

# Methylalumoxane (MAO)-Derived MeMAO<sup>−</sup> Anions in Zirconocene-Based Polymerization Catalyst Systems – A UV-Vis Spectroscopic Study

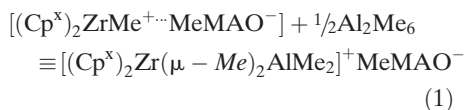
Ulrich Wieser, Frank Schaper, Hans-Herbert Brintzinger\*

**Summary:** Reaction of Me<sub>2</sub>Si(Ind)<sub>2</sub>ZrCl<sub>2</sub> with excess methylalumoxane (MAO) gives rise to ion pairs containing zirconocenium cations of the type [Me<sub>2</sub>Si(Ind)<sub>2</sub>ZrMe]<sup>+</sup> in contact with two types of anions, MeMAO<sub>A</sub><sup>−</sup> and MeMAO<sub>B</sub><sup>−</sup>, which differ in their coordinative strengths: More strongly coherent contact-ion pairs [Me<sub>2</sub>Si(Ind)<sub>2</sub>ZrMe<sup>+</sup>⋯MeMAO<sub>B</sub><sup>−</sup>] are converted by a sufficiently high excess of MAO to more easily separable contact-ion pairs [Me<sub>2</sub>Si(Ind)<sub>2</sub>ZrMe<sup>+</sup>⋯MeMAO<sub>A</sub><sup>−</sup>], which react with AlMe<sub>3</sub> to form the outer-sphere ion pairs [Me<sub>2</sub>Si(Ind)<sub>2</sub>Zr(μ-Me)<sub>2</sub>AlMe<sub>2</sub>]<sup>+</sup> MeMAO<sub>A</sub><sup>−</sup>, and are likely to be required also for the formation of the olefin-containing reaction complexes responsible for catalytic activity.

**Keywords:** metallocene catalysts; methylalumoxane; polymerization catalysis; reaction intermediates; UV-vis spectroscopy

## Introduction

Highly active polymerization catalysts are formed by activation of zirconocene precatalysts of the type (Cp<sup>x</sup>)<sub>2</sub>ZrCl<sub>2</sub> (Cp<sup>x</sup> = substituted, annelated and/or bridged cyclopentadienyl ligands) with methylalumoxane (MAO) at sufficiently high [Al]<sub>MAO</sub>/[Zr] ratios.<sup>[1]</sup> NMR and UV/Vis studies have shown that ion pairs of (Cp<sup>x</sup>)<sub>2</sub>ZrMe<sup>+</sup> cations in direct contact with MAO-derived MeMAO<sup>−</sup> anions, [(Cp<sup>x</sup>)<sub>2</sub>ZrMe<sup>+</sup>⋯MeMAO<sup>−</sup>], and heterobimetallic cations [(Cp<sup>x</sup>)<sub>2</sub>Zr(μ-Me)<sub>2</sub>AlMe<sub>2</sub>]<sup>+</sup>, now in outer-sphere association with MeMAO<sup>−</sup> anions, are present in these systems in Al<sub>2</sub>Me<sub>6</sub>-dependent equilibria (eq. 1).<sup>[2–9]</sup>



That these reaction systems might involve several distinct MeMAO<sup>−</sup> species has

been deduced from effects of changing c(Al<sub>MAO</sub>)/c(Zr) ratios on <sup>1</sup>H-NMR shifts of the zirconocene cation in [(Cp<sup>x</sup>)<sub>2</sub>ZrMe<sup>+</sup>⋯MeMAO<sup>−</sup>] ion pairs.<sup>[4,5]</sup> In order to characterize the roles of different types of MeMAO<sup>−</sup> anions in zirconocene-based catalyst systems, we have undertaken a UV-vis spectroscopic study on equilibrium reactions according to eq. 1.

## Results and Discussion

As a typical *ansa*-zirconocene precatalyst, dimethylsilylbis(indenyl)zirconium dichloride, Me<sub>2</sub>Si(Ind)<sub>2</sub>ZrCl<sub>2</sub>,<sup>[10]</sup> was chosen for this study. When a 6.0·10<sup>−4</sup> M toluene solution of this complex is treated with solid MAO, from which most of its free trimethylaluminum (TMA) content had been removed by heating *in vacuo*,<sup>[11]</sup> one observes, instead of the absorption band of the initial dichloride complex at 447 nm, a new band at 458 nm. This bathochromic shift can be assigned, as previously established,<sup>[7–9]</sup> to the formation of a contact-ion pair [Me<sub>2</sub>Si(Ind)<sub>2</sub>ZrMe<sup>+</sup>⋯MeMAO<sup>−</sup>]. A ratio of at least c(Al<sub>MAO</sub>)/c(Zr) = 120 is

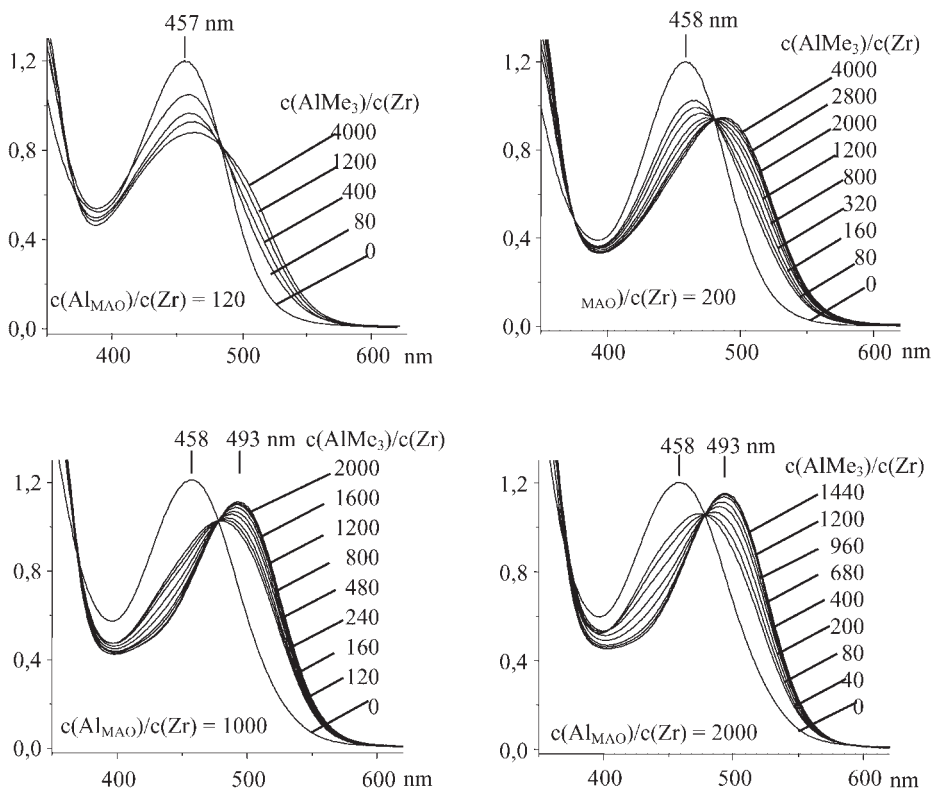
Fachbereich Chemie, Universität Konstanz, D-78457 Konstanz, Germany

required to induce complete transformations of the dichloride  $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2$ , via an intermediate  $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrClMe}$ , to the ion pair  $[\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrMe}^{+\cdots} \text{MeMAO}^-]$ ; only minimal changes of the absorption band of this contact-ion pair are produced by further additions of TMA-free solid MAO, up to a ratio of  $c(\text{Al}_{\text{MAO}})/c(\text{Zr}) = 2000$  (Figure 1).

These solutions were then treated with  $\text{Al}_2\text{Me}_6$  to induce the formation of the heterodinuclear cation  $[\text{Me}_2\text{Si}(\text{Ind})_2\text{Zr}(\mu\text{-Me})_2\text{AlMe}_2]^+$ . When a solution of the contact-ion pair  $[\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrMe}^{+\cdots} \text{MeMAO}^-]$ , obtained at a ratio of  $c(\text{Al}_{\text{MAO}})/c(\text{Zr}) = 2000$ , is treated with increasing proportions of TMA, the absorption at 458 nm is replaced by a new band at

493 nm (Figure 1, bottom right), in accord with the second bathochromic shift expected for the formation of the cationic TMA adduct  $[\text{Me}_2\text{Si}(\text{Ind})_2\text{Zr}(\mu\text{-Me})_2\text{AlMe}_2]^+$ .<sup>[4,9]</sup> The formation of the band at 493 nm is essentially complete at a  $c(\text{AlMe}_3)/c(\text{Zr})$  ratio of about one thousand. Very similar spectral changes occur when an increasing excess of TMA is added to a solution of the contact-ion pair  $[\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrMe}^{+\cdots} \text{MeMAO}^-]$  obtained at a ratio of  $c(\text{Al}_{\text{MAO}})/c(\text{Zr}) = 1000$ .

When a solution of the contact-ion pair obtained at a ratio of only  $c(\text{Al}_{\text{MAO}})/c(\text{Zr}) = 200$ , however, is treated with TMA, one observes, instead of the expected absorption band at 493 nm, only a limited absorption increase in this spectral region.



**Figure 1.**

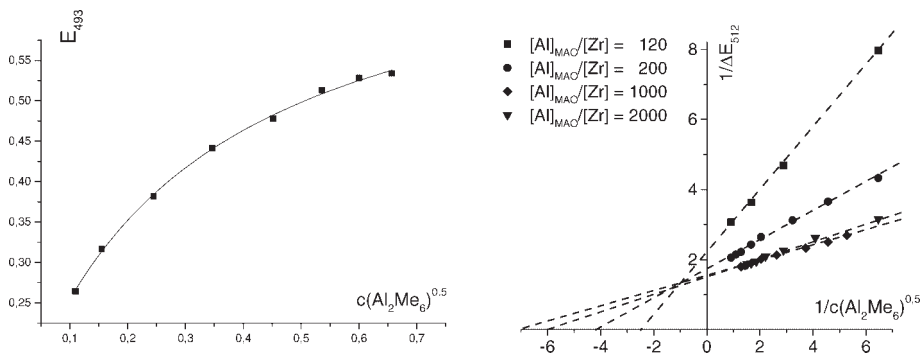
UV/Vis spectra of  $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2$  ( $6 \times 10^{-4}$  M in toluene solution) in the presence of TMA-free MAO (top left: 0.072 M, top right: 0.12 M, bottom left: 0.6 M, bottom right: 1.2 M) before and after addition of  $\text{Al}_2\text{Me}_6$  in  $c(\text{AlMe}_3)/c(\text{Zr})$  ratios as indicated.

At the minimal ratio of  $c(\text{Al}_{\text{MAO}})/c(\text{Zr}) = 120$  finally, which is required to produce the contact-ion pair  $[\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrMe}^+\cdots\text{MeMAO}^-]$ , only an absorption shoulder on the long-wavelength side of the band at 458 nm is produced by excess TMA, even at a  $c(\text{AlMe}_3)/c(\text{Zr})$  ratio of 4000 (Figure 1, top left). In these cases, even a high TMA excess appears to induce only a partial formation of the heterodinuclear cation  $[\text{Me}_2\text{Si}(\text{Ind})_2\text{Zr}(\mu\text{-Me})_2\text{AlMe}_2]^+$  from the prevailing contact-ion pair  $[\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrMe}^+\cdots\text{MeMAO}^-]$ .

Plots of the absorption values at 493 nm as a function of  $c(\text{AlMe}_3)$ , i. e. as a function of the square root of  $c(\text{Al}_2\text{Me}_6)$ , for solutions containing  $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2$  and MAO at  $c(\text{Al}_{\text{MAO}})/c(\text{Zr}) = 2000$  show the saturation behavior expected for an equilibrium according to eq. 1 (Figure 2, left). A more quantitative analysis by means of Hildebrand-Benesi plots, <sup>[12]</sup> i. e. of reciprocal absorption changes at 512 nm (where all difference spectra have their maxima) against the reciprocal of  $c(\text{Al}_2\text{Me}_6)^{0.5}$ , yields a linear relation for each of the  $c(\text{Al}_{\text{MAO}})/c(\text{Zr})$  ratios studied (Figure 2, right) and, hence, apparent equilibrium constants  $K_{\text{obs}}$  (as the negative of the abscissa intercepts) and maximal absorption increases (as the reciprocal of the ordinate intercept) for each of these reaction systems.

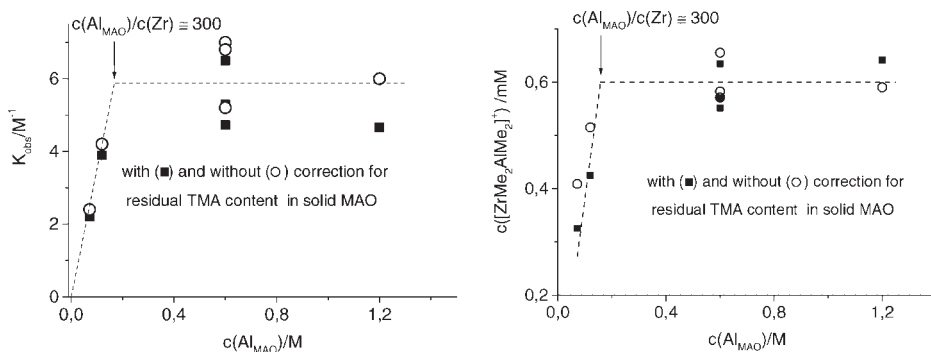
Plots of these data, i. e. either of  $K_{\text{obs}}$  or of the maximal attainable concentration of the TMA adduct (which is proportional to the maximal absorption increase at 512 nm), as a function of the MAO concentration  $c(\text{Al}_{\text{MAO}})$  increase at low  $c(\text{Al}_{\text{MAO}})$  and become rather constant at higher  $c(\text{Al}_{\text{MAO}})$  values (Figure 3). The capability of TMA to convert the initially formed contact-ion pairs to outer-sphere ion pairs containing the cationic TMA adduct,  $[\text{Me}_2\text{Si}(\text{Ind})_2\text{Zr}(\mu\text{-Me})_2\text{AlMe}_2]^+ \text{MeMAO}^-$ , thus exhibits a titration-type dependence on the concentration of MAO: A value of  $c(\text{Al}_{\text{MAO}}) \approx 0.18$  M is required to allow all of the inner ion pairs  $[\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrMe}^+\cdots\text{MeMAO}^-]$  present to be completely converted to  $[\text{Me}_2\text{Si}(\text{Ind})_2\text{Zr}(\mu\text{-Me})_2\text{AlMe}_2]^+ \text{MeMAO}^-$  by excess TMA in an equilibrium reaction according to eq. 1.

The value of  $c(\text{Al}_{\text{MAO}}) \approx 0.18$  required for complete displacement of  $\text{MeMAO}^-$  by excess TMA corresponds, at the zirconocene concentration of  $6.0 \cdot 10^{-4}$  M used throughout this study, to a ratio of  $c(\text{Al}_{\text{MAO}})/c(\text{Zr}) \approx 300$ . This is substantially higher than the ratio of  $c(\text{Al}_{\text{MAO}})/c(\text{Zr}) = 120$  required to convert all initially present zirconocene species to ion pairs of the type  $[\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrMe}^+\cdots\text{MeMAO}^-]$ . To explain this discrepancy, we propose that at least two distinct types of MAO species, designated as  $\text{MAO}_A$



**Figure 2.**

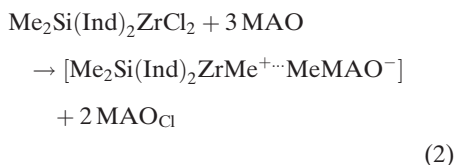
Absorption at 493 nm as a function of  $c(\text{Al}_2\text{Me}_6)^{0.5}$  in a solution of  $6 \cdot 10^{-4}$  mol/l  $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2$  and MAO with  $c(\text{Al}_{\text{MAO}})/c(\text{Zr}) = 2000$  (left), and analysis of the data from Figure 1 by Hildebrand-Benesi plots of  $1/\Delta E_{512}$  against  $1/c(\text{Al}_2\text{Me}_6)^{0.5}$  (right).

**Figure 3.**

Apparent equilibrium constants for displacement of  $\text{MeMAO}^-$  from contact-ion pairs  $[\text{Me}_2\text{Si}(\text{Ind})_2\text{-ZrMe}^{+\cdots}\text{MeMAO}^-]$  by TMA according to eq. 1 (left) and maximal concentrations of outer-sphere ion pairs  $[\text{Me}_2\text{Si}(\text{Ind})_2\text{Zr}(\mu\text{-Me})_2\text{AlMe}_2]^+ \text{MeMAO}^-$  (right) in dependence on the MAO concentration  $c(\text{Al}_{\text{MAO}})$ .

and  $\text{MAO}_\text{B}$ , participate in the following sequence of activation reactions:

Up to a ratio of  $c(\text{Al}_{\text{MAO}})/c(\text{Zr}) = 120$ , MAO is primarily consumed by conversion of  $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2$  to  $[\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrMe}^{+\cdots}\text{MeMAO}^-]$ , presumably under formation of two MAO-derived units in which a methyl group is replaced by Cl. This and the formation of a  $\text{MeMAO}^-$  anion could consume up to 3 MAO units for each zirconocene (eq. 2).



At this point, excess TMA can displace the anion from about half of the contact-ion pairs present; we designate this type of species as  $[\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrMe}^{+\cdots}\text{MeMAO}_\text{A}^-]$ . In an about equal portion of ion pairs, designated as  $[\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrMe}^{+\cdots}\text{MeMAO}_\text{B}^-]$ , the anion appears to be so strongly coordinated to the Zr center that it cannot be displaced even by the highest excess of TMA. The differing coordination strengths of the two anions  $\text{MeMAO}_\text{A}^-$  and  $\text{MeMAO}_\text{B}^-$  must be related to different Lewis acidities of the MAO species from which they are derived: More Lewis-acidic methylalumoxane clusters  $\text{MAO}_\text{A}$  appear to bind a methide unit so strongly that the

counter anion  $\text{MeMAO}_\text{A}^-$  has only minimal residual basicity, while  $\text{MeMAO}_\text{B}^-$ , derived from  $\text{MAO}_\text{B}$  units with lower Lewis acidity, retains finite basicity and remains thus strongly bound to its counter-cation.

When more MAO is added to these systems, the proportion of the cleavable ion pairs  $[\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrMe}^{+\cdots}\text{MeMAO}_\text{A}^-]$  increases at the expense of the more coherent pairs  $[\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrMe}^{+\cdots}\text{MeMAO}_\text{B}^-]$ . These “uncleavable” ion pairs have apparently totally disappeared when the MAO excess has reached a ratio of  $c(\text{Al}_{\text{MAO}})/c(\text{Zr}) \approx 300$ . At this “titration end point”, enough of the more Lewis-acidic  $\text{MAO}_\text{A}$  clusters appear to be present in the reaction system to displace the less acidic  $\text{MAO}_\text{B}$  according to eq. 3 completely:



Despite its dramatic effects on the ease of anion displacement by TMA, the anion exchange according to eq. 3 is hardly reflected in the spectral data shown in Figure 1: Very slight shifts of the absorption maxima from 457 nm to 458 nm and of the isosbestic points, which accompany the conversion of contact-ion pairs to TMA adducts, from 372 and 483 nm to 370 and 479 nm, indicate that the more

weakly bound ion pairs  $[\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrMe}^+\cdots\text{MeMAO}_A^-]$  absorb at marginally different wavelengths than their more strongly bound counterparts  $[\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrMe}^+\cdots\text{MeMAO}_B^-]$ . Similar observations with different counter-anions, such as  $\text{B}(\text{C}_6\text{F}_5)_4^-$  or  $\text{MeMAO}^-$ , have been reported already in previous studies.<sup>[13]</sup>

With regard to the nature of the more Lewis-acidic species  $\text{MAO}_A$ , which reaches the total zirconocene concentration at  $c(\text{Al}_{\text{MAO}})/c(\text{Zr}) \approx 300$ , previous Pulsed-Field-Gradient NMR studies have shown that weakly coordinated  $\text{MeMAO}^-$  anions associated with the TMA adduct  $[(\text{C}_5\text{H}_5)_2\text{Zr}(\mu\text{-Me})_2\text{AlMe}_2]^+$  each comprise about 150–200  $\text{Al}_{\text{MAO}}$  units.<sup>[5]</sup> Of the ca. 300  $\text{Al}_{\text{MAO}}$  units required for complete formation of the weakly bound contact ion pair, about half would thus make up its  $\text{MeMAO}_A^-$  anion, while the other half appears to make up mostly the  $\text{MAO}_B$  clusters. The mean molar mass of MAO, which is in the order of one thousand, would require that  $\text{MAO}_B$  molecules are more abundant and contain substantially fewer  $\text{Al}_{\text{MAO}}$  units than  $\text{MAO}_A$ . A mean composition of  $\text{MAO}_B$  such as  $\text{Al}_{16}\text{O}_{12}\text{Me}_{24}$ , as proposed by Sinn,<sup>[14]</sup> would be in reasonable accord with this assumption and would imply that  $\text{MAO}_B$  molecules are about ten times more abundant than those of  $\text{MAO}_A$ . Several of these  $\text{MAO}_B$  molecules might then be consumed by the pre-activation of  $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2$  to  $[\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrMe}^+\cdots\text{MeMAO}_B^-]$  according to eq. 2.

Only after conversion to their less strongly bound  $[\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrMe}^+\cdots\text{MeMAO}_A^-]$  congeners by the relatively rare species  $\text{MAO}_A$  can these zirconocenium ion pairs be cleaved by  $\text{AlMe}_3$  or, by implication, by an olefin substrate, which is presumably even less efficient in this regard than  $\text{AlMe}_3$ . The necessity to convert major parts of the zirconocene precatalyst to the  $\text{MeMAO}_A^-$ -containing ion pair as a prerequisite for the formation of a cationic olefin complex is the most likely cause for the rather high  $c(\text{Al}_{\text{MAO}})/c(\text{Zr})$  ratios required for full activation of these catalyst systems. From our data we cannot exclude, however, that

further, even rarer and more Lewis-acidic species  $\text{MAO}_{A+}$  are also present, which might explain further increases in the activity of zirconocene-based catalysts with increasing excess of MAO up to  $c(\text{Al}_{\text{MAO}})/c(\text{Zr})$  values of  $10^4$  and more.<sup>[15]</sup>

## Experimental Part

All glassware in contact with zirconocene complexes was dried by prolonged heating to 150 °C in a dynamic vacuum. Sample manipulations were conducted either in a nitrogen-filled glove box or in Schlenk vessels under argon protection. Dimethylsilylbis(indenyl)-zirconium dichloride,  $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2$ , was prepared according to ref. 10. A solution of MAO in toluene (mean molar mass ca. 800, total Al-concentration 1.8 M, 30% of which as  $\text{AlMe}_3$ ) was obtained as a gift from Crompton GmbH, Bergkamen. From this solution, TMA-free solid MAO was prepared by removal of solvent and subsequent heating to 50 °C in a dynamic vacuum for 16 h.<sup>[11]</sup> Toluene solutions containing  $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2$  and MAO in different  $c(\text{Al}_{\text{MAO}})/c(\text{Zr})$  ratios were prepared by dissolving the required amounts of solid MAO in 10 ml of a  $6.0 \cdot 10^{-4}$  M toluene solution of  $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2$ . UV-Vis spectra of these solutions were recorded in teflon-stoppered 10-mm quartz cuvettes using a Cary-50 UV-Vis spectrometer. To these solutions successive increments either of a 2.0 M solution of trimethyl aluminum (TMA) in toluene or of neat TMA, both obtained from Sigma-Aldrich Chemie GmbH, were added in a glove box under nitrogen. UV-Vis spectra obtained from these solutions were numerically corrected for the effects of dilution by the added volumes of TMA solution.

**Acknowledgements:** We thank Crompton GmbH for a gift of MAO and BASSELL GmbH for financial support.

[1] W. Kaminsky, *J. Polym. Sci., Part A: Polym. Chem.* **2004**, 42, 3911.

[2] M. Bochmann, J. Lancaster, *Angew. Chem. Int. Ed.* **1994**, 33, 1634.

- [3] I. Tritto, R. Donetti, M.C. Sacchi, P. Locatelli, G. Zannoni, *Macromolecules* **1997**, 30, 1247.
- [4] D.E. Babushkin, N.V. Semikolenova, V.A. Zakharov, E.P. Talsi, *Macromol. Chem. Phys.* **2000**, 201, 558.
- [5] D.E. Babushkin, H.H. Brintzinger, *J. Am. Chem. Soc.* **2002**, 124, 12869.
- [6] D. Coevoet, H. Cramail, A. Deffieux, *Macromol. Chem. Phys.* **1998**, 199, 1451.
- [7] D. Coevoet, H. Cramail, A. Deffieux, C. Mladenov, J.N. Pedetour, F. Peruch, *Polym. Int.* **1999**, 48, 257.
- [8] J.N. Pedetour, D. Coevoet, H. Cramail, A. Deffieux, *Macromol. Chem. Phys.* **1999**, 200, 1215.
- [9] U. Wieser, H.H. Brintzinger, in *Organometallic Catalysts and Olefin Polymerization*, E. Blom, A. Follestad, E. Rytter, M. Tilset, M. Ystenes eds., Springer Berlin, 2001, p. 3.
- [10] W.A. Herrmann, J. Rohrmann, E. Herdtweck, W. Spaleck, A. Winter, *Angew. Chem.* **1989**, 101, 1536.
- [11] G.L. Crossetti, C. Bormioli, A. Ripa, A. Giarrusso, L. Porri, *Macromol. Rapid Commun.* **1997**, 18, 801.
- [12] H.A. Benesi, J.H. Hildebrand, *J. Am. Chem. Soc.* **1949**, 71, 2703.
- [13] L. Schröder, H.H. Brintzinger, D.E. Babushkin, D. Fischer, R. Mülhaupt, *Organomet.* **2005**, 24, 867.
- [14] H.J. Sinn, *Macromol. Symp.* **1995**, 97, 27.
- [15] N. Herfert, G. Fink, *Makromol. Chem.* **1992**, 193, 1359.