Chain End Isomerization as a Side Reaction in Metallocene-Catalyzed Ethylene and Propylene Polymerizations

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ABSTRACT: The relevance of chain end isomerization in ethylene and propylene homopolymerizations has been investigated using four C_2 symmetric methylaluminoxane (MAO)-activated metallocene catalysts: *rac*-ethylenebis(1-indenyl)zirconium dichloride (**1**), *rac*-ethylenebis(2-(*tert*-butyldimethylsiloxy)-1-indenyl)zirconium dichloride (**2**), *rac*-ethylenebis(4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride (**3**), and *rac*-ethylenebis(1-(*tert*-butyldimethylsiloxy)-3-indenyl)zirconium dichloride (**4**). The amount of *trans*-vinylene groups in polyethylene and the amount of stereoinverted CH_2D groups in poly(1-*d*-propylene) were used as a measure for chain end isomerization. The isomerization process was more favored for **3**/MAO than for **1**/MAO, **2**/MAO, and **4**/MAO. The presence of the bulky electron-donating 2-siloxy substituent in **2**/MAO drastically suppresses the isomerization reaction. Formation of *trans*-vinylene groups in polyethylene and *d*-[*mrrm*] stereoerrors in polypropylene were concluded to be mechanistically related. Monomer-assisted chain termination after isomerization is proposed to explain the presence of chain end bound *trans*-vinylene groups in polyethylenes produced with **1**/MAO, **2**/MAO, and **4**/MAO.

Introduction

Macroscopic properties of a polymer are determined by its chain microstructure. The recent revolutionary development in metallocene-catalyzed olefin polymerization has allowed the rational tailoring of catalyst precursors to produce well-defined polymer microstructures ranging from atactic to stereoregular and stereoblock poly-α-olefins.[1] Careful examination of the microstructure gives insight into the reaction mechanisms involved in the catalytic olefin polymerization process.

In the case of polyethylenes, mechanistic information can be obtained from end group analysis. Vinyl end groups, formed by β-H abstraction to the metal or to a coordinated monomer, are common in polyethylenes prepared with metallocene catalysts. In addition to these, Thorshaug et al. have observed by FT IR measurements *trans*-vinylene double bonds in metallocene-catalyzed polyethylenes.[2] The proposed isomerization mechanism resulting in the formation of *trans*-2-vinylene groups is presented in the upper part of Scheme 1a.

In propylene polymerization with isospecific C_2-symmetric metallocene catalysts, isomerization of the last inserted monomer unit with subsequent chain growth results in the formation of [*mrrm*] stereoerrors (Scheme 1b), as demonstrated by Brintzinger et al.[3] and Busico and co-workers.[4] In addition, 3,1-propylene insertions resulting in the formation of a tetramethylene unit into the polypropylene chain have been proposed to originate from a reaction sequence with some analogy to Scheme 1b. In this process, initial β-H abstraction from the methyl group after 2,1-insertion is followed by rotation of the unsaturated chain end and 1,2-reinsertion into the Zr−H bond with subsequent regular 1,2-monomer insertion.[5]

The exact isomerization mechanisms in ethylene and propylene polymerizations are still under debate. One of the open questions is whether the isomerization proceeds via rotation of the π-complex before reinsertion[2,4] or via an allylic activation mechanism.[6−8] The latter alternative would explain the formation of internal vinylene bonds in polyethylene (Scheme 1a), although the actual reaction path may largely depend on the studied catalyst system. Nevertheless, it is tempting to assume—independent of the exact isomerization mechanism—that for a specific metallocene catalyst similar reaction steps are, at least to some extent, involved in both ethylene and propylene polymerizations.[2,9]

The aim of this study was to compare ethylene and propylene polymerizations with various metallocene catalysts in order to gain information on the isomerization reactions involved in the polymerization process. The understanding of isomerization mechanisms in ethylene polymerization may provide a means to control the fraction of reactive vinyl end groups for production of long-chain branched[10] or end group functionalized polyethylenes.[11] In our earlier studies,[10] we observed mainly vinyl and *trans*-vinylene unsaturations in polyethylenes prepared with stereorigid metallocene catalysts. The *trans*-vinylene groups were assumed to originate from isomerization reactions.[2] Figure 1 summarizes briefly our earlier findings in ethylene polymerization using three methylaluminoxane (MAO)-activated *ansa*-metallocene catalysts: *rac*-ethylenebis(1-indenyl)zirconium dichloride (**1**), *rac*-ethylenebis(2-(*tert*-butyldimethylsiloxy)-1-indenyl)zirconium dichloride (**2**),

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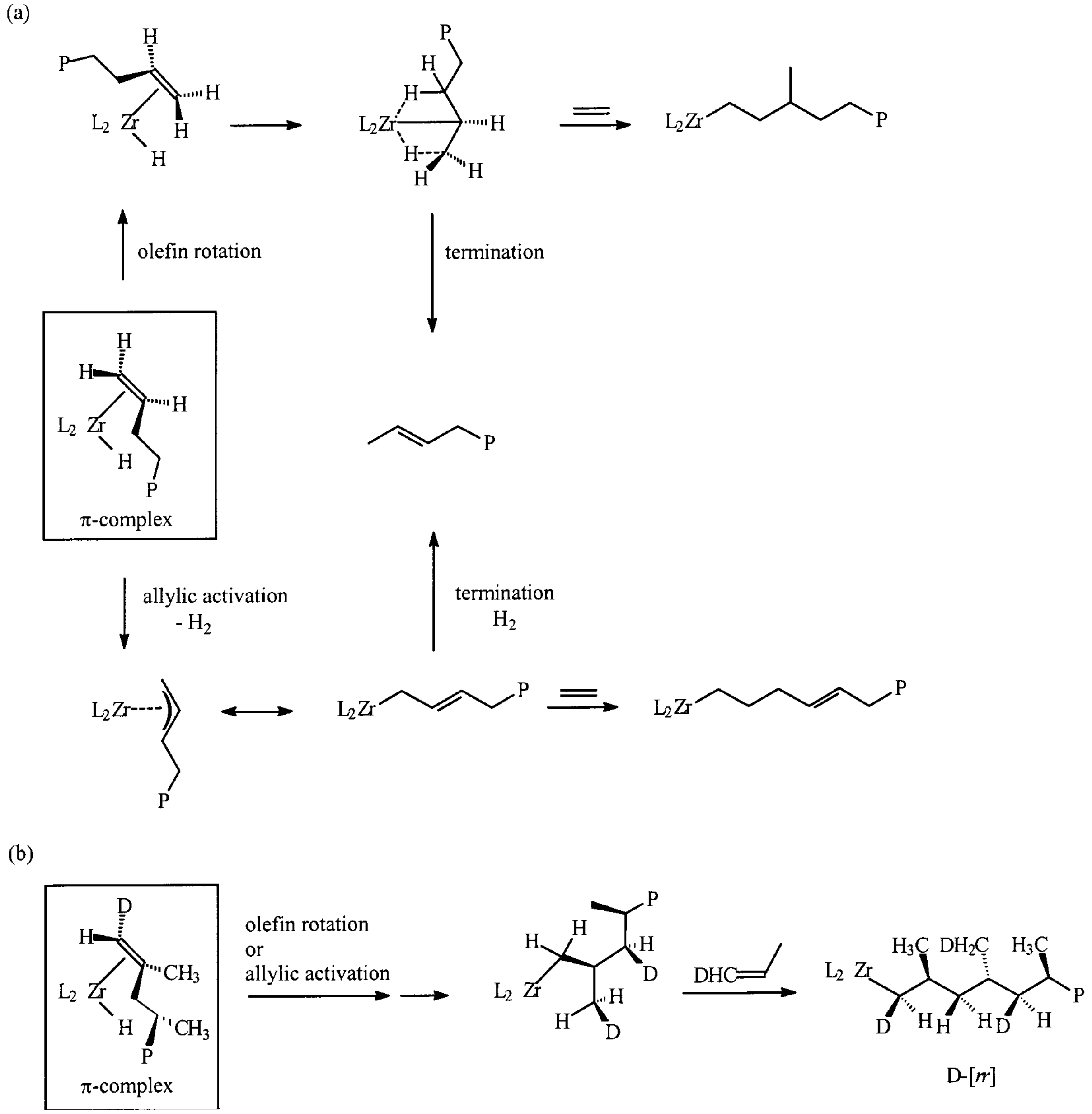
Scheme 1. Influence of Isomerization on Polymer Structure in (a) C_2 and (b) C_3 Polymerization According to Prevailing Mechanistic Concepts: Olefin Rotation[2,4] and Allylic Activation;[6] the Cationic Charge of Zr Has Been Omitted for Clarity



and *rac*-ethylenebis(4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride (**3**) (Figure 2).[10a,b] The vinyl selectivity of **1**/MAO decreased with monomer concentration ranging from 85% at $[C_2H_4] = 0.04$ M to 100% at $[C_2H_4] = 0.24$ M, as measured by FTIR. **2**/MAO exhibited a higher vinyl selectivity corresponding to approximately 95% at $[C_2H_4] = 0.04$ M. In contrast to these results, the selectivity of **3**/MAO is below 30% and independent of monomer concentration.

To obtain more information on the nature of the *trans*-vinylenes of these polymers, we have now studied the fine structures of the polyethylenes prepared with **1-3**/MAO by ^{1}H NMR and ^{13}C NMR. For comparison, we have also investigated the vinyl selectivity and its temperature dependency for *rac*-ethylenebis(1-(*tert*-butyldimethylsiloxy)-3-indenyl)zirconium dichloride (**4**)/MAO, which from earlier studies[10a] was known to produce *trans*-vinylene unsaturated polyethylenes at low monomer concentrations. To extend the scope of our investigations, we have also examined the role of stereoerror forming isomerization reactions in propylene polymerizations for **1-3**/MAO using deuterium-labeled monomer.

Experimental Section

Materials. Metallocene catalyst precursors **1**, **2**, and **4** were prepared according to literature procedures.[12] Metallocene complex **3**, triisobutylaluminum (TIBA), and MAO were obtained from Witco GmbH. Ethylene (grade 3.5) was obtained from AGA, and a mixture of *cis*/*trans*-1-*d*-propylene was prepared from *cis*/*trans*-1-bromopropylene (Aldrich, 98%) and MeOD (Aldrich, 99.5%) in analogy to literature procedures.[3] A detailed description of the synthesis and purification steps is given elsewhere.[13]

Polymerization. Ethylene and 1-*d*-propylene polymerizations were performed in 0.5 L and 50 mL steel autoclaves, respectively. The detailed polymerization procedures are described elsewhere.[10a,13] The overall reaction rates and polymer yields were kept low to avoid mass and heat transfer problems.

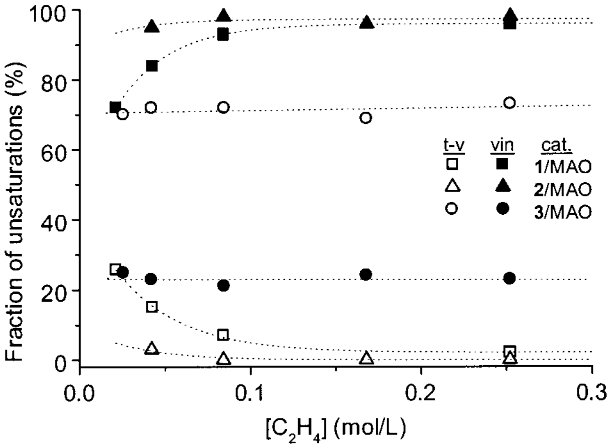


Figure 1. *trans*-Vinylene (t-v, open symbols) and vinyl (vin, solid symbols) bonds as a function of ethylene concentration in polyethylenes obtained at 80 °C with the complexes **1**/MAO, **2**/MAO, and **3**/MAO.

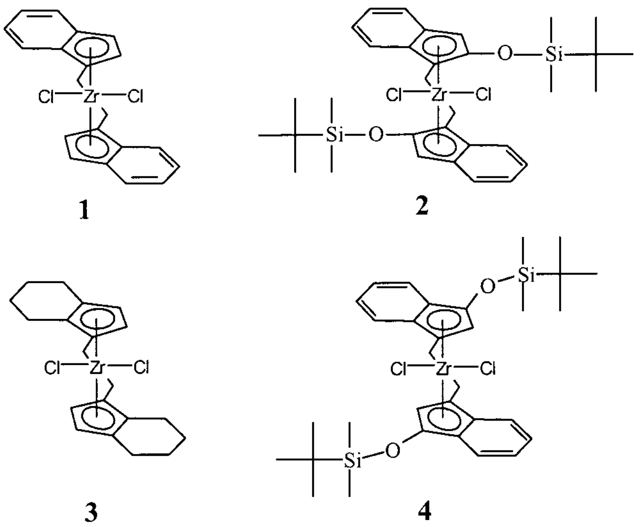


Figure 2. Catalyst precursors examined in this study.

Polymer Analysis. ^{13}C NMR spectra were recorded on a Varian GEMINI 2000 spectrometer (PP in $C_2D_2Cl_4$, PE in 1,2,4-$C_6H_3Cl_3$/C_6D_6 or C_7D_8, 100 °C, 75 MHz, 10 mm probe) or on a Bruker AMX 500 spectrometer ($C_2D_2Cl_4$, 80 °C, 125 MHz, 5 mm probe). Spectra of the deuterated polypropylenes were recorded in the inverse gated decoupling mode with a 4.5 s pulse repetition time and a 45° pulse. For polyethylene samples full NOE, a 7.8 s pulse repetition time and 45° pulse were applied. The number of transients accumulated was at least 6000. Double bonds in the polyethylenes were analyzed by ^1H NMR spectroscopy or Fourier transform infrared spectroscopy (Nicolet Magna 750 FT IR) from melt-pressed thin films. Isomerization of vinyl or vinylidene groups to *trans*-vinylene groups during polymer workup or polymer film preparation was concluded to be insignificant, since polymers containing only vinyl (>98%) or only vinylidene (>98%) unsaturations could be produced.

Results and Discussion

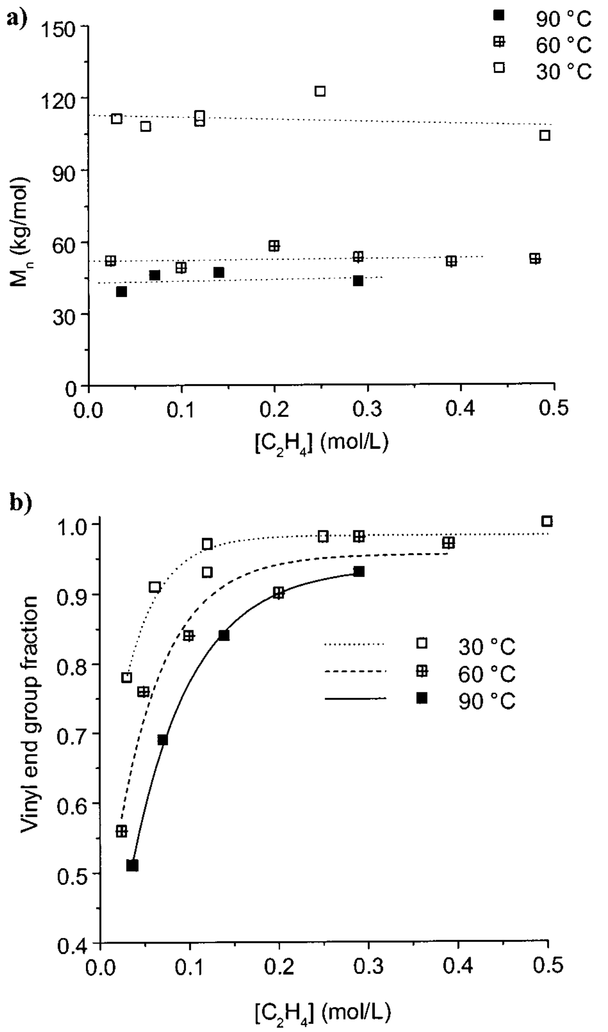


Figure 3. Dependency of (a) molecular weight and (b) vinyl end group selectivity on temperature and monomer concentration for complex **4**/MAO.

Ethylene Polymerization with 4/MAO. Figure 3 displays the molecular weights and vinyl bond contents of polyethylenes produced with **4**/MAO as functions of polymerization temperature and monomer concentration. The molecular weights decreased with increasing temperature but were independent of the employed ethylene concentration. The fraction of vinyl bonds decreased with decreasing ethylene concentration and increasing polymerization temperature. Notably, the decline in the vinyl bond content was largely compensated by a comparable increase in the *trans*-vinylene content.[14] Moreover, the overall content of unsaturations remained practically unchanged, corresponding to approximately one double bond per chain.

Chain transfer to monomer, β-H elimination, and σ-bond metathesis are the predominant chain transfer mechanisms producing vinyl-terminated polyethylene chains.[1,15] The ethylene concentration independent molecular weight results from a constant ratio of chain propagation and termination and indicates that for **4**/MAO chain transfer to monomer was the prevailing termination mechanism, as previously observed for **1**/MAO and **2**/MAO.[10] Monomer-assisted chain transfer is also reflected by the monomer concentration dependent vinyl bond fraction in the polyethylenes produced with these complexes. Apparently, formation of *trans*-vinylenes by chain end isomerization[16] was for **1**/MAO, **2**/MAO, and **4**/MAO kinetically competitive only at low monomer concentrations. Increase in the polymerization temperature may lower the energy barrier required for the isomerization reaction, thus favoring the formation of *trans*-vinylene bonds. In the case of **3**/MAO, for which chain transfer mainly occurs by β-H transfer to the metal,[10] both vinyl formation and isomerization induced *trans*-vinylene formation are unimolecular. This is

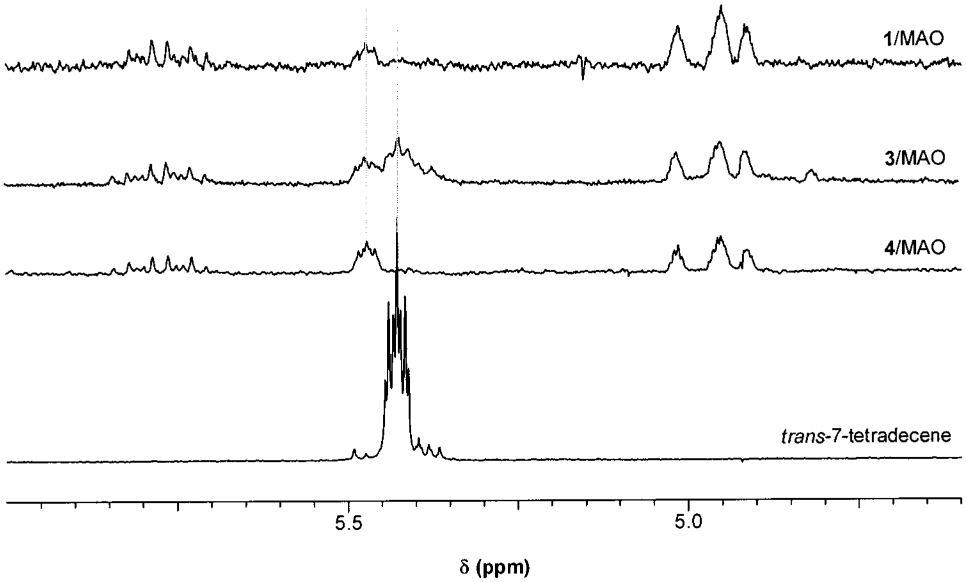


Figure 4. ^{1}H NMR spectra measured at 100 °C (δ(toluene) = 7.07 ppm) for selected polyethylenes and *trans*-7-tetradecene as reference compound.

reflected in the constant ratio of vinyl to vinylene unsaturations in the studied concentration range. The ease of Zr−H formation for **3**/MAO, as also reflected in its higher sensitivity toward chain termination by hydrogen,[10b,c] may be the cause for its higher tendency toward isomerization.

Analysis of the Polyethylene Microstructure. Analysis of the polyethylene double-bond regions by ^{1}H NMR provided information on the *trans*-vinylenes detected earlier by FTIR. Figure 4 shows the ^{1}H NMR spectra of the double-bond region of selected polyethylenes obtained with **1**/MAO, **3**/MAO, and **4**/MAO. It is evident that the major part of *trans*-vinylenes in **3**-PE are different to those of **1**-PE and **4**-PE.[17] In ^{13}C NMR analysis, signals from the methyl carbon (CH$_3$CH═CH−) of a 2-*trans*-vinylene chain end (17.6 ppm) were not detected in any of these polymers, whereas in all cases signals from carbon atoms neighboring an internal vinylene bond (−CH$_2$−CH═CH−CH$_2$−) (32.8 ppm) were clearly observed. The difference of the vinylene peak positions in the ^{1}H NMR spectra could be explained by different distances from the chain end.[18] The major part of the vinylenes in the polyethylene produced with **3**/MAO seems to be internal, as seen by the peaks that overlap with the double-bond peaks of the model substance *trans*-7-tetradecene (Figure 4). The vinylenes of **1**-PE and **4**-PE and a minor fraction of the vinylenes of **3**-PE, shifted downfield, seem to be closer to the chain end. The ^{13}C NMR spectra revealed peaks at 34.1/130.6 ppm and 25.9/131.8 ppm, possibly originating from 4- and 3-*trans*-vinylene bonds,[19] respectively. Further studies with catalysts producing lower molecular weight polyethylene should clarify this point.

At this stage, we believe that the differences in the vinylene peaks of **3**-PE compared to **1**-PE and **4**-PE are related to the differences in their predominant chain transfer mechanisms, which in turn influence the isomerization reactions. The absence of 2-*trans*-vinylenes in our polyethylenes cannot directly be explained by the rotation mechanism presented in the upper part of Scheme 1a. Therefore, we suggest that in ethylene polymerizations with catalysts undergoing β-H transfer to a monomer the isomerization process has to be monomer assisted as shown in Scheme 2. For **1**/MAO and **4**/MAO the β-H is transferred to a monomer, thus creating a Zr-bound ethyl group. After rotation, 2,1-reinsertion of the chain to the Zr−ethyl bond with subsequent β-H transfer to a new monomer molecule may explain vinylenes formed at the 3- or 4-position.

In the ^{13}C NMR spectrum of polyethylene obtained with **3**/MAO signals arising from isolated methyl side groups were detected at 37.5, 33.2, 27.4, and 19.9 ppm in a 2:1:2:1 ratio. The amount of methyl branching was less than one branch per three polymer molecules. In polyethylenes obtained with **1**/MAO and **2**/MAO methyl side groups were not detected, whereas for **4**/MAO a low amount of ethyl branches was observed.[20] The very low methyl side group content for **3**/MAO and the absence of branching for **1**/MAO and **2**/MAO suggests that the methyl branches may have originated from monomer insertion into the Zr−C(2) bond of the isomerizing chain end with subsequent chain growth (Scheme 1a). The presence of both internal vinylenes and methyl branches in **3**-PE suggests—according to Scheme 1a—more than one reaction pathway to take part in the isomerization process.

To undergo a *trans*-vinylene forming isomerization reaction, the π-complex formed by β-H elimination (Scheme 1) has to remain bound to the metal until the isomerization process is invoked. Since the isomerization in propylene polymerization is also understood to originate from a metal-bound π-complex (Scheme 1b), we were interested in studying the sensitivity of the four complexes **1-4**/MAO toward stereoerror formation by isomerization.

Propylene Polymerizations. The results of 1-*d*-propylene polymerizations are shown in Table 1 and Figure 5.[21] The ^{13}C NMR spectra of the deuterium-containing polypropylenes showed, in addition to the triplet of the main chain CHD-methylenes at 45.5 ppm, a triplet centered at 19.3 ppm ($J(^{13}C,^2H) = 19$ Hz) which can be assigned to stereoinverted CH$_2$D groups.[3] These *d*-[*mrrm*] stereoerrors originate from chain end isomerization (Scheme 1b), and their amount can thus be seen as a measure of the isomerization tendency of the applied catalyst. The undeuterated [*mrrm*] pentad results from wrong enantiofacial insertion of the prochiral monomer and can be observed downfield at 19.6 ppm.

Scheme 2. Tentative Mechanism for Formation of (A) *trans*-3-Vinylenes and (B) *trans*-4-Vinylenes; the Cationic Charge of Zr Has Been Omitted for Clarity

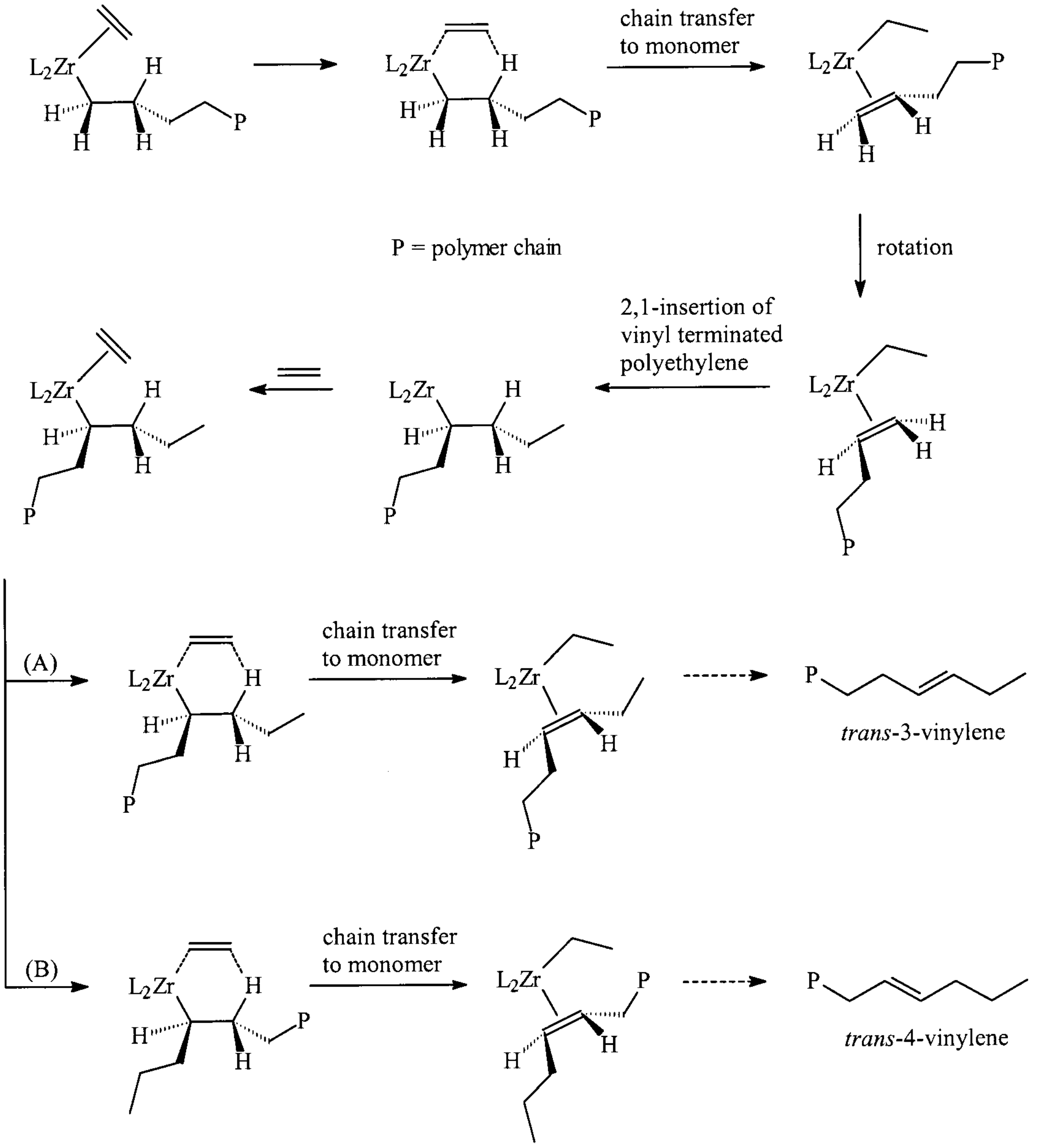


Table 1. 1-*d*-Propylene Polymerization Results[a]

catalyst	*T* (°C)	[d-C_3] (mol/L)	Al/Zr	pentad distributions[b] (%) [*mmmm*]	[*mmrr*]	[*mrrm*]	*d*-[*mrrm*]
1/MAO	30	0.4	500	82	4.2	1.5	0.4
1/MAO	50	0.4	1500	69	9.5	1.9	2.6
1/MAO	50	0.85	1500	79	6.4	2.0	1.3
1/MAO	50	1.3	1500	82	5.5	2.0	<0.5
1/MAO	70	0.4	1500	65	9.7	2.8	2.2
2/MAO	30	0.4	750	91	2.5	0.9	<0.5
2/MAO	50	0.4	750	80	5.2	1.6	0.7
2/MAO	50	0.85	750	81	4.0	1.4	0.5
2/MAO	70	0.4	750	66	8.5	2.1	1.2
3/MAO	30	0.4	200	69	6.1	1.1	2.1
3/MAO	50	0.4	200	50	16.4	3.3	6.7

[a] [Zr] = 3.3×10^{-4} mol/L for **1**/MAO and **2**/MAO, [Zr] = 2.5×10^{-3} mol/L for **3**/MAO. [b] By ^{13}C NMR.

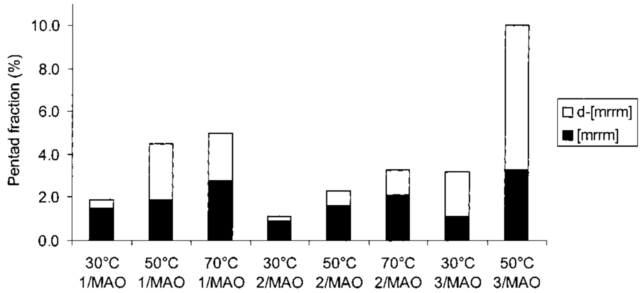


Figure 5. Fraction of deuterated *d*-[*mrrm*] and undeuterated [*mrrm*] error pentads as a function of polymerization temperature for polypropylenes obtained at 0.4 mol/L propylene concentration with the complexes **1**/MAO, **2**/MAO, and **3**/MAO.

Comparison of the amounts of *d*-[*mrrm*] stereoerrors for the three complexes indicates that the isomerization process was most favorable for **3**/MAO. This is in agreement with findings of Kaminsky et al.,[22] that in bulk polymerizations isomerization induced 3,1-insertions were only produced with **3**/MAO and not with **1**/MAO. At 30 °C the amount of isomerization induced *d*-[*mrrm*] stereoerrors for **3**/MAO was 5-fold compared to the two non-hydrogenated complexes. At 50 °C ([1-*d*-propylene] = 0.4 mol L^{-1}) the amounts of intrinsic and isomerization induced *d*-[*mrrm*] stereoerrors were for **3**/MAO 3.3% and 6.7%, respectively, which was already higher than the corresponding values for **1**/MAO and **2**/MAO at 70 °C.

Isospecificities of C_2 symmetric metallocenes generally decrease with increasing polymerization temperature and decreasing monomer concentration,[4] as can also be seen from Table 1 and Figure 5. It is interesting to evaluate the influence of temperature and monomer concentration on stereoregularity by differentiating between the contributions of intrinsic and isomerization-induced stereoerrors. We observed that the amount of intrinsic stereoerrors was, as expected,[3] independent of monomer concentration and increased with polymerization temperature. Furthermore, the amount of isomerization-induced stereoerrors increased with decreasing monomer concentration as the lower frequency of monomer insertions increased the probability of isomerization of the metal-bound π-complex. For **2**/MAO and **3**/MAO elevation of the polymerization temperature promoted the formation of isomerization-induced stereoerrors, which was, however, not observable for **1**/MAO at 50−70 °C.

Summary and Conclusions. A clear correlation between the isomerization tendency of a metallocene catalyst in ethylene and propylene polymerizations has been observed. The results demonstrate that the formation of *trans*-vinylene bonds in polyethylene and the formation of [*mrrm*] stereoerrors in polypropylene, both due to chain end isomerization, are more favored processes for **3**/MAO than for **1**/MAO, **2**/MAO, and **4**/MAO. The formation of *trans*-vinylenes via chain end isomerization in polyethylenes produced with **1**/MAO, **2**/MAO, and **4**/MAO is kinetically competitive only at low monomer concentrations. In ethylene polymerizations, the high vinyl end group selectivity, even at low monomer concentrations (Figure 1), suggested that for the siloxy-substituted **2**/MAO catalyst system the isomerization reaction is not competitive. The reason for the suppression of the isomerization reaction for **2**/MAO may be seen in its 2,2′-substituents, which increase its regiospecificity and interfere with the 2,1-reinsertion of a macromonomer during isomerization according to Scheme 2. A further reason might be the electronic influence of the siloxy groups, which enhances polymerization activity[10a] and possibly makes the regular chain propagation reaction more competitive. In propylene polymerizations, the amount of *d*-[*mrrm*] pentads was for **2**/MAO at all temperatures clearly lower than for any of the other complexes (Figure 5). This indicated likewise the unfeasibility of the isomerization reaction for this complex as expected from previous reports[3] on 2,2′-substituted metallocene systems.

For **3**/MAO, the very high *trans*-vinylene content and the presence of methyl branches in polyethylenes, together with the high amount of *d*-[*mrrm*] stereoerror pentads in polypropylene, indicate the feasibility of isomerization for this catalyst system. The higher tendency toward isomerization for the hydrogenated **3**/MAO seems to result, in addition to its lower regiospecificity, from its preference to undergo chain termination via β-H transfer to the metal, in contrast to the other catalysts of this study. This results for **3**/MAO in formation of a Zr−H bond prior to isomerization.

We consider our results as indirect experimental evidence and suggest that the formation of [*mrrm*] stereoerrors in metallocene-catalyzed propylene polymerization and the formation of *trans*-vinylene groups in ethylene polymerization are mechanistically related in the sense that they both involve some common elementary steps such as formation of a metal-bound π-complex after β-H abstraction. The role of chain end isomerization in olefin polymerization is charasteristic for a specific catalyst system and determines, at least to some extent, its potential for vinyl end group selectivity in ethylene polymerization and stereoselectivity in propylene polymerization.

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(16) Vinylene formation by termination after 2,1-insertion of a vinyl-ended macromonomer to a growing polymer chain can be outruled as chain termination by comonomer in ethylene−α-olefin copolymerizations preferentially leads to vinylidene and not to vinylene unsaturations.

(17) In the ^{13}C NMR spectrum of the polyethylene obtained with **3**/MAO we could detect only traces of *cis*-vinylenes, which cannot explain the difference in the vinylene peaks observed

in the ^1H NMR spectrum. The *trans*-vinylene pattern (^1H NMR) of **3**-PE and of polyethylene produced with (*n*-butylCp)$_2$ZrCl$_2$ is alike, which correlates it to catalysts undergoing chain termination in ethylene polymerizations preferentially by β-H elimination to the metal.[10b]

(18) The vinylene peaks of *trans*-3-octene and *trans*-4-octene overlapped with the peaks of *trans*-7-tetradecene. However, increasing the alkyl chain length from 4 carbons in 1-hexene to 14 carbons in 1-hexadecene was found to shift vinyl peaks 0.03 ppm downfield. Therefore, we do not consider short chain alkenes as appropriate model substances for exact comparison with polymers.

(19) The ^{13}C NMR spectrum of *trans*-3-octene and *trans*-4-octene revealed peaks at 132.0/25.7 ppm and 130.5/34.8 ppm, respectively.

(20) The formation of ethyl branching in polyethylene for the nonstereoselective *meso*-Et(Ind)$_2$ZrCl$_2$ has recently been proposed by Izzo et al. to occur via a bimolecular mechanism with monomer-assisted β-H abstraction (Izzo, L.; Caporaso, L.; Senatore, G.; Oliva, L. *Macromolecules* **1999**, *32*, 6913). Complex **4** is likewise nonstereoselective, in contrast to the other catalysts of this study, which might explain its propensity to form ethyl branched polyethylene.

(21) The activity of **4**/MAO toward propylene was too low for obtaining a representative homopolymer (see e.g. ref 12c or Leino, R.; Luttikhedde, H. J. G. In *Olefin Polymerization, Emerging Frontiers*; Arjunan, P., McGrath, J. E., Hanlon, T. L., Eds.; ACS Symposium Series 749; American Chemical Society: Washington, DC, 2000; pp 31−47). However, introducing ethylene as comonomer afforded a copolymer containing 90 mol % of deuterated propylene. The ^{13}C NMR spectrum of this copolymer showed atactic polypropylene blocks with a very low fraction of *d*-[*mrrm*] stereoerrors, difficult to integrate due to partial overlapping with the strong [*mrrm*] pentad.

(22) Schupfner, G.; Kaminsky, W. *J. Mol. Catal. A* **1995**, *102*, 59.

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