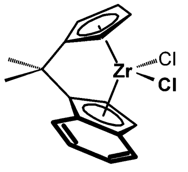
ABSTRACT: Addition of aluminum or zinc alkyls (AlR_3 or ZnR_2, R = Me or Et) lowers the molar masses of norbornene−ethene (N/E) copolymers obtained with the catalyst systems $Me_2C(Ind)(Cp)ZrCl_2$/MAO or *rac*-$C_2H_4(2\text{-}{}^tBuMe_2SiO\text{-}Ind)_2ZrCl_2$/MAO to different degrees. These chain-shortening effects and changes in relative end-group abundance indicate the degree to which E/N copolymers growing at a Zr catalyst center are transferred to Al or Zn centers by alkyl−polymeryl exchange. Increased molar masses of copolymers obtained in the presence of added $Al(^iBu)_3$ indicate that this reagent suppresses polymer chain exchange between Zr catalyst centers and methylaluminum species contained in the MAO activator. These observations are interpreted in terms of reversible adduct formation between Al or Zn alkyls and cationic zirconocene alkyl species.

Introduction

Zirconocene-catalyzed norbornene/ethene (N/E) copolymerizations, which produce thermoplastic and highly transparent materials,[1] have been studied in detail over the past 10 years, in particular with regard to the microstructure of the copolymers thus obtained.[2−4] Chain-growth termination and chain-transfer reactions, on the other hand, have not been studied for these copolymerization systems in similar detail as for homopolymerizations with related catalyst systems.[5] Since the reactivity of different types of chain ends would be essential for any functionalization or further grafting of these copolymers, we have set out to clarify how the growth of N/E copolymer chains at typical zirconocene catalysts is terminated and, in particular, under which conditions and to which degree termination occurs by polymeryl exchange with Al alkyl centers under formation of alkylaluminum-functionalized copolymer chain ends.

Exchange between catalyst-bound polymer chains and aluminum-bound alkyl groups has been noted to occur in heterogeneous Ziegler−Natta catalyst systems, from decreased polymer chain lengths and reduced abundances of unsaturated chain ends,[6] as well as by isotopic labeling studies.[7] Similar effects of polymeryl vs alkyl exchange between catalyst and aluminum centers have been observed for several zirconocene-based catalyst systems[8] as well as for catalysts based on bis(imino)iron complexes.[9] Diethylzinc has been reported to be a particularly effective chain-transfer agent for conventional Ziegler−Natta catalysts,[10] as for metallocene and late-transition-metal catalysts.[11,12]

High degrees of polymerization, reported for some N/E polymerization catalysts,[3] would make the observation of end groups rather difficult. We have thus chosen the catalyst systems $Me_2C(Ind)(Cp)ZrCl_2$/MAO (**1**) and *rac*-$C_2H_4(2\text{-}{}^tBuMe_2SiO\text{-}Ind)_2ZrCl_2$/MAO (**2**) to study how aluminum and zinc alkyls affect N/E copolymerization, since the relatively short copolymer chains obtained with these catalysts might facilitate the identification of polymer end groups: Catalyst **1** has been shown by Ruchatz and Fink to give rather short-chained N/E copolymers,[2b] while for catalyst **2** extensive chain transfer to aluminum has been observed in ethene polymerization.[8e−g]



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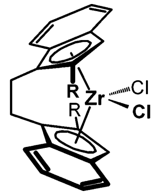

2 R = ^{t}BuMe$_2$SiO-

Results and Discussion

1. Assignment of End-Group NMR Signals. Since the reactions responsible for chain-growth termination in a given catalyst system are primarily indicated by the relative amounts of various types of chain ends, we have sought to identify the NMR signals of typical end groups in ethene−norbornene (E/N) copolymers by comparison with suitable model species.

In metal complex-catalyzed E/N copolymerization, each insertion of a first E or N unit will lead to a

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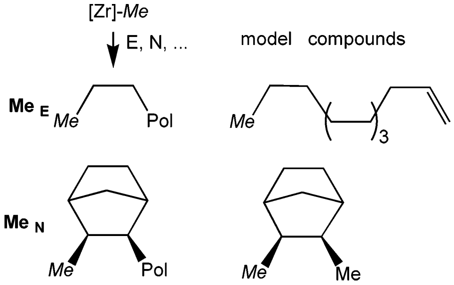
Scheme 1. Saturated Chain Starts Derived from Zr−Me Units



Scheme 2. Saturated Chain Starts Derived from Zr−H Units (A) and Saturated Chain Ends Derived from Me_2Al End Groups (B)

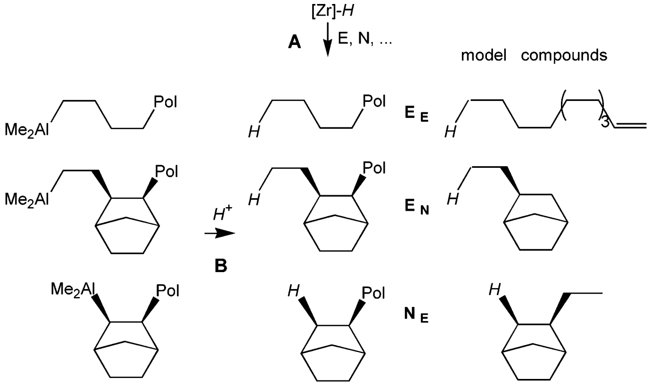
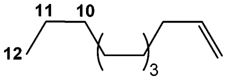
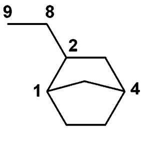
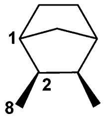


Table 1. Significant NMR Signals for Saturated Chain-End Models

Model compound	^{1}H NMR signals (ppm)	^{13}C NMR signals (ppm)	End group indicated
	0.89 (-CH$_3$)	29.1 (C-**10**) * 22.8 (C-**11**) * 14.2 (C-**12**) *	$\mathrm{E_E}$, $\mathrm{Me_E}$
	0.90 (-CH$_3$)	29.2 (C-**8**) 12.7 (C-**9**)	$\mathrm{E_N}$
	1.97, 2.18 (H-**1**, H-**4**)	41.0 (C-**1**) 44.6 (C-**2**) 36.8 (C-**4**)	$\mathrm{N_E}$
	-	44.5 (C-**1**) [a] 39.9 (C-**2**) [a] 15.9 (C-**8**) [a,*]	$\mathrm{Me_N}$

[a] From ref 13. *Used to identify the respective chain-end groups.

saturated chain start (Scheme 1). Ethyl or 2-norbornyl end groups of type $\mathrm{E_E}$/$\mathrm{E_N}$ and $\mathrm{N_E}$/$\mathrm{N_N}$ will arise as chain starts when a first E or N unit inserts into a zirconocene hydride, [Zr]−H, or when a β-H atom is transferred to one of the monomers. The same groups can also arise as chain ends, however, when AlR_x- or ZnR-terminated polymer chains, generated by alkyl exchange between [Zr]−polymer and Al−Me or Zn−Me species, are subject to hydrolysis (Scheme 2). In Table 1, we list relevant ^{1}H and ^{13}C NMR signals, derived from those of the model compounds 1-dodecene and 2-ethylnorbornane, which would indicate the presence of these types of end groups.

Each exchange between a [Zr]−polymer and a [Al]−Me or [Zn]−Me species will also generate a [Zr]−Me unit, however, which, upon insertion of E or N, gives rise to chain starts $\mathrm{Me_E}$ and $\mathrm{Me_N}$. While $\mathrm{Me_E}$ is practically indistinguishable from $\mathrm{E_E}$, a chain start $\mathrm{Me_N}$ is indicated by a ^{13}C methyl signal at 15.9 ppm, as in *exo,exo*-2,3-dimethylnorbornane (Table 1).[13]

Scheme 3. Unsaturated Chain Ends Arising from β-H Transfer

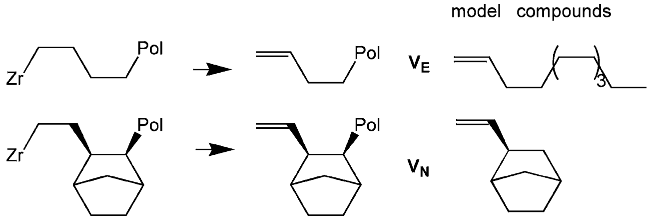
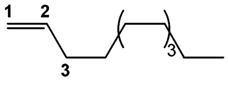
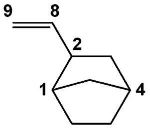
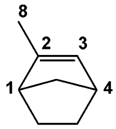
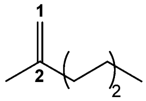


Table 2. Significant NMR Signals for Unsaturated Chain-End Models

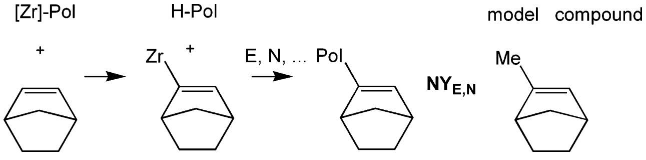
Model compound	^{1}H NMR signals (ppm)	^{13}C NMR signals (ppm)	End group indicated
	4.98 (H-**1a**)* 4.93 (H-**1b**) * 5.80 (H-**2**) * 2.05 (H-**3**a,b)	114.1 (C-**1**) 139.2 (C-**2**) 33.9 (C-**3**)	$\mathrm{V_E}$
	2.25 (H-**1**) 2.11 (H-**2**) 2.08 (H-**4**) 5.77 (H-**8**) * 4.86 (H-**9a**) * 4.93 (H-**9b**) *	46.0 (C-**2**) 144.5 (C-**8**) 111.8 (C-**9**)	$\mathrm{V_N}$
	2.60, 2.75 (H-**1**, H-**4**) 5.50 (H-**3**) [a, *]	145.5 (C-**2**) 128.3 (C-**3**)	$\mathrm{NY_E}$, $\mathrm{NY_N}$
	4.67 (H-**1**a,b) *	109.7 (C-**1**) * 146.2 (C-**2**) *	$\mathrm{VD_E}$

[a] The olefinic proton of 2-(2′-norbornenyl)norbornane also has an ^{1}H NMR shift of 5.50 ppm. *Used to identify the respective chain-end groups.

More informative than these saturated-end-group signals, with regard to their origin from a specific termination reaction, are unsaturated-end-group signals. Vinyl chain ends, such as $\mathrm{V_E}$ or $\mathrm{V_N}$, which arise by β-H transfer from a last-inserted E unit, either to the metal or to a monomer (Scheme 3),[5] are characterized by olefinic ^{1}H and ^{13}C signals close to those of 1-dodecene and 2-vinylnorbornane, respectively (cf. Table 2).

As seen in 2-methyl- or 2-norbornylnorbornene (Table 2), unsaturated norbornenyl end groups $\mathrm{NY_E}$/$\mathrm{NY_N}$ are detectable by rather low-field ^{13}C signals at 128 and 145.5 ppm and rather high-field ^{1}H signals at ca. 5.5 ppm as well as by rather low-field ^{1}H signals of their bridge-head protons at 2.6−2.8 ppm. As noted before,[2f,g] norbornenyl end groups cannot arise by β-H transfer from a last-inserted N unit, since the metal−carbon bond in the *exo* position and the β-hydrogen−carbon bond in the *endo* position cannot become coplanar to form the required four-centered transition state[14] and since formation of a carbon−carbon double bond by transfer of the other β-H atom at the bridge-head position is prohibited by Bredt's rule.[15] The only conceivable way for norbornenyl end groups to arise is thus a vinylic C−H bond activation, i.e., a σ-bond metathesis

Scheme 4. Norbornenyl Chain Start from Vinylic C−H Activation



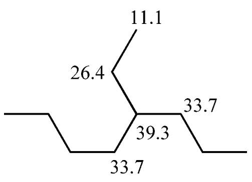
beween a Zr−polymer species and one of the olefinic CH units of a norbornene substrate molecule (Scheme 4).[5,16] This reaction would thus generate an unsaturated norbornenyl chain start together with one of the saturated chain ends shown in Scheme 1.

If each of the saturated chain ends discussed above would be generated—via transfer of a β-H atom—simultaneously with the formation of one of the unsaturated chain ends shown in Scheme 3, the total amounts of saturated and unsaturated end groups should be equal to each other.[17] Chain growth termination by alkyl−polymeryl exchange with AlMe or ZnR units, on the other hand, would manifest itself by an excess of saturated over unsaturated end groups.

2. N/E Copolymerization with Catalysts 1 and 2. Norbornene incorporation increased with increasing [N]/[E] concentration ratios in the reaction feed for both catalyst systems, but more so for catalyst **1** than for catalyst **2**. Under the reaction conditions used (30 °C, $[\mathrm{Al}]_{\mathrm{MAO}}/[\mathrm{Zr}] = 2000$), norbornene incorporation reached a limiting value of ca. 50 mol % N for catalyst **1** at the highest used feed ratio of $[\mathrm{N}]/[\mathrm{E}] \approx 20$,[2] while 19 mol % N was the highest norbornene incorporation reached with catalyst **2**. ^{13}C NMR spectra of the copolymers show, in accord with previous reports,[2] that increasing N contents of the copolymer are accompanied by a decrease of isolated norbornene (-E-E-N-E-E-) signals at 47.0 ppm and by an increase of alternating-sequence (-E-N-E-N-E-) signals at 47.7 ppm. Weak signals of NN diads (at 49.0 ppm) and NNN triads (at 54.7 ppm) become observable at high norbornene incorporations. At a [N]/[E] feed ratio of 10.4, copolymers obtained with catalyst **1** contained 42 mol % N, of which 17% are present as isolated and 72% as alternating N units, while NN diads represent 10% and NNN triads 1% of the total norbornene content. Copolymers obtained under the same conditions with catalyst **2** contained 7.5 mol % N, of which 60% was present as isolated and 40% as alternating N units. ^{13}C NMR signals of NN diads and NNN triads were not detectable in polymers obtained at a feed ratio of $[\mathrm{N}]/[\mathrm{E}] \approx 10$, but raised to a level of 7.4% and 1.3%, respectively, when the total N content was increased to its maximal value of ca. 20 mol % by elevating the feed ratio to $[\mathrm{N}]/[\mathrm{E}] \approx 20$, while 43% of the total N content was then present as isolated and 48% as alternating N units.

Copolymers obtained with catalyst **1** at low [N]/[E] feed ratios, which contain less than 15 mol % N, give rise to ^{13}C NMR signals at 22.6 and 14.0 ppm, which can be assigned to the last two carbons in saturated $-(CH_2)_xCH_3$ ($x \geq 2$) chain ends. In addition, we observe in these polymers atypical ^{13}C signals at 11.1, 26.4, 33.7, and 39.3 ppm. By empirical increment rules,[18] by DEPT NMR spectra, and from literature data for branched polyethenes,[19] these signals are assigned to ethyl branches (Scheme 5). Most likely, 1-butene is formed via ethene dimerization by this catalyst system and incorporated into the growing polymer chain.[20]

Scheme 5. ^{13}C NMR Signals Assigned to Ethyl Branches in PE and N/E Copolymers with Low N Content Prepared with Catalyst 1



Vinylidene groups, VD_E/VD_N, identified by a ^{1}H NMR signal at 4.8 ppm and by ^{13}C NMR signals at 107.6 and 147.0 ppm, appear to be the only unsaturated groups present in these copolymers. We assume that ethyl−polymeryl-substituted vinylidene end groups arise via β-H transfer after insertion of a 1-butene unit.[21] Under these conditions, chain growth thus appears to be terminated mainly by a (more facile) β-H transfer from the tertiary C atom of one of the rare ethyl branches, rather than from a secondary C atom of the more abundant straight-chain CH_2 groups.

With increasing norbornene contents (ca. 30−50 mol % N) increasing fractions of normal vinylic end groups give rise to ^{1}H NMR multiplets at 5.0 and 5.9 ppm, while norbornenyl end groups are apparent, from their olefinic proton signal at 5.5 ppm, with comparable intensity. At these higher norbornene concentrations, chains appear to be frequently started via vinylic C−H bond activation by norbornene; vinylic end groups could be derived either from vinylic C−H bond activation by ethene or via chain growth termination by β-H abstraction from a last-inserted E unit.

For copolymers obtained at low [N]/[E] feed ratios with catalyst system **2**, on the other hand, NMR data show the presence of vinylic as well as saturated *n*-alkyl end groups. This observation and the absence of ethyl branches and vinylidene end groups indicate that insertion of 1-butene and formation of vinylidene end groups do not occur to any significant degree with this crowded catalyst and that normal β-H transfer from straight-chain CH_2 groups, either via the metal center or directly to a monomer, dominates under these reaction conditions.

At higher [N]/[E] feed ratios, increasing proportions of norbornenyl chain starts became apparent again by their ^{1}H NMR signal at 5.5 ppm.[22] In this regard, catalyst **2** thus behaved similar to the one discussed above: As norbornene incorporation into the copolymer chain approached its limit at higher [N]/[E] feed ratios, metathetic CH activation under formation of a norbornenyl chain start becomes an increasingly prevalent alternative to β-H transfer.

The transfer of polymer chains from the Zr centers of a zirconocene catalyst to Al centers of MAO-derived methylaluminum species should manifest itself by an excess of saturated over unsaturated end groups in the hydrolyzed polymer product. While this excess cannot always be reliably assessed, due to the limited accuracy of the end group signal integrations, significant effects of added aluminum or zinc alkyls on various properties of the copolymers indicate that polymeryl exchange occurs to a substantial extent in both of the catalyst systems studied.

3. Effects of Aluminum and Zinc Alkyls. When studied at a fixed [N]/[E] feed ratio of 10.4 and a temperature of 30 °C with catalyst **1**, addition of TMA caused a moderate increase of N/E copolymerization activities by a factor of ca. 2 (Table 3, runs 1−9 and 1−10, Figure 1). Molar mass as well as N incorporation

Table 3. Effects of Trialkylaluminum Compounds on Norbornene−Ethene Copolymerization with Catalyst 1[a]

run	R	[AlR$_3$], mol	AlR$_3$/Zr	P,[b] g	N,[c] mol %	Act[d]	M_w,[e] kg/mol	M_n,[e] kg/mol	DI[e]
1-7		0	0	2.3	42.0	63.1	48.7	24.9	2.0
1-8	Me	0.002	200	3.5	46.6	98.1	55.2	30.3	1.8
1-9	Me	0.004	400	4.3	42.4	119.7	50.4	24.9	2.0
1-10	Me	0.006	600	5.1	46.3	142.2	47.7	24.1	2.0
1-11	Et	0.002	200	2.8	43.0	78.6	18.9	11.4	1.7
1-12	Et	0.004	400	2.0	44.6	55.0	14.1	8.9	1.6
1-13	Et	0.006	600	1.8	45.6	50.8	12.3	7.9	1.6
1-14	^{i}Bu	0.002	200	9.4	43.9	260.8	69.6	26.6	2.6
1-15	^{i}Bu	0.004	400	13.9	42.0	386.1	93.6	48.3	1.9
1-16	^{i}Bu	0.006	600	15.4	42.5	427.2	98.0	47.9	2.1

[a] Reactions conditions: temperature 30 °C, reaction time 1 h, [N] = 1.56 mol/L, P_E = 1.2 bar, [E] = 0.15 mol/L, [N]/[E] = 10.4, in 100 mL of toluene, [Zr] = 100 μmol/L, [Al(MAO)] = 200 mmol/L, [Al (MAO)]/[Zr] = 2000. [b] Polymer yield. [c] Norbornene incorporated, determined from copolymer ^{13}C NMR spectra. [d] Activity in g of polymer/(mol of Zr s). [e] From high-temperature GPC measurements.

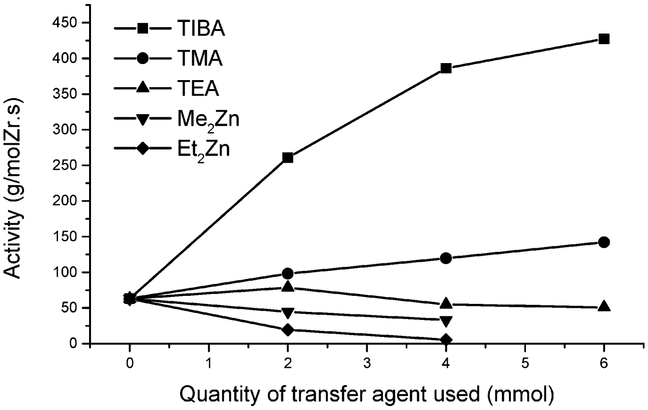


Figure 1. Effects of metal alkyl reagents on activities of norbornene−ethene copolymerizations with catalyst **1**.

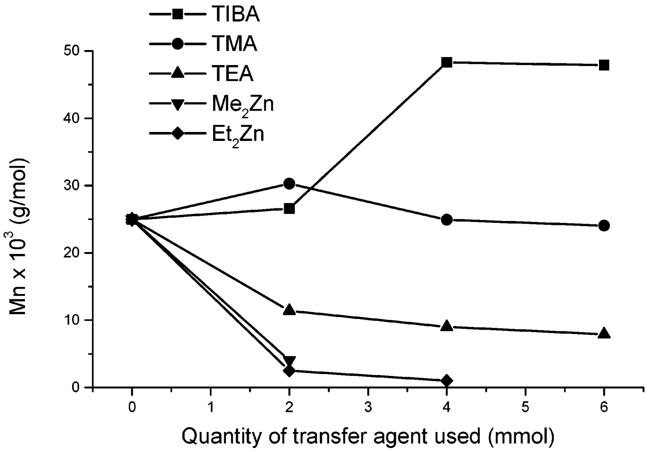


Figure 2. Effects of metal alkyl reagents on molar masses (M_n) of norbornene−ethene copolymers obtained with catalyst **1**.

values were not significantly affected by addition of TMA (Figure 2).[23]

Added TMA normally decreases the activity of zirconocene/MAO catalyst systems,[8k,24,25a,b] most likely by formation of heterobinuclear cations of the type Cp$^x_2$Zr(μ-Me)$_2$AlMe$_2^+$ and/or Cp$^x_2$Zr(μ-polymeryl)(μ-Me)AlMe$_2^+$.[25,26] One might speculate that this inhibitory effect is possibly compensated here by a removal of occasionally arising NN or NNN microblocks,[2d] which might otherwise tie up parts of the catalyst due to a decreased reactivity with further monomer. Their escape from the Zr center by exchange with an Al−Me unit would then explain the modest increase of activity caused by addition of TMA. The frequency with which such bulky microblock chain ends are excised from the metal center must be rather small, however, since no significant decrease of copolymer molar mass or N incorporation is caused by addition of TMA.

Addition of triethylaluminum (TEA) left activities and N incorporation values largely unchanged but caused a monotonic decrease in copolymer molar mass by factors of ca. 3. This chain-shortening effect would indicate, prima facie, nonnegligible exchange of Zr-bound, growing copolymer chains against Al-bound Et units.[27]

Addition of triisobutylaluminum (TIBA), finally, caused a striking increase in the activity of catalyst system **1**, by factors of up to 7 and of molar mass values by a factor of ca. 2 (Table 3, runs 1−16), while N incorporation remained essentially unchanged.[28] Causes for these remarkable effects of TIBA additions are to be discussed, together with those observed for catalyst system **2**, in a subsequent section below.

Addition of Me$_2$Zn to catalyst system **1** strongly decreased catalyst activities as well as copolymer molar masses, such that in some cases only oligomers were produced. Et$_2$Zn gave a similar decrease in activity and an even more pronounced lowering of copolymer molar masses (Table 4). In all of these cases, the dispersity indices remain close to (or even below) the value of 2, as expected for single-site polymerization catalysis with mass-independent chain-growth and -termination rates.

The dramatic chain-shortening effects caused by both zinc alkyls indicate a rather efficient exchange of their alkyl groups with Zr-bound, growing copolymer chains. The concomitant activity decrease indicates, furthermore, that zinc alkyls form rather strong heterodinuclear adducts with zirconocene alkyl (methyl or polymeryl) cations, Me$_2$C(Ind)(Cp)Zr(μ-alkyl)(μ-R)Zn(R)$^+$, from which the zinc dialkyl ZnR$_2$ is not easily displaced by an entering olefin substrate. The stability of these adducts (and their accessibility for further reaction with ZnR$_2$) would undoubtedly facilitate polymer transfer from Zr to Zn and would thus explain why polymer chains are exchanged with a Zn-bound methyl or ethyl group to a greater extent than with an Al-bound alkyl group.

For the copolymers produced in the presence of ZnMe$_2$ (runs 1-17 to 1-20), a new ^{13}C NMR signal was detected at 15.9 ppm. By comparison with *exo,exo*-2,3-dimethylnorbornane,[12] this signal can be assigned to the −**C**H$_3$ group of a methylnorbornane chain end (Me$_N$), which must arise from insertion of norbornene in the [Zr]−CH$_3$ bond of the methylated zirconocene catalyst. For copolymer 1−20, signals at 14.0 and 22.6 ppm, typical for the last two C atoms of *n*-alkyl end groups with at least three C atoms were observed, along with the signal at 15.9 ppm. These observations indicate that in the

Table 4. Effects of Dialkylzinc Compounds on Norbornene−Ethene Copolymerization with Catalyst 1[a]

run	R	[R_2Zn], mol	Zn/Zr	P,[b] g	N,[c] mol %	Act[d]	M_w,[e] kg/mol	M_n,[e] kg/mol	DI[e]
1-7		0	0	2.3	42.0	63.1	48.7	24.9	2.0
1-17	Me	0.002	200	1.6	47.3	44.7	6.9	4.0	1.7
1-18	Me	0.004	400	1.2	46.3	33.1	*f*	*f*	*f*
1-19	Et	0.002	200	0.7	43.7	19.4	*f*	*f*	*f*
1-20	Et	0.004	400	0.2	43.9	5.6	1.7	1.0	1.7

[a] Reaction conditions as in Table 3. [b] Polymer yield. [c] Norbornene incorporated, determined from copolymer ^{13}C NMR spectra. [d] Activity (g of polymer/(mol of Zr s)). [e] From high-temperature GPC measurements. [f] Molar masses of these copolymers were too low for GPC measurements.

Table 5. Effect of Trialkylaluminum Compounds on Norbornene−Ethene Copolymerization with Catalyst 2[a]

run	R	[AlR_3], mol	AlR_3/Zr	P,[b] g	N,[c] mol %	Act[d]	M_w,[e] kg/mol	M_n,[e] kg/mol	DI[e]
2-6		0	0	0.2	7.5	5.6	266.4	87.2	3.1
2-7	Me	0.002	200	0.1	28.9	2.5	225.5	64.1	3.5
2-8	Me	0.004	400	0.2	13.2	5.6	148.5	23.3	6.4
2-9	Me	0.006	600	0.2	2.5	5.3	128.9	23.1	5.6
2-10	Et	0.002	200	0.3	23.0	7.2	240.8	33.6	7.2
2-11	Et	0.004	400	0.7	10.7	18.3	198.8	29.2	6.8
2-12	Et	0.006	600	0.8	9.2	23.1	175.9	27.2	6.5
2-13	^iBu	0.002	200	1.9	17.9	51.4	275.6	85.8	3.2
2-14	^iBu	0.004	400	1.2	37.5	33.1	413.9	115.7	3.6
2-15	^iBu	0.006	600	2.2	36.1	60.6	414.7	171.5	2.4

[a] Reaction conditions as in Table 3. [b] Polymer yield. [c] Norbornene incorporated, determined from copolymer ^{13}C NMR spectra. [d] Activity (g of polymer/(mol of Zr s)). [e] From high-temperature GPC measurements.

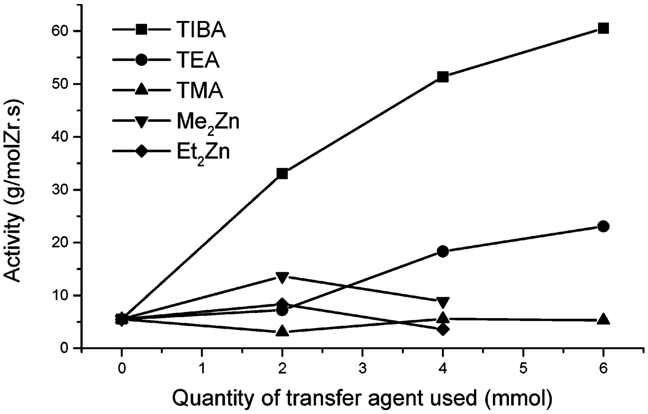


Figure 3. Effects of metal alkyl reagents on activities of norbornene−ethene copolymerizations with catalyst **2**.

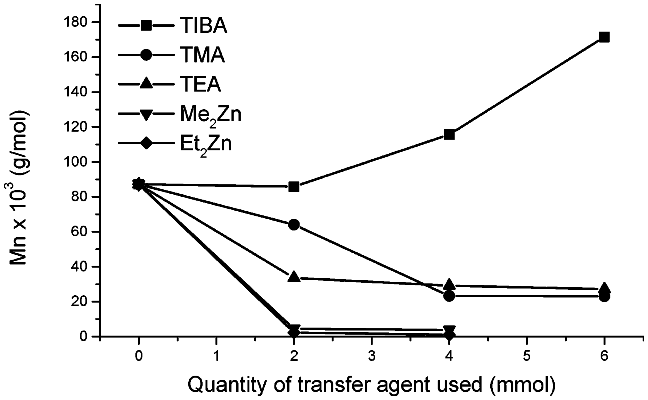


Figure 4. Effects of metal alkyl reagents on molar masses (M_n) of norbornene−ethene copolymers obtained with catalyst **2**.

presence of $ZnMe_2$ *n*-propyl-terminated chain ends and/or starts occur together with methyl-derived Me_N chain starts.

Catalyst **2**, *rac*-$C_2H_4(2\text{-}^tBuMe_2SiO\text{-}Ind)_2ZrCl_2$/MAO, differs markedly from catalyst **1** in its response to added aluminum alkyls. Addition of TMA, while not affecting activities greatly, caused a decrease in copolymer molar masses by a factor of ca. 4 (Table 5, runs 2-8 and 2-9, Figures 3 and 4). We have to assume, therefore, that this catalyst exchanges its growing polymer chains with [Al]−Me units of added TMA rather efficiently, as had been noted before when it was used for homopolymerizations of ethene and propene.[8e−g]

Together with this chain shortening, added TMA caused a significant broadening of the molar mass distribution, as shown by an increase of the polydispersity index from DI ≈ 3 to DI ≈ 6. Another difference to catalyst **1** concerns significant changes in the incorporation of norbornene, which increased by a factor of ca. 4 upon addition of modest amounts of TMA, but decreased to about one-third of its initial value when TMA was added in larger excess (Table 5, runs 2-7 and 2-9). Addition of TEA caused rather similar changes as found for TMA, with regard to activities, molar masses, mass distribution, and N incorporation.

Addition of excess of TIBA caused a remarkable activity increase, by a factor of ca. 10, similar to that observed with catalyst **1**, and an increase in molar mass M_n by a factor of ca. 2 (Table 5, Figure 4). At the same time, mass distributions became more narrow, with the polydispersity index moving toward DI ≈ 2. While the norbornene content in copolymers produced with catalyst **1** was not significantly affected by added TIBA, norbornene incorporation by catalyst **2** was remarkably increased, by a factor of up to 5, in the presence of added TIBA (Table 5, runs 2−14 and 2−15). Copolymers produced in the presence of TIBA contained, instead of an upper limit of ca. 20 mol % N in its absence, close to 40 mol % N. Of these, 40% corresponded to isolated and 54% to alternating N units and 4% and 2% to NN diblocks and NNN triblocks, respectively. The doubling of the copolymer N content caused by addition of TIBA is thus accompanied only by modest changes with regard to the distribution of N units within the copolymer chain.

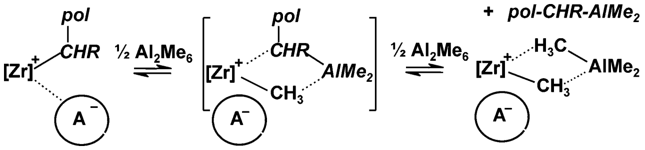
Addition of Me_2Zn or Et_2Zn had rather similar effects on catalyst **2** as noted above for catalyst **1**, especially with regard to chain shortening and suppression of unsaturated chain ends.[29] In the presence of $ZnEt_2$, catalyst **2** gave polymers consisting almost exclusively

Table 6. Effect of Dialkylzinc Compounds on Norbornene/Ethene Copolymerization with Catalyst 2[a]

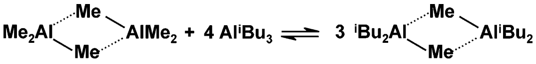
run	R	$[R_2Zn]$, mol	Zn/Zr	P,[b] g	N,[c] mol %	Act[d]	M_w,[e] kg/mol	M_n,[e] kg/mol	DI[e]
2-6		0	0	0.2	7.5	5.5	266.4	87.2	3.1
2-16	Me	0.002	200	0.5	7.2	13.6	46.4	4.5	10.4
2-17	Me	0.004	400	0.3	8.5	8.9	33.4	3.9	8.6
2-18	Et	0.002	200	0.3	2.7	8.3	13.7	2.3	6.0
2-19	Et	0.004	400	0.1	1.5	3.6	5.2	1.1	4.9

[a] Reaction conditions as in Table 3. [b] Polymer yield. [c] Norbornene incorporated, determined from copolymer ^{13}C NMR spectra. [d] Activity (g of polymer/(mol of Zr s)). [e] From high-temperature GPC measurements.

Scheme 6



Scheme 7



of ethene units, even at a rather high [N]/[E] feed ratio of ca. 10:1 (Table 6, run 2−19). This suggests that chain transfer to Zn competes particularly efficiently with insertions involving norbornene either as the substrate or as the last-inserted unit.

A remarkable difference between the catalyst systems **1** and **2** concerns the copolymer polydispersity indices: While addition of Me_2Zn to catalyst **1**, despite severe chain-shortening effects, had left the polydispersity index close to DI $\approx$ 2, added Me_2Zn increases this value toward DI $\approx$ 10 for catalyst **2**. Similarly broadened or even bimodal mass distributions, recently observed for Fe(II)-based polymerization catalysts, have been shown to arise from polymer transfer to aluminum and/or zinc alkyls[12] and might thus be regarded as a diagnostic sign for extensive polymeryl/alkyl exchange between catalysts and cocatalysts.

Conclusions

Most of the data presented above appear to be in accord with the assumption that aluminum alkyls and—even more so—zinc alkyls interact with the reactive alkyl zirconocenium cations, thought to be responsible for the activity of zirconocene-based polymerization catalysts, by forming heterobinuclear, cationic adducts of the type represented in Scheme 6.[25,26] Particularly stable adducts, as those containing $ZnMe_2$ and $ZnEt_2$, will lead to pronounced catalyst inhibition as well as to efficient polymer chain transfer. With added TMA, polymer transfer according to Scheme 6 appears to be contingent on steric factors, being more substantial for the more crowded catalyst **2** than for **1** and, in the case of the latter, probably restricted to species where bulky NN or NNN units are attached to the Zr center.

Most intriguing in this context are the effects of added TIBA on both catalyst systems, namely increases in polymerization activity by about 1 order of magnitude and the molar mass of the polymers by a factor of ca. 2. While these data are in accord with the prima-facie assumption that a $[Al]-{}^iBu$ unit has no tendency to exchange with a [Zr]−polymer unit, as no free energy gain is to be expected for exchange of a bulky ^iBu group against a polymer chain at the Zr center,[8k] additional factors are required to explain the activating and chain-lengthening effects of added TIBA.

Activating effects of TIBA, previously observed for propene homopolymerization with various *ansa*-zirconocene/MAO catalyst systems,[24] can be ascribed to its tendency to scavenge TMA and possibly also other [Al]−Me species present in MAO and/or in MAO-derived anions. Because of its mononuclear, tricoordinate geometry enforced by its bulky alkyl ligands, TIBA tends to react with TMA under formation of mixed $Me_x{}^iBu_{(3-x)}Al$ species, which can form stable dimers with bridging Me groups (Scheme 7),[30] but are probably too bulky to react with catalytically active alkyl zirconocene cations under formation of heterobinuclear adducts of the type shown in Scheme 6. Such a scavenging of the TMA content of MAO—and hence the suppression of any catalyst inhibition and/or polymer transfer due by it—might be the cause, at least in part, of increases in activities and chain lengths, as well as of decreased DI values, brought about by additions of TIBA.

Even the increase in N content in N/E copolymers obtained with catalyst **2** in the presence of TIBA might be subsumed to this interpretation: While TMA might be displaced from its adduct with the reactive alkylzirconocene cation more easily by ethene than by norbornene, a TMA-free contact-ion pair of the type *rac*-$C_2H_4(2\text{-}{}^tBuMe_2SiO\text{-}Ind)_2Zr(poly)^+MeMAO^-$, favored by reaction of TMA with $^iBu_3Al$ (Scheme 7), might react more evenly with ethene and with norbornene.

A reasonable extension of these lines of thinking would be the possibility that the anion $MeMAO^-$, assumed to arise by extraction of Me^- from a dimethylzirconocene precursor by a particularly Lewis acidic MAO species, might serve as a source for a—presumably exergonic—methyl/isobutyl exchange with TIBA. An anion $^iBu\text{-}MAO^-$ produced by such an exchange is likely to be less strongly coordinated to the reactive alkylzirconocene cation and more easily displaced even by norbornene and might thus be an alternative cause for the increases in catalyst activities and in norbornene contents of the N/E copolymers prepared in the presence of added TIBA.

Experimental Part

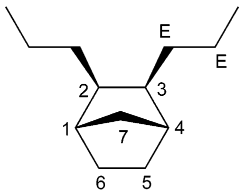
All work involving air- or moisture-sensitive compounds was carried out using standard Schlenk, vacuum line (argon atmosphere), and glovebox (nitrogen atmosphere) techniques. Samples of *rac*-$C_2H_4(2\text{- }Me_2SiO\text{-}Ind)_2ZrCl_2$ and $Me_2C(Ind)(Cp)ZrCl_2$ were kindly provided by Borealis AG and Ticona GmbH, respectively, the cocatalyst MAO (30 wt % in toluene) by Crompton GmbH, and ethene (grade 3.5) from BASF AG. TMA (2 M in toluene), TEA (1.9 M in toluene), TIBA (1 M in toluene), Me_2Zn (2 M in toluene), Et_2Zn (1.1 M in toluene), and 1-dodecene were purchased from Aldrich and used as received. Norbornene (purchased from Aldrich) and toluene were dried and distilled over CaH_2 and sodium, respectively, under an argon atmosphere. The following model compounds were synthesized according to literature reports: 2-methylnorborn-2-ene,[31] 2-ethylidenenorbornane,[32] 2-(2′-norbornenyl)norbornane,[33] 2-ethylnorbornane.[34] ^1H and ^{13}C NMR spectra of the model compounds were recorded on a Bruker AC 250

(250 MHz) instrument in $C_2D_2Cl_4$ which was predried over 4 Å molecular sieves.

Copolymerization Procedures. Stock solutions containing 3.3×10^{-3} mol/L of zirconocene dichlorides **1** or **2** (i.e., 10 μmol in 3 mL) and of norbornene (50 mol/L) were prepared in toluene. A 250 mL Schlenk vessel was charged with toluene (100 mL) and the cocatalyst MAO (5 mL) followed by norbornene and, where appropriate, by variable amounts (e.g., 2 mmol) of the trialkylaluminum or dialkylzinc compounds as toluene solutions. The mixture was degassed in vacuo, thermostated to 30 °C, and saturated with ethene at a pressure of 0.2 bar above atmosphere. In a second Schlenk vessel, 3 mL of the catalyst solution (10 μmol) was preactivated with MAO (5 mL) for 10 min and then added to the reaction to start the copolymerization. The copolymerization was stopped after 1 h by turning off the ethene feed, degassing the reaction vessel and then quenching the copolymerization solution in acidified methanol. By this procedure, norbornene conversion was generally kept below 10%, so as to keep [N]/[E] ratios constant, except for runs **1**−**15** and **1**−**16** (Table 3), which had much higher activities. The copolymer products were left stirring overnight, filtered, washed thoroughly with methanol, and dried in vacuo at 80 °C.

The concentration of ethene in toluene was evaluated according to Henry's law:[35] $C_{\mathrm{ethene}} = P_{\mathrm{ethene}}H_0 \exp(\Delta H_{\mathrm{L}}/(RT))$, where C_{ethene} = ethene concentration (mol/L), P_{ethene} = ethene pressure (atm), H_0 = the Henry coefficient, 0.001 75 mol L^{-1} atm^{-1}, ΔH_{L} = enthalpy of solvation of ethene in toluene, 2569 cal mol^{-1}, R = universal gas constant, 1.989 cal mol^{-1} K^{-1}, and T = solution temperature (K).[36] For a total ethene pressure of 1.2 bar, an ethene concentration of 0.15 mol/L is thus obtained.

Copolymer Characterization. Copolymer ^{1}H and ^{13}C NMR spectra were measured in $C_2D_2Cl_4$ at 120 °C on a Bruker Avance DRX 600 spectrometer. The norbornene content of the copolymers was determined by use of the signal integrals assigned to the following copolymer positions



according to eq 1:[37]

$$\text{mol \% norbornene} = 100(1/3)(2I_{\mathrm{C7}} + I_{\mathrm{C1,C4}} + I_{\mathrm{C2,C3}})/(I_{\mathrm{E}} + I_{\mathrm{C5,C6}}) \quad (1)$$

where I_{E} and $I_{\mathrm{C5,C6}}$ = integral of the signals between 28 and 32.5 ppm, I_{C7} = integral of the signals between 33 and 36.5 ppm, $I_{\mathrm{C1,C4}}$ = integral of the signals between 37 and 44 ppm, and $I_{\mathrm{C2,C3}}$ = integral of the signals between 44.5 and 56 ppm.

Molar masses of the copolymers were determined at the Max-Planck-Institut für Polymerforschung, Mainz, on a PL 220 chromatograph from Polymer Laboratories, at 140 °C with Waters Styragel columns (HT 2-6), using polystyrene standards, with 1,2,4-trichlorobenzene as solvent (3 mg of copolymer in 1.3 mL of solvent) at a flow rate of 1 mL/min.

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Note Added after ASAP Publication. This article was posted ASAP on January 11, 2005. The following information was added: The formation of ethyl branches, occasionally observed in ethene polymerization by *ansa*-zirconocene catalysts with one unobstructed coordination site, has been shown to occur by β-H transfer to ethene and subsequent insertion of the unsaturated polymer end into the Zr−ethyl bond, rather than by intermediate formation of 1-butene [Melillo, G.; Izzo, L.; Zinna, M.; Tedesco, C.; Oliva, L. *Macromolecules* **2002**, *35*, 9256 and references cited therein]. The revised version was posted on February 17, 2005.

References and Notes

(1) (a) Kaminsky, W.; Bark, A.; Arndt, M. *Makromol. Chem., Macromol. Symp.* **1991**, *47*, 83. (b) Kaminsky, W.; Arndt, M.; Bark, A. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1991**, *32*, 467. (c) Kaminsky, W. *Catal. Today* **1994**, *20*, 257. (d) Kaminsky, W. *Macromol. Chem. Phys.* **1996**, *197*, 3907.

(2) (a) Herfert, N.; Montag, P.; Fink, G. *Makromol. Chem.* **1993**, *194*, 3167. (b) Ruchatz, D.; Fink, G. *Macromolecules* **1998**, *31*, 4669. (c) *Macromolecules* **1998**, *31*, 4674. (d) *Macromolecules* **1998**, *31*, 4681. (e) *Macromolecules* **1998**, *31*, 4684. (f) Ruchatz, D. Dissertation, Heinrich-Heine-Universität Düsseldorf, 1997.

(3) (a) Cherdron, H.; Brekner, M. J.; Osan, F. *Angew. Makromol. Chem.* **1994**, *223*, 121. (b) Shiono, T.; Yoshida, K.; Soga, K. *Makromol. Chem. Rapid Commun.* **1990**, *11*, 169. (c) Hasan, T.; Nishii, K.; Shiono, T.; Ikeda, T. *Macromolecules* **2002**, *35*, 8933. (d) Hasan, T.; Shiono, T.; Ikeda, T. *Macromol. Symp.* **2004**, *213*, 123.

(4) (a) Bergström, C. H.; Väänänen, T. L. J.; Seppälä, J. V. *J. Appl. Polym. Sci.* **1997**, *63*, 1071. (b) Kaminsky, W.; Arndt, M.; Beulich, I. *Polym. Mater. Sci. Eng.* **1997**, *76*, 18. (c) Arndt, M.; Beulich, I. *Macromol. Chem. Phys.* **1998**, *199*, 1221. (d) Lasarov, H.; Mönkkönen, K.; Pakkanen, T. T. *Macromol. Chem. Phys.* **1998**, *199*, 1939. (e) Janiak, C.; Lassahn, P. G. *Macromol. Rapid Commun.* **2001**, *22*, 479. (f) Tritto, I.; Marestin, C.; Boggioni, L.; Sacchi, M. C.; Brintzinger, H.-H.; Ferro, D. R. *Macromolecules* **2001**, *34*, 5770. (g) Forsyth, J.; Perena, J. M.; Benavente, R.; Pérez, E.; Tritto, I.; Boggioni, L.; Brintzinger, H.-H. *Macromol. Chem. Phys.* **2001**, *202*, 614.

(5) Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* **2000**, *100*, 1253 and references quoted therein.

(6) (a) Bukatov, G. D.; Zakharov, V. A.; Yermakov, Yu. I. *Makromol. Chem.* **1978**, *179*, 2097. (b) Chien, J. C. W.; Kuo, C. I. *J. Polym. Sci., Part A* **1985**, *23* 731; *J. Polym. Sci., Part A* **1986**, *24*, 1779.

(7) (a) Zambelli, A.; Sacchi, M. C.; Locatelli, P.; Zannoni, G. *Macromolecules* **1982**, *15*, 211. (b) Zambelli, A.; Locatelli, P.; Sacchi, M. C.; Tritto, I. *Macromolecules* **1982**, *15*, 831.

(8) (a) Zambelli, A.; Longo, P.; Grassi, A. *Macromolecules* **1989**, *22*, 2186. (b) Resconi, L.; Bossi, S.; Abis, L. *Macromolecules* **1990**, *23*, 4489. (c) Resconi, L.; Waymouth, R. M. *J. Am. Chem. Soc.* **1990**, *112*, 4953. (d) Mogstad, A. L.; Waymouth, R. M. *Macromolecules* **1992**, *25*, 2282. (e) Leino, R.; Luttikhedde, H.; Wilén, C. E.; Sillanpää, R.; Näsman, J. H. *Organometallics* **1996**, *15*, 2450. (f) Leino, R.; Luttikhedde, H. J. G.; Lehmus, P.; Wilén, C. E.; Sjöholm, R.; Lehtonen, A.; Seppälä, J. V.; Näsman, J. H. *Macromolecules* **1997**, *30*, 3477. (g) Lehmus, P.; Kokko, E.; Härkki, O.; Leino, R.; Luttikhedde, H. J. G.; Näsman, J. H.; Seppälä, V. *Macromolecules* **1999**, *32*, 3547. (h) Naga, N.; Mizunuma, K. *Polymer* **1998**, *39*, 5059. (i) Byun, D. J.; Shin, D. K.; Kim, S. Y. *Macromol. Rapid Commun.* **1999**, *20*, 419. (j) Byun, D.-J.; Kim, S. Y. *Macromolecules* **2000**, *33*, 1921. (k) Lieber, S.; Brintzinger, H. H. *Macromolecules* **2000**, *33*, 9192.

(9) (a) Small, B. L.; Brookhart, M.; Bennett, A. M. A. *J. Am. Chem. Soc.* **1998**, *120*, 4049. (b) Small, B. L.; Brookhart, M. *Macromolecules* **1999**, *32*, 2120. (c) Britovsek, G. J. P.; Bruce, M.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; Mastroianni, S.; McTavish, S. J.; Redshaw, C.; Solan, G. A.; Strömberg, S.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **1999**, *121*, 8728. (d) Werne, G. Dissertation, Universität Konstanz, 1999.

(10) (a) Firsov, A. P.; Ter-Gazaryan, A. D.; Chirkov, N. M. *Polym. Sci. (U.S.S.R.)* **1964**, *6*, 408. (b) Burfield, D. R. *Polymer* **1984**, *25*, 1817.

(11) Kim, J. D.; Soares, J. B. P. *Macromol. Rapid Commun.* **1999**, *20*, 347.

(12) (a) Britovsek, G. J. P.; Cohen, S. A.; Gibson, V. C.; Maddox, P. J.; van Meurs, M. *Angew. Chem.* **2002**, *114*, 507. (b) Britovsek, G. J. P.; Cohen, S. A.; Gibson, V. C.; van Meurs, M. *J. Am. Chem. Soc.* **2004**, *126*, 10701.

(13) Stothers, J. B.; Tan, C. T.; Teo, K. C. *Can. J. Chem.* **1973**, *51*, 2893.

(14) Since norbornene insertion follows a stereospecific *cis*-2,3-*exo* mechanism: (a) Arndt, M.; Kaminsky, W. *Macromol. Symp.* **1995**, *97*, 225. (b) Bergström, C. H.; Sperlich, B. R.; Ruotoistenmäki, J.; Seppälä, J. V. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 1633.

(15) Kobrich, G. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 464.

(16) Woo, T. K.; Fan, L.; Ziegler, T. *Organometallics* **1994**, *13*, 2252.

(17) Ethyl head groups and vinyl end groups of essentially equal concentration were determined e.g. for N/E copolymers obtained with the catalyst $(PPh_2CH{=}C(O)Ph)Ni(Ph)(PPh_3)$: Benedikt, G. M.; Elce, E.; Goodall, B. L.; Kalamarides, H. A.; McIntosh, L. H.; Rhodes, L. F.; Selvy, K. T.; Andes, C.; Oyler, K.; Sen, A. *Macromolecules* **2002**, *35*, 8978.

(18) Friebolin, H. *Ein- und zweidimensionale NMR-Spektroskopie*; Verlag Chemie: Weinhein, 1988.

(19) Koenig, J. L. *Spectroscopy of Polymers*; American Chemical Society: Washington, DC, 1992.

(20) These ethyl branch signals are also observed in ethene homopolymer prepared with catalyst **1**. Chain walking of the Zr center, from which ethyl branches might also arise, would be expected to yield also methyl as well as longer alkyl branches, for which no ^{13}C NMR signals are observable.

(21) Vinylidene end groups might arise also from 1,2-reinsertion of a vinyl-terminated chain into a Zr−polymer bond, followed by β-H elimination.

(22) A weaker signal at 5.3 ppm was assigned to small amounts of isomerized norbornenyl groups, based on a comparison with the model compound 2-ethylidenenorbornane.

(23) Because of the rather high molar masses of the copolymers, end groups were not detected by NMR.

(24) Kleinschmidt, R.; van der Leek, Y.; Reffke, M.; Fink, G. *J. Mol. Catal. A* **1999**, *148*, 29.

(25) (a) Bochmann, M.; Lancaster, S. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1634. (b) Bochmann, M.; Lancaster, S. J. *J. Organomet. Chem.* **1995**, *497*, 55. (c) Tritto, I.; Donetti, R.; Sacchi, M. C.; Locatelli, P.; Zannoni, G. *Macromolecules* **1997**, *30*, 1247. (d) *Macromolecules* **1999**, *32*, 264. (e) Babushkin, D. E.; Semikolenova, N. V.; Zakharov, V. A.; Talsi, E. P. *Macromol. Chem. Phys.* **2000**, *201*, 558. (f) Pedeutour, J. N.; Cramail, H.; Deffieux, A. *J. Mol. Catal.* **2001**, *176*, 87. (g) Wieser, U.; Brintzinger, H. H. *Organometallic Catalysts and Olefin Polymerization*; Blom, E., Follestad, A., Rytter, E., Tilset, M., Ystenes, M., Eds.; Springer-Verlag: Berlin, 2001; p 3.

(26) Tritto et al.[25c,d] have shown polymeryl-bridged species such as $Cp^x{}_2Zr(\mu\text{-polymeryl})(\mu\text{-Me})_2AlMe_2{}^+$ to be not abundant enough for NMR detection in MAO-activated catalyst systems, but added TMA might increase their concentration to a level sufficient as exchange intermediates.

(27) Alternatively (and in distinction to TMA), TEA might contain also a finite fraction of Al−H units, possibly derived from Al−Et in the presence of the zirconocene catalyst; such an Al−H unit might have a greater tendency than its Al−Me (or Al−Et) counterparts to undergo exchange with a Zr−polymer unit of the polymerization catalyst.

(28) A decrease in the molar mass of the copolymers by a factor of ca. 2 was observed upon addition of TIBA, when similar copolymerization experiments were conducted at 70 °C.[2g] At this elevated temperature, Al hydride species might be formed by loss of isobutene from Al^iBu_3 and induce polymer transfer to Al under formation of Zr hydride species. This assumption is supported by the observation of heterodinuclear hydride complexes in TIBA-containing zirconocene catalyst systems: Götz, C.; Rau, A.; Luft, G. *J. Mol. Catal. A: Chem.* **2002**, *184*, 95.

(29) Neither saturated nor unsaturated chain ends were detectable in the NMR spectra of copolymers **2-16** and **2-17**. In the ^{13}C NMR spectra of copolymers **2-18** and **2-19**, however, *n*-propyl chain terminals were identified by signals at 14.0 and 22.6 ppm, while signals representing unsaturated chain ends were not detected.

(30) (a) Hoffmann, E. G. *Trans. Faraday Soc.* **1962**, *58* 642. (b) Yamamoto, O.; Hayamizu, K. *J. Phys. Chem.* **1968**, *72*, 822.

(31) (a) Kolonko, K. J.; Shapiro, R. H. *J. Org. Chem.* **1978**, *43*, 1404. (b) Posner, G. H.; Shulman-Roskes, E. M. *Tetrahedron* **1992**, *48*, 4677. (c) Farnum, D. G. *J. Org. Chem.* **1963**, *28*, 870.

(32) Adams, W. R.; Trecker, D. J. *Tetrahedron* **1972**, *28*, 2361.

(33) (a) Tenaglia, A.; Terranova, E.; Waegell, B. *J. Mol. Catal.* **1987**, *40*, 281. (b) Ito, M.; Ishii, Y.; Hamanaka, S.; Ogawa, M. *Sekiyu Gakkaishi* **1986**, *29*, 246.

(34) Dzhemilev, U. M. *Tetrahedron* **1995**, *51*, 4333.

(35) McKnight, A. L.; Waymouth, R. M. *Macromolecules* **1999**, *32*, 2816.

(36) Krauss, V. W.; Gestrich, W. *CHEMTECH* **1977**, *6*, 513.

(37) Tritto, I.; Marestin, C.; Boggioni, L.; Zetta, L.; Provasoli, A.; Ferro, D. R. *Macromolecules* **2000**, *33*, 8931.

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