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Dialkylaminoethyl-Functionalized *ansa*-Zirconocene Dichlorides: Precatalysts for the Regulation of the Molecular Weight Distribution of Polyethylene[**]

Christian Müller, Dieter Lilge, Marc Oliver Kristen,[*] and Peter Jutzi[*]

Dedicated to Professor Reinhard Schmutzler on the occasion of his 65th birthday

The synthesis of metallocene derivatives which can be used as precatalysts in the methylalumoxane (MAO)-activated polymerization of α-olefins is a rapidly growing research area. Special attention is directed to the design of the metal coordination sphere: variations in the substitution pattern and in the connection of cyclopentadienyl (Cp) ligands may be utilized for synthesizing tailor-made single-site catalysts. Thus, polymer parameters such as stereochemical microstructure (tacticity), molecular weight distribution, crystallinity, and copolymer incorporation can be influenced systematically.[1, 2] This new generation of catalysts therefore is playing an important role in the development of new polyolefin-based materials.

The molecular weights of polymers produced with $[Cp_2ZrCl_2]$/MAO catalysts range between 100 000 and 1 000 000 g mol^{-1} for polyethylenes and between 200 and 1000 g mol^{-1} for polypropylenes. Polymers made by the conventional Ziegler–Natta process have broad molecular weight distributions with high polydipersities of $M_w/M_n = 5-10$, whereas single-site metallocene catalysts usually produce polyolefins with a unimodal molecular weight distribution and polydispersities of about 2. With respect to these features, there are no differences between unbridged, bridged, or Cp-substituted systems.[1a, 3]

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[*] Prof. Dr. P. Jutzi, Dipl.-Chem. C. Müller
Fakultät für Chemie der Universität
Universitätsstrasse 25, 33615 Bielefeld (Germany)
Fax: (+49) 521-106-6026
E-mail: peter.jutzi@uni-bielefeld.de
Dr. M. O. Kristen, Dr. D. Lilge
BASF Aktiengesellschaft, Kunststofflaboratorium
Forschung Polyolefine
67056 Ludwigshafen (Germany)

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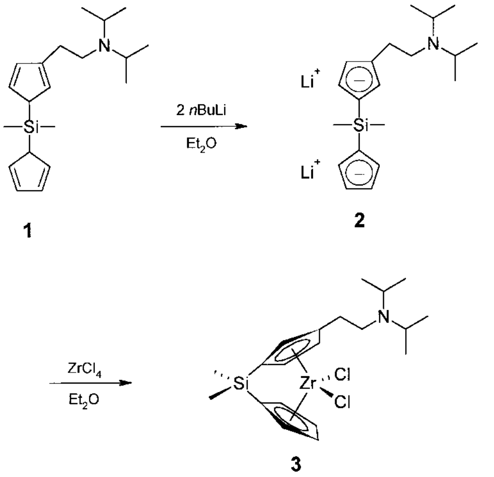
We report here on the polymerization of ethylene with amino-functionalized *ansa*-zirconocene dichlorides, activated with MAO.[4] These systems provide the possibility of regulating the molecular weight distribution of polyethylene systematically. Using only one precatalyst, high-molecular-weight as well as low-molecular-weight polyethylene with a classical unimodal molecular weight distribution is obtained. Furthermore, it is possible to produce polyethylenes with variable amounts of high- and low-molecular weights; these polymers show bimodal molecular weight distributions.

The silicon-bridged, diisopropylaminoethyl-functionalized zirconocene dichloride **3** was synthesized according to Scheme 1, and obtained as a beige, air- and moisture- sensitive solid in 43 % yield. The polymerization of ethylene with the catalyst **3**/MAO (Zr:Al = 1:1000) was performed at $T = 30, 45, 50, 60$, and 90 °C. The polyethylene samples were analyzed by gel permeation chromatography (GPC). Table 1 gives a summary of the polymerization results with regard to activity of the catalyst, M_w, M_n, and viscosity of the polymers. The molecular weight distribution as a function of the polymerization temperature is shown in Figure 1. The unimodal distribution at $T = 90$ °C is typical for the polymerization with single-site catalysts. Lowering the temperature to $T = 60$ °C resulted in the formation of a high-molecular-weight "shoulder", with a decrease in the low-molecular-weight area. This effect was intensified at a polymerization temperature of $T = 50$ °C. At $T = 45$ °C, the bimodal distribution is obvious; the maxima are located at $M = 45000$ g mol^{-1} and 1430000 g mol^{-1}, respectively. At $T = 30$ °C, high-molecular-weight polyethylenewas formed predominantely, while the low-molecular-weight fraction was decreased dramatically. At $T = 20$ °C, high-molecular-weight polyethylene was obtained, which could not be analyzed by GPC. As judged from the trend in Figure 1, one would expect that this polymer shows a unimodal molecular-weight distribution again.



Scheme 1. Synthesis of **3**.

Table 1. Results of the ethylene polymerization with the catalyst system **3**/MAO.

T [°C]	M_w	M_n	M_w/M_n	Yield [g]	Activity[a]	η[b] [dl g^{-1}]
30	1821768	144989	12.6	0.80	16	10.70
45	1193864	72504	16.5	1.50	30	6.80
50	584946	42869	13.6	2.50	50	4.78
60	389131	22306	17.5	4.45	89	3.75
90	54731	12939	4.2	19.7	394	1.00

[a] Activity in kg$_{PE}$(mol$_{Zr}$ h bar)$^{-1}$, [b] viscosity in decaline at $T = 180$ °C..

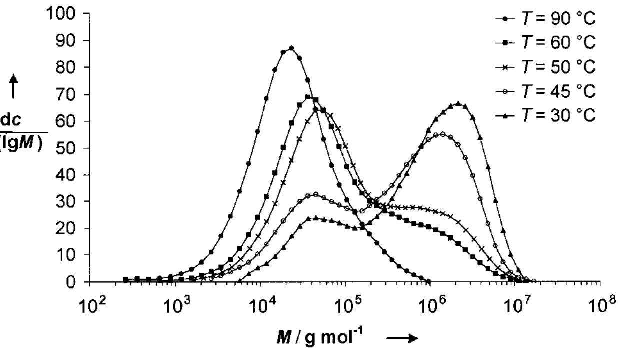
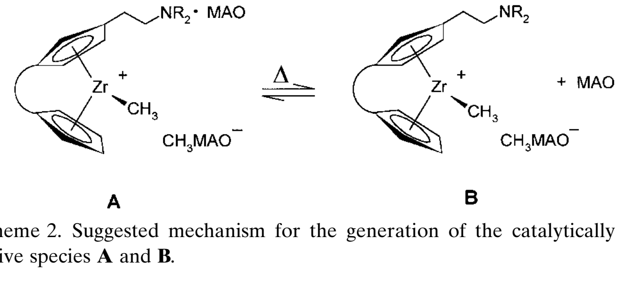


Figure 1. Molecular weight distribution of polyethylene as a function of the polymerization temperature.

We have demonstrated that it is possible to produce polyethylenes with different amounts of low- ($M = 30000$–60000 g mol^{-1}) as well as high-molecular-weight ($M = 1000000$–2500000 g mol^{-1}) polymer chains by varying the polymerization temperature and using a catalyst system consisting of an amino-functionalized *ansa*-zirconocene dichloride and MAO.[5] Thus, polymer properties can be influenced more effectively than by using conventional single-site catalysts.

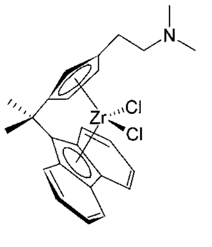
We propose that the dialkylaminoethyl functionality plays an important role in the polymerization process: the cocatalyst MAO not only acts as a methylating agent and as a Lewis acid to build the catalytically active, cationic complex, but it can also coordinate to the nitrogen atom of the dialkylaminoethyl group.[6] This results in the formation of the active species **A**, which produces high-molecular-weight polyethylene (Scheme 2). In the high-temperature region the catalytically active species **B** is formed in which the MAO does not coordinate to the amino group any more. **B** produces low-molecular-weight polyethylene. An equilibrium between **A** and **B** leads to the formation of a bimodal molecular-weight distribution in the polymerization process. Chain propagation and termination processes are obviously influenced by the differently structured side chain in **A** and **B**.[7] The assumption of a reversible temperature-dependent adduct formation (N →MAO) is supported by ^{1}H and ^{27}Al NMR spectroscopic investigations on a model system: a solution of diisopropyl-



Scheme 2. Suggested mechanism for the generation of the catalytically active species **A** and **B**.

amine and MAO (N:Al = 1:2) in [D$_8$]toluene as solvent shows a temperature-dependent equilibrium between amine · MAO adducts and dissociated species in the temperature range between $T = -80\,^\circ$C to $+80\,^\circ$C.

The 3-position of the dialkylaminoethyl substituent as well as the *ansa* bridge seem to be essential for the results reported here: only in this constellation is the amino group directed to the open sector of the catalytically active center; thus, chain propagation and chain termination processes can be effected by altering the donor functionality. This assumption is proven by the fact that unbridged, amino-functionalized zirconocene dichlorides as precatalysts do not show this phenomenon in the polymerization of olefins at all.[8]



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The results reported here are not restricted to the system **3**/MAO. In combination with MAO the carbon-bridged, dimethylaminoethyl-functionalized zirconocene dichloride **4**[4] produces polyethylene which shows a bimodal molecular weight distribution at $T = 50\,^\circ$C.[9] For the system **4**/MAO, it was additionally shown by Schulz–Zimm statistical methods[10] that the observed distribution was generated by a superposition of two independent distributions: the experimentally obtained data and the curve-fit, calculated from two different single-site catalysts ($M_w/M_n = 2.9$ and 2.3, respectively), are in good agreement (Figure 2). Although a single-component precatalyst was used for the polymerization process, two catalyst systems have to be present which produce a polyethylene with a bimodal molecular weight distribution in the selected temperature region (Table 2).

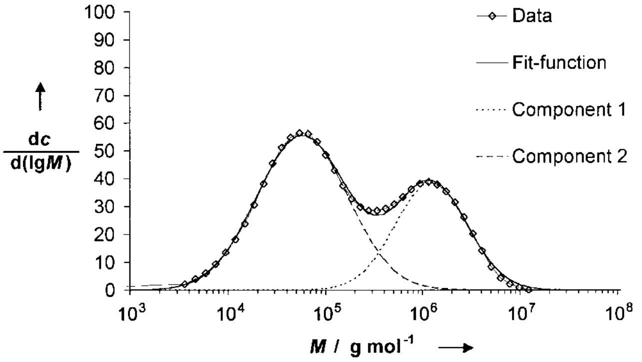

Figure 2. GPC curve of a polyethylene sample in comparison to a calculated molecular weight distribution consisting of two independent components; catalyst system: **4**/MAO, polymerization temperature: $T = 50\,^\circ$C.

Table 2. Experimentally obtained data and calculated molecular weight parameters M_w and M_w/M_n of polyethylene; catalyst system **4**/MAO, polymerization temperature $T = 50\,^\circ$C.

	M_w	M_w/M_n	Amount
data	824884	15.2	–
calculated-fit	817849	16.1	–
component 1	1850057	2.3	41 %
component 2	88049	2.9	59 %

Similar effects should be generally possible in other dialkylaminoethyl-functionalized and sterically fixed catalyst systems.

Experimental Section

All manipulations were carried out under purified argon atmosphere using standard Schlenk techniques. The solvents were commercially available, purified by conventional methods, and distilled immediately prior to use.

3: *n*BuLi (4.5 mL, 7.0 mmol) was added dropwise at 0 °C to a solution of **1**[11] (1.08 g, 3.4 mmol) in diethyl ether (10 mL). A white suspension of the dilithium salt **2** was formed immediately. The mixture was stirred for 18 h at room temperature. Subsequently, compound **2** was filtered off, dried in vacuo (1.00 g, 3.0 mmol; 89 %), and then suspended again in diethyl ether (10 mL). ZrCl$_4$ (0.70 g, 3.0 mmol) was added slowly at $-60\,^\circ$C. The yellow suspension was allowed to warm to room temperature and stirred for a further 18 h. The solvent was removed in vacuo and the residue was extracted with toluene (20 mL). After filtration the solvent was again removed in vacuo. The remaining yellow oil solidified by addition of pentane (10 mL). The orange solid was recrystallized from dimethoxyethane/acetonitrile (10:1). Compound **3** was obtained as a beige, air- and moisture-sensitive solid (0.61 g, 1.3 mmol, 43 %); M. p. 124 °C; ^{1}H NMR (500.1 MHz, C$_6$D$_6$, 25 °C): $\delta = 0.14$ (s, 3 H; SiCH$_3$), 0.15 (s, 3 H; SiCH$_3$), 0.91 (d, ^3J(H,H) = 6.3 Hz, 6 H; CHCH_3), 0.92 (d, ^3J(H,H) = 6.3 Hz, 6 H; CHCH_3), 2.64–2.68, 2.89–2.96 (2 × m, 6 H; CHCH$_3$, CH_2CH_2), 5.37 (pt, $^{3,4}J$(H,H) = 2.5 Hz, 1 H; C$_5H_3$), 5.44 (m, 1 H; C$_5H_4$), 5.57 (m, 1 H; C$_5H_4$), 5.59 (pt, $^{3,4}J$(H,H) = 2.5 Hz, 1 H; C$_5H_3$), 6.70 (pt, $^{3,4}J$(H,H) = 2.5 Hz, 1 H; C$_5H_3$), 6.78 (m, 1 H; C$_5H_4$), 6.85 (m, 1 H; C$_5H_4$); ^{13}C{^{1}H} NMR (125.8 MHz, C$_6$D$_6$, 25 °C): $\delta = -5.7$ (SiCH$_3$), 20.9, 21.0 (NCHCH$_3$), 32.3 (NCH$_2$$CH_2$), 45.5 (N$CH_2CH_2$), 48.1 (N$C$H), 107.2, 107.5, 113.6, 113.8, 114.4, 114.8, 127.3, 128.3, 128.5, 141.9 (CpC). ^{29}Si{^{1}H} NMR (99.4 MHz, C$_6$D$_6$, 25 °C): $\delta = -13.8$; MS (CI): *m*/*z* (%): 476 (13) [M^+], 114 (100) [i(C$_3$H$_7$)$_2$NCH$_2^+$]; elemental analysis (%): C$_{20}$H$_{31}$Cl$_2$NSiZr (475.68): calcd: C 50.51, H 6.57, N 2.94; found: C: 50.21, H: 6.96, N: 2.76.

General procedure for the polymerization of ethylene: A 1 L-Büchi autoclave, equipped with mass-flow and pressure-controller was filled under argon with toluene (194 mL) and MAO solution (3 mL; 4.9 % aluminum, $\rho \approx 0.9$ g mL^{-1}, 1 mmol Al = 0.6 mL). The interior was pressurized with ethylene (5 bar) and thermostated to the desired temperature. The ethylene pressure was kept constant during the polymerization process. Compound **3** (4.8 mg, 1×10^{-5} mol) was preactivated for 10 min with MAO solution (3 mL) and injected into the autoclave. The polymerization process was terminated after 1 h by injecting 2-propanol (20 mL). The suspension containing the polymer was poured into methanol/HCl (200 mL; 5:1) and stirred for 18 h. After filtration the polymer was dried in the air.

Determination of the molecular weight distribution: The polyethylenes were analyzed by high-temperature gel permeation chromatography using a Waters 150 C apparatus with an IR detector at $\lambda = 3.5$ µm; the solvent was 1,2,4-trichlorobenzene at 135 °C. Calibration was performed by using narrow and broad distributed linear polyethylene standards.

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[3] Exceptions have been observed, if, for example, more than one catalytically active species is present because of conformational changes. This results in the formation of polyolefins with different molecular weights. Thus, a superposition of narrow distributions

generally leads to the generation of a broad molecular weight distribution with one or more "shoulders". See also: a) R. Leino, H. J. G. Luttikhedde, P. Lehmus, C.-E. Wilén, R. Sjöholm, A. Lehtonen, J. V. Seppälä, J. H. Näsman, *J. Organomet. Chem.* **1998**, *559*, 65–72; b) D. W. Stephan, J. C. Stewart, F. Guérin, R. E. v. H. Spence, W. Xu, D. G. Harrison, *Organometallics* **1998**, *18*, 1116–1118; c) G. H. Llinas, R. O. Day, M. D. Rausch, J. C. W. Chien, *Organometallics* **1993**, *12*, 1283–1288, and references therein; d) A. Yano, S. Hasegawa, T. Kaneko, M. Sone, M. Sato, *Macromol. Chem. Phys.* **1999**, *200*, 1542–1553; C. Janiak, K. C. H. Lange, U. Versteeg, D. Lentz, P. H. M. Budzelaar, *Chem. Ber.* **1996**, *129*, 1517–1529.

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[7] The intramolecularly donor-stabilized complex $[\{\eta^5\text{-}C_5H_3(CH_2CH_2NMe_2)CMe_2\text{-}\eta^5\text{-}C_{13}H_8\}ZrCH_3]^+B(C_6F_5)_4^-$ was isolated and is not active in the polymerization catalysis. However, after addition of AlR_3, a catalytically active species was obtained.

[8] a) P. Jutzi, T. Redeker, B. Neumann, H.-G. Stammler, *Organometallics* **1996**, *15*, 4153–4161; b) P. Jutzi, T. Redeker, B. Neumann, H.-G. Stammler, *Chem. Ber.* **1996**, *129*, 1509–1515.

[9] Polymerization of ethylene with **4**/MAO: see Experimental Section; Zr:Al = 1:1000, $n(\mathrm{Zr}) = 3\times10^{-5}$ mol. Polymerization temperature: $T = 50\,^{\circ}\mathrm{C}$, activity: 59 $\mathrm{kg_{PE}\,(mol_{Zr}\,h\,bar)^{-1}}$.

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Real Space Observation of a Chiral Phase Transition in a Two-Dimensional Organic Layer[**]

Matthias Böhringer,[*] Wolf-Dieter Schneider, and Richard Berndt

Chiral discrimination between mirror-image stereoisomers can lead to the spontaneous separation of a racemic mixture into enantiomerically pure phases.[1] In three-dimensional systems the formation of these conglomerates is the exception rather than the rule; most racemic mixtures crystallize as racemates with the unit cell composed of an equal number of molecules with opposite chirality or as random solid solutions. It was originally proposed by Stewart and Arnett that confinement to two dimensions (2D) enhances chiral discrimination between enantiomers.[2] Most racemic 2D systems investigated experimentally so far, with respect to spontaneous breaking of the mirror symmetry, are Langmuir films of amphiphilic molecules with one or more asymmetric carbon atoms.[2–7] Atomic force microscopy (AFM) observations by Eckhardt et al. of enantiomorphic supramolecular structures evolving from a racemic mixture of a chiral amphiphile have been interpreted in terms of chiral segregation.[4] However, chiral packing of achiral molecules has also been observed to cause enantiomorphous structures.[8–12] Therefore, the observation of chiral supramolecular structures alone does not prove chiral phase separation.

A straightforward proof for chiral segregation is the direct determination of the chirality of individual molecules. Scanning-tunneling microscopy (STM) has been successfully applied to determine the conformation and chirality of individual molecules.[13, 14] Lopinski et al. used STM to determine the absolute configuration of isolated chiral centers.[14] The same technique was employed by de Feyter et al. to identify the positions of asymmetric carbon atoms within homochiral domains of a chiral terephthalic acid derivative.[15] In the present paper, we report the first real space observation of a coverage-driven chiral phase transition from a conglomerate to a racemate at low and high molecular coverages, respectively. The chirality of individual molecules is determined from high resolution STM images which closely reflect the asymmetric electronic structure of the molecules. From the STM data, models are deduced for the distinct chiral and achiral phases, revealing the driving force for chiral symmetry breaking.

The substrate used is reconstructed Au(111) which is comprised of uniaxial domains of alternating face centred cubic (fcc) and hexagonal close packed (hcp) stacking of the surface atoms (Figure 1 a). The domain walls form a herringbone pattern visible as bright stripes in the STM topographs.

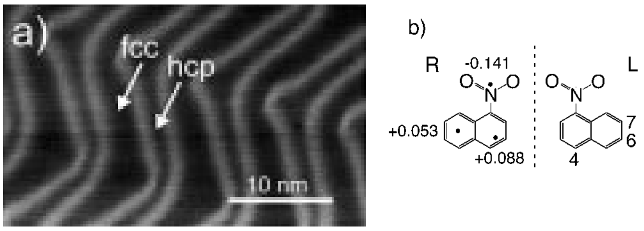

Figure 1. a) STM topograph of the reconstructed Au(111) surface. Broad and narrow dark stripes correspond to domains with surface atoms in fcc or hcp positions, respectively. The transition regions (domain walls) separating fcc and hcp regions appear as bright stripes. b) 1-Nitronaphthalene (NN) in a planar adsorption geometry on Au(111) is 2D chiral. Molecules with the nitro group attached to the left/right carbon ring are denoted as L/R-enantiomers. The nitro group has a net negative charge; the two carbon rings are positively charged.[17] The centres of mass of the respective charges are marked with dots.

1-Nitronaphthalene (NN, Figure 1 b) adsorbs with the naphthalene system parallel to the Au(111) surface.[16] This geometry imposes a chirality onto the NN molecules which is not present in the gas phase. An adsorbed molecule and its mirror image can not be superimposed by rotation and translation within the surface plane (Figure 1 b). On the

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[*] Dr. M. Böhringer,[+] Prof. Dr. W.-D. Schneider
Institut de Physique de la Matière Condensée
Université de Lausanne
1015 Lausanne (Switzerland)
E-mail: Matthias.Boehringer@de.bosch.com

Prof. Dr. R. Berndt
Christian-Albrechts-Universität Kiel
Institute for Experimental and Applied Physics

[+] New address:
Robert Bosch GmbH, RtW1/FIW4
Postfach 1342, 72703 Reutlingen (Germany)
Fax: (+49) 7121-35-1593

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