Spectrophotometric study of zirconocene/polymethylalumoxane catalytic systems: principal component analysis and parametric modeling

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Transformation of electronic absorption spectra of zirconocene catalytic systems $Ph_2CCpFluZrCl_2$ —polymethylalumoxane (MAO) and *rac*-Me_2Si(2-Me,4-PhInd)_2ZrCl_2—MAO (Flu is fluorenyl, Ind is indenyl) in toluene was studied upon a change in the ratio of reactants Al_{MAO}/Zr from 0 to 3000 mol mol⁻¹. Analysis of the spectroscopic data using statistical methods determined the number of reaction products in each system. A reaction model including three equilibria and being common for the both systems was proposed. Effective equilibrium constants and absorption spectra of individual reaction products were determined by parametric self-modeling of the experimental spectra.

Key words: zirconocene, polymethylalumoxane, transformation of spectra, principal component analysis, parametric modeling.

Highly efficient homogeneous catalytic systems for olefin polymerization based on metallocene complexes of IVB Group elements are formed from a metallocene precursor complex and a cocatalyst (activator). Polymethylalumoxane (MAO) is most frequently used as the latter. MAO is a mixture of oligomeric compounds (Al(Me)O—)_n (n = 4-30), which are capable of forming three-dimensional structures. In addition, MAO contains a considerable amount (up to 30 mol.% Al) of free or partially bound trimethylaluminum.¹ The action of the cocatalyst produces single-type active species, which form uniform macromolecules during catalyzed polymerization and a polymeric product with narrow molecular-weight characteristics and high compositional and fractional uniformity.

Exact data on the qualitative and quantitative composition of the reaction products of the metallocene catalyst with MAO under the conditions close to catalysis are lacking. Several reaction products can be formed by the interaction of MAO with catalyst, and the efficiency of one or another route depends on the structure and concentration of the metallocene component, MAO/catalyst molar ratio, polarity of the solvent, and several other factors.

Cationic metal alkyl complexes, which are active sites of polymerization, are formed in a high excess of MAO $(1 \cdot 10^3 - 1 \cdot 10^4 \text{ mol mol}^{-1})$ (Scheme 1, reaction (3)). The formation of the cationic intermediates is preceded by the monoalkylation of metallocene dichloride²⁻⁴ (reaction (1)), which proceeds efficiently even at low molar ratios (Al_{MAO}/M \approx 10–50). However, the formation of dimethylated metallocene derivatives cannot be excluded.^{5,6} Neutral or polarized complexes (reaction (2)) are formed in an intermediate range of the Al_{MAO}/M molar ratios (to ~10²).^{7,8}

Scheme 1

L ₂ ZrCl ₂	MAO	L ₂ ZrMeCl	()	1)
-2-: 0-2		-2	(-,

 $L_2 Zr MeCl + MAO \implies L_2 Zr MeCl \cdot MAO$ (2)

$$L_2ZrMeCl \cdot MAO + MAO \implies L_2Zr^+Me...ClMAO^-$$
 (3)

The formation of binuclear coordinatively saturated complexes $L_2Zr^+Me(\mu-Me)AlMe_2]^+...CIMAO^-$, which involves $AlMe_3$ present in MAO, and $L_2ZrMe(\mu-Me)MeZrL_2]^+...MeMAO^-$, was confirmed by NMR spectroscopy.^{9,10} Except for the dimethylated derivative, all above-listed reaction products of the metallocene complex with MAO were detected only under NMR conditions when the metallocene concentrations are by two—three orders of magnitude higher than the concentrations of the catalyst used in polymerization. Thus, questions about the number and nature of catalytic intermediates and the influence of the Al_{MAO}/M molar ratio on the routes of their formation still needs a clear answer.

Spectrophotometry has recommended itself as an efficient tool for studying the formation of a homogeneous catalytic system by the interaction of a metallocene complex with MAO.^{2-4,11-14} The long-wavelength absorption band of metallocenes or catalytic metallocene—activator systems is related to an electron transition accom-

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panied by the charge transfer from the π -ligand to the transition metal (ligand-to-metal charge transfer, LMCT).^{15,16}

The high sensitivity of this electron transition to structural changes in metallocene^{4,14,17} and rather high molar absorption coefficients for the metallocene complexes provide a possibility for spectrophotometric observation of reactions of a precursor complex with an activator at the catalyst concentrations by one-two orders of magnitude lower than those in NMR spectroscopy, *i.e.*, close to catalytic concentrations. Earlier,¹⁴ for a series of structurally similar metallocenes of the IVB Group we have shown that the change in the LMCT energy (position of the absorption band maximum) under the action of different factors, such as solvation, the electronic effect of a π -system of bridging groups, the nature of a transition metal, and the formation of precursor complexes of the catalytic system and cationic complexes, is additive and can be used for analytical purposes when studying metallocene catalytic systems.

In the present work, we studied the effect of the cocatalyst/precatalyst molar ratio on the electronic absorption spectra of the catalytic systems $Ph_2CCpFluZrCl_2$ (1)—MAO (Flu is fluorenyl) and *rac*-Me₂Si(2-Me,4-PhInd)₂ZrCl₂ (2)—MAO (Ind is indenyl) in toluene. The observed transformations of the spectra were interpreted using a method of multi-dimensional statistics: principal component analysis. It was of interest to determine the number of reaction products in each system, elucidate the general and specific properties of the compared catalytic systems, and draw some conclusions about the nature of catalytic intermediates.



Toluene (special purity grade) was used. The solvent was distilled from LiAlH₄, degassed in a high-vacuum line, and kept over molecular sieves 4A in an argon atmosphere. Polymethylalumoxane (Witco) was used as a 10% solution in toluene. Zirconocenes 1 and 2 (Boulder Scientific Co.) were pre-purified by recrystallization. Compounds *rac*-Me₂Si(2-Me,4-PhInd)₂ZrMeCl and *rac*-Me₂Si(2-Me,4-PhInd)₂ZrMe₂ were synthesized according to a standard procedure.¹⁸ All works on the preparation of solutions of the metallocene complexes and reaction products with MAO and filling of cells were carried out in a flow of purified and dried argon. Absorption spectra of catalytic systems 1–MAO and 2–MAO in toluene were recorded on a Specord M-40 spectrophotometer. For each system, 11 spectra were measured at different molar ratios of the reactants (Al_{MAO}/Zr). The Al_{MAO}/Zr value was varied from 0 to 3000 mol mol⁻¹, and the zirconocene concentration was maintained at $8 \cdot 10^{-4}$ mol L⁻¹. The spectra were recorded in the interval from 25 000 to 15 000 cm⁻¹ (1–MAO) or from 26 000 to 16 000 cm⁻¹ (2–MAO) with an increment of 40 cm⁻¹. Each spectrum included 251 absorbance values.

The following procedure of statistical processing of spectra was used. A matrix of experimental spectra with a dimensionality of 11 columns per 251 rows was composed for each catalytic system. The spectra were normalized in such a way that the sum of all absorbances in the spectrum was equal to unity. Then the average spectrum was subtracted from each spectrum. After the data matrix was normalized and the average spectrum was subtracted, the matrix was subjected to singular decomposition over the QR algorithm, ¹⁹ *i.e.*, singular vectors and the corresponding singular values σ of this matrix were calculated. The program for performing this method is available.²⁰ Singular decomposition makes it possible to considerably decrease the dimensionally of the spectra representation. For example, in our case, each spectrum formally is a 251-dimensional vector-column or a point in the 251-dimensional space, whose coordinates are absorbances

of the solution. It is impossible to conceive and analyze the mutual arrangement of 11 points in the 251-dimensional space. The program used gives an image in which each spectrum is a point in the three-dimensional space, due to which the spatial arrangement of points, being the initial spectra, can easily be analyzed. The main specific feature and advantage of this program as compared to other commercial software is that the program repro-

	a_1
	a_2
	:
	a_k
k	= 25

duces just the three-dimensional pattern, which can be turned in the full-display regime, and precisely these turns provide the three-dimensional perception of the pattern analyzed.

The absorption spectra of the products were estimated from the proposed reaction model by the parametric self-modeling of the spectral matrix (PSSM).^{21,22}

Results and Discussion

Principal component analysis as applied to treatment of spectroscopic data. The procedure of principal component analysis^{23,24} provides a decrease in the dimensionality of a data array containing many mutually related variables. The dimensionality is reduced by plotting of spectra in the basis of the first three singular vectors of the data matrix. The singular vectors are numerated in the order of decreasing the corresponding singular values σ . Each experimental spectrum is presented in the basis of singular vectors as a linear combination

$$\begin{bmatrix} a_1 \\ a_2 \\ \vdots \\ a_k \end{bmatrix} = x_1 \begin{bmatrix} p^1_1 \\ p^1_2 \\ \vdots \\ p^1_k \end{bmatrix} + x_2 \begin{bmatrix} p^2_1 \\ p^2_2 \\ \vdots \\ p^2_k \end{bmatrix} + \dots + x_n \begin{bmatrix} p^n_1 \\ p^n_2 \\ \vdots \\ p^n_k \end{bmatrix}, \begin{bmatrix} p^j_1 \\ p^j_2 \\ \vdots \\ p^j_k \end{bmatrix} = \mathbf{p}^j, \quad (1)$$

where \mathbf{p}^{j} is the *j*th singular vector. Expression (1) describes the particular spectrum {A}. The coefficients

 $x_1, x_2, ..., x_n$ are the coordinates of the point that represents this spectrum in the singular basis. This representation, whose sum contains all singular vectors, reproduces quite exactly the experimental spectrum. Equation (1) expresses the transition from one system of coordinates to another. There are infinitely many such transformations but the singular decomposition gives the fastest decrease in the significance of summands in this sum. The σ_i singular values are a measure of this significance. Since in this sum the singular vectors are numerated in the order of decreasing their singular values, the last terms in this sum, which reflect only measurement errors, can be neglected and thus the dimensionality of representation can be decreased. In addition, the first coordinates x_1 , x_2 , and x_3 in the above-presented Eq. (1) reflect in the best way tendencies in changes in the spectra and allow one to display the three-dimensional image of spectra as points in the basis of singular vectors on a monitor. To illustrate this fact, let us consider several simple cases.

For instance, let one substance be gradually converted during the reaction to another substance, and we are successively recording the spectra of this system. It is assumed that the reactants in the system absorb in the detected wavelength range, and the spectra of these reactants differ. Then the recorded spectra are the sums of two spectra: the spectrum of the starting substance and the spectrum of the product. From the mathematical point of view this means that all spectra are linear combinations of the spectra of the starting and final substances. This also implies that all the spectra, although they are multi-dimensional (in our case, 251-dimensional), can be placed, in fact, in a one-dimensional subspace, and their changes can mathematically be described by only one variable. In our case, for the normalization used, all point-spectra would lie on the same straight line (Fig. 1, a). If the matrix of normalized spectra is subjected to singular decomposition, it turns out that only one singular vector is essential. Its singular value becomes higher, and other singular values would be lower by several orders of magnitude. The direction of this singular vector corresponds exactly to the difference between the outermost spectra (see Fig. 1). It is clear that all points will not fall onto the same line because of errors in spectra recording, and small deviations will result in the appearance of other singular vectors with small but nonzero singular values. As a result, the program gives a three-dimensional pattern displaying this straight line. The scatter of points representing the experimental spectra along this line (along the first singular vector) will be just that as it was in the multidimensional space, *i.e.*, the variability during a decrease in the dimensionality is completely reflected. It is an important fact that the spectra of neither starting nor intermediate substances are needed to be known to display this image. No additional information except for the array of spectra itself is required. If the points are numerated in



Fig. 1. Trajectories of the point-spectra in the basis of singular vectors: one substance is converted to another (*a*); at first one and then another substance is formed in the process (*b*); ξ_1 and ξ_2 are the singular vectors, Δ_i^i are the deviations of a point from the point of origin along the singular vectors (the superscript corresponds to the number of the singular vector, and the subscript corresponds to the number of the point-spectrum). The singular value σ^2 is equal to the sum $\Sigma \Delta_i^2$, where the summation is conducted over all points. The errors are strongly increased for clarity.

the order of recording the corresponding spectra, one can monitor the motion of these points in time, *i.e.*, to obtain a trajectory that describes a chemical process. In this case, the distance between the points is directly related to the depth of conversion in this system. In addition, the direction of motion of a point-spectrum is also significant.

For example, if another reaction forming the third product is included into the process, then from the moment of involving the second reaction the motion of the point-spectrum would deviate from the primary direction of motion, and the trajectory would transform into a curve lying on the plane (Fig. 1, b). Now the minimum dimensionality of the space in which this totality of the spectra can be placed without losses in information is equal to two. Correspondingly, if this whole array of the spectra is subjected to singular decomposition, it will turn out that the second singular value is also significant. In this case, the direction of the first singular vector would change to reflect the scatter of experimental spectra in its entirety. The singular value equals the sum of squared deviations of point-spectra from the center of gravity along the corresponding singular vector (see Fig. 1). The occurrence of three reactions in the system results in a situation when the whole set of points of the spectra lies already not on the plane but in the three-dimensional space. In this case, a change in the spectra can also be observed in the threedimensional space of the basic singular vectors as trajectories of motion of the point-spectra.

In the two-dimensional image, the coordinates of a point-spectrum (the x_1 and x_2 values in Eq. (1)) are the projections of the experimental vector-spectrum onto the

first and second singular vectors to form a plot named the score plot, because this representation is not an absolutely exact representation but is the first and second approximations (see Eq. (1)).

Thus, analyzing changes in the experimental data by their arrangement in the singular space, one can determine the number of products formed in the system and the sequence of their conversions. If at most three these substances are formed, then this analysis can be visualized as a 3-D pattern and further analyzed on the computer display. However, if more substances are formed during the process, then special algorithms should be used to determine their number (or the minimum dimensionality of the space).

In the present work, the RSD-F criterion²⁵ was used to check spectrophotometric data. This criterion is based on an assumption that the last and lowest singular values reflect only measurement errors, which are described by the Gaussian distribution. Note once more that the singular vectors are ordered in the sequence of decreasing the corresponding singular values. Analyzing an increase in a singular value with a decrease in its number, this criterion allows one to easily find the moment of its jumpwise increase caused by the appearance of an additional factor of spectral variability. This means that the correct representation of an experimental spectrum requires singular vectors beginning from the first number to the number at which the jumpwise increase in the criterion was observed.

Analysis of transformation of the absorption spectra for the 1-MAO and 2-MAO systems in toluene at the varied AI_{MAO}/Zr ratio. The transformation of the spectra for the 1-MAO system with a change in the Al_{MAO}/Zr molar ratio from 0 to 60 and from 120 to 3000 is shown in Figs 2, a and b, respectively. The zirconocene concentration in these experiments was maintained at $8 \cdot 10^{-4}$ mol L⁻¹. The spectra were numerated in the order of increasing the Al_{MAO}/Zr ratio. The same figures show the spectra of individual reaction products (designated by dashes), which were calculated by the PSSM method (see below). The scales of the calculated spectra were selected in such a way that they would not superimpose with the experimental spectra. The two-dimensional image of the experimental and calculated spectra in the basis of the two first singular vectors $(p_1 \text{ and } p_2)$ is shown in Fig. 2, c.

It is seen that the absorption spectra of the 1–MAO system are a superposition of broad absorption bands (see Fig. 2, *a* and *b*). As mentioned above, many products can be formed in the reactions under study. It is difficult to determine the number of these products by visual analysis. Therefore, first of all, let us consider the mutual arrangement of the point-spectra for the 1–MAO system in the basis of the two first singular vectors (see Fig. 2, *c*). It is seen that spectra 1-3 (Al_{MAO}/Zr = 0, 10, and 20 mol mol⁻¹) lie on the straight line 1-1'. Therefore, spectra 2 and 3 can be presented as a linear combination



Fig. 2. Absorption spectra (*A*) of the **1**—MAO system in toluene at different molar ratios AI_{MAO}/Zr : 0 (*I*), 10 (*2*), 20 (*3*), 40 (*4*), and 60 (*5*) (*a*); 120 (*6*), 240 (*7*), 500 (*8*), 1000 (*9*), 1650 (*10*), and 3000 (*11*) (*b*); two-dimensional image of the experimental and calculated spectra in the basis of the two first singular vectors p_1 and p_2 (*c*). Here and in Fig. 3, the spectra are normalized in such a manner that the sum of all absorbances in the spectrum would equal unity; curves 1'-3' are the absorption spectra of individual reaction products calculated by the PSSM (the scale is arbitrary).

of the spectrum of the starting metallocene (1) and the calculated spectrum of one of the reaction products (1'). This means that at the molar ratios $AI_{MAO}/Zr \le 20$ the system contains only one reaction product along with the starting metallocene. It will be shown below for the 2–MAO system that model spectrum 1' corresponds to the spectrum of the monomethylated metallocene derivative.

When the Al_{MAO}/Zr ratio increases further from 40 to 120 mol mol⁻¹ (points 4–6), the formation of one more substance is "involved" and, as shown by the analysis of the three-dimensional image, points 1-6, as well as points 1' and 2' corresponding to the calculated spectra of the individual products, lie on the same plane. Therefore, in the system presented by spectra 3-6 contains, in addition to intermediate 1', only one new product with spectrum 2' is available.

A subsequent increase in the Al_{MAO}/Zr molar ratio from 240 to 3000 "involves" one more reaction that gives the third product, whose spectrum corresponds to curve 3'calculated by the PSSM method. It should be mentioned that points 7–11 and points 1'-3' lie on the same plane, which crosses the plane formed by points 1-6 and points 1' and 2' along the line 1'-2'. This implies that the system presented by points 7-11 simultaneously contains only three reaction products of zirconocene dichloride with MAO, whose spectra correspond to the calculated spectra 1'-3'. Turning the pattern in the threedimensional space, we find that point 6 somewhat deviates down from line 1'-2'. In other words, the system at $Al_{MAO}/Zr = 120 \text{ mol mol}^{-1}$ (spectrum 6) simultaneously contains four substances (the starting metallocene and three products of the reaction with MAO) but the relative concentrations of the compounds with spectra 1 and 3'are low.

The RSD-F criterion showed that only three significant factors are present in the whole set of 11 experimental spectra, *i.e.*, the concentrations of only four substances change in the system. Using this objective criterion, one checks whether the remaining deviation can be explained by measurement errors or not. The singular decomposition of the data matrix gives the following singular values: 1.129, 0.529, 0.010, and 0.0008. The first of them (1.129) is the root mean of scatter squares of points 1-11 along the first singular vector (see Fig. 2, c, axis p_1), the second vector (0.529) is the scatter along the second singular vector (axis p_2), and the third value (0.010) is the data scatter along the p_3 axis, which reflects the degree of relative rotation of the planes. Finally, the last value (0.0008) indicates that the error of three-dimensional description of the given array of the spectra has a value comparable with the accuracy of spectrum recording. Thus, the RSD-F criterion demonstrates that the described array of spectra can be presented by a combination of only four spectra.

Figure 3 shows the transformation of spectra for the 2-MAO system with the AI_{MAO}/Zr ratios varied from 0 to 240 (see Fig. 3, *a*, spectra 1-7) and from 500 to 3000 (see Fig. 3, *b*, spectra 8-11) and the image of the spectra in the basis of singular vectors (see Fig. 3, *c*). The spectra of the individual reaction products calculated by the PSSM method are also given. It should be mentioned that the absorption bands of the starting dichloride and the reac-



Fig. 3. Absorption spectra (*A*) of the **2**—MAO system in toluene at different molar ratios AI_{MAO}/Zr : 0 (*I*), 10 (*2*), 20 (*3*), 40 (*4*), 60 (*5*), 120 (*6*), and 240 (*7*) (*a*); 500 (*8*), 1000 (*9*), 1650 (*10*), and 3000 (*11*) (*b*); two-dimensional image of the experimental and calculated spectra in the basis of the two first singular vectors p_1 and p_2 (*c*).

tion products for this system are shifted toward higher frequencies (lower wavelengths) compared to those in the **1**-MAO system. Nevertheless, the transformations of the spectra observed in these systems with a change in the Al_{MAO}/Zr ratio are general. It is seen that at low Al_{MAO}/Zr molar ratios (0-40) in the basis of singular vectors spectra 1-3 of the reaction products lie on line 1-1'. This



Fig. 4. Comparison of the experimental absorption spectra of rac-Me₂Si(2-Me,4-PhInd)₂ZrClMe (1) and rac-Me₂Si(2-Me,4-PhInd)₂ZrMe₂ (2) and calculated absorption spectra of the reaction products (1'-3') in toluene solutions.

implies that they are a linear combination of the spectra of the starting dichloride and the product with spectrum 1'. An increase in the Al_{MAO}/Zr ratio in a range of 40–500 mol mol⁻¹ gives the reaction products, whose spectra are described by a linear combination of spectra 1, 1', and 2'. The linear combination of spectra 1'-3'makes it possible to exactly represent spectra 8-11 of the products obtained in high excess MAO. It can be asserted that only three products are formed in the 2–MAO system depending on the Al_{MAO}/Zr ratio. At the same time, the formation of products 1' and 2' in this system requires a higher excess of MAO than that in the 1–MAO system.

To identify the reaction products of zirconocene 2 $(\lambda_{max} = 464 \text{ nm}, \epsilon = 5.7 \cdot 10^6 \text{ mL mol}^{-1} \text{ (toluene)})$ with MAO, we synthesized the monomethyl monochloride $(\lambda_{max} = 432 \text{ nm}, \epsilon = 5.4 \cdot 10^6 \text{ mL mol}^{-1} \text{ (toluene)})$ and dimethylated $(\lambda_{max} = 404 \text{ nm}, \epsilon = 6.1 \cdot 10^6 \text{ mL mol}^{-1} \text{ (toluene)})$ derivatives of complex 2 as reference compounds. The spectra of these compounds along with the calculated spectra of the reaction products are presented in Fig. 4.

For the 2–MAO system, spectrum 1 of the synthesized monoalkylated zirconocene derivative corresponds to the calculated spectrum I' (see Fig. 4): their maxima coincide at 23 240 cm⁻¹, *i.e.*, at low Al_{MAO}/Zr molar ratios the main reaction products of the dichloride complex with MAO is the monomethylated zirconocene derivative, which is intermediate in the formation of the reaction products with MAO at high Al_{MAO}/Zr molar ratios. We also can assert that the dialkylated form of zirconocene (spectrum 2) is not formed in this system at any Al_{MAO}/Zr molar ratios. According to the principal component analysis, the whole set of experimental spectra 1-11 (see Fig. 2) is rigidly described by a linear combination of only four spectra, namely, by the spectrum of the starting zirconocene dichloride (see Fig. 3, *a*, spectrum *I*) and three calculated spectra of the products (1'-3').

The λ_{max} values for different forms of zirconocenes in the 1-MAO and 2-MAO systems and a change in the LMCT energy (ΔE_{LMCT}) upon the conversion of zirconocene from one form to another (see Scheme 1, reactions (1)-(3) are presented in Table 1. The monoalkylation of zirconocene 1 increases the LMCT energy by 0.16 eV due the replacement of the electron-withdrawing Cl ligands by the electron-releasing Me ligands. Going from the monomethyl derivative of compound 1 (the product with spectrum 1') to the polarized complex (the product with spectrum 2') is accompanied by a decrease in the energy of the electron transition by 0.21 eV. The subsequent "cationization" of the catalyst (the formation of the product with spectrum 3') results in an additional decrease in the LMCT energy by 0.20 eV. Similar processes occur in the 2–MAO system, and the ΔE_{LMCT} values for all the three reactions in this system differ slightly from the corresponding values in the 1–MAO system. It should be noted that all the reactions discussed occur in the plane of the ZrXY fragment (X = Cl or Me; Y = Me) in which the lowest molecular orbitals of the complex are localized and determined mainly by the empty orbital of the $Zr(4d_{x^2-\nu^2})$ type, which is overlapped with the orbitals of the σ -bonded ligands and is a nonbonding with respect to the π -ligands of the complex.²⁶ Therefore, the energy parameters of similar processes that occur without a substantial influence of the π -bonded ligands give approximately the same contribution to a change in the

Table 1. The λ_{max} values for different forms of zirconocene in the 1-MAO and 2-MAO systems and the change in the LMCT energy (ΔE_{LMCT}) upon the conversion of zirconocene from one form to another (see Scheme 1, reactions (1)-(3))

Form of zircono-	1		2	
cene	$\lambda_{\text{max}}/\text{nm}$	$\Delta E_{\rm LMCT}/{\rm eV}$	λ_{max}/nm	$\Delta E_{\rm LMCT}/{\rm eV}$
$L_2ZrCl_2(1)$	498	_	463	_
L_2 ZrMeCl (1')	468	-0.16	431	-0.20
L_2 ZrMeCl • MAO (2')	508	0.21	479	0.29
$L_2^{-}Zr^+MeClMAO^-(3')$	554	0.20	525	0.22

LMCT energy for two zirconocenes with different structures.

Parametric self-modeling of the absorption spectra for the 1—MAO and 2—MAO systems. If the content of photoabsorbing components in a multicomponent system changes according to the system of equilibrium reactions, then the observed transformations of the absorption spectra can be simulated by the PSSM method.^{21,22} The modeling makes it possible to determine both the equilibrium constants and unknown spectra of individual components. The parametric modeling of spectra was conducted on the basis of the reaction model, which is almost completely identical to that presented in Scheme 1. However, it was assumed that all the reactions are reversible.

It is impossible to determine the true values of the equilibrium constants of reactions (1)–(3) $(K_1-K_3, \text{ re-}$ spectively) for the 1-MAO and 2-MAO systems, because MAO is not an individual compound and the concentrations of the active components in MAO involved in reactions (1)—(3) are unknown. However, let us assume that the concentration of the active MAO components is proportional to the MAO concentration and that the active MAO components are in high excess with respect to zirconocene at all values of the total MAO concentration. Then, operating with the normalized spectra, one can obtain the effective equilibrium constants and with the use of the latter compare the steps in the proposed model and reveal differences in the 1-MAO and 2-MAO systems. Taking into account these assumptions, the partial concentrations of four photoabsorbing components, viz., L₂ZrCl₂, L₂ZrMeCl, L₂ZrMeCl·MAO, and $L_2Zr^+Me...ClMAO^-$ (c_1-c_4 , respectively), should change according to the equations

$$\begin{cases} c_1 = (1 + K_1 C_M + K_1 K_2 C_M^2 + K_1 K_2 K_3 C_M^3)^{-1}, \\ c_2 = c_1 K_1 C_M, \\ c_3 = c_2 K_2 C_M, \\ c_4 = 1 - c_1 - c_2 - c_3, \end{cases}$$
(2)

where $C_{\rm M}$ is the total concentration of MAO.

The unknown parameters K_1-K_3 in the system of equations (2) can be considered as the effective equilibrium constants of reactions (1)–(3) (see Scheme 1). These parameters are a combination of the true equilibrium constant, the coefficient caused by uncertainty in the concept of "concentration of the active MAO component," and the coefficient related to the fact that the normalized spectra were modeled. Normalization was used to avoid the effect of random deviations (±10%) in the total concentration of zirconocene on the process of parametric modeling.

At low Al_{MAO}/Zr molar ratios, the spectra calculated by the PSSM method based on the system of equations (2) insufficiently well reproduced the corresponding experimental spectra for the both systems (1–MAO and 2–MAO). The character of deviations assumes that the induction concentration of MAO can exist for reaction (2), *i.e.*, the concentration below which the MAO component involved in reaction is deactivated for some reasons. The existence of such an induction concentration can be explained by the fact that the MAO component involved in reaction (2) is deactivated by some admixture until the concentration of this component would exceed the admixture concentration (one of the probable admixtures of the MAO \cdot Cl product formed in reaction (1)).

Good agreement between the experimental and theoretical spectra was obtained after the system of equations (2) was corrected as follows:

$$\begin{cases} c_1 = (1 + K_1 C_M + K_1 K_2 C_M C_{\text{corr}} + K_1 K_2 K_3 C_M C_{\text{corr}}^2)^{-1}, \\ c_2 = c_1 K_1 C_M, \\ c_3 = c_2 K_2 C_{\text{corr}}, \\ c_4 = 1 - c_1 - c_2 - c_3, \\ C_{\text{corr}} = C_M - C_{\text{ind}}, \end{cases}$$
(3)

where C_{ind} is the induction concentration of MAO.

The theoretical spectra were obtained for the values of effective equilibrium constants presented below.

System	K_1	<i>K</i> ₂	K_3
		$L mol^{-1}$	
1-MAO	120	70	1.4
2–MAO	190	4.8	1.7

For the both systems, the induction MAO concentration corresponds to the molar ratio $Al_{MAO}/Zr = 33$.

Differences between the two systems are especially pronounced when the effective equilibrium constants K_2 for reaction (2) are compared. For the 1-MAO system, the K_2 constant is by an order of magnitude higher than the corresponding constant for the 2–MAO system. This means that the conversion of the monoalkylated form of zirconocene 1 to an intermediate complex occurs at much lower values of Al_{MAO}/Zr as compared to zirconocene 2. The K_1 constants for the both systems are high. This indicates that the monoalkylation is efficient at low equilibrium concentrations of MAO. The K_3 constants for the both systems are similar in values and very low. Simple estimations based on the obtained K_3 constants show that the complete conversion (>99%) of zirconocene to the L₂Zr⁺Me...ClMAO⁻ product cannot virtually be achieved in both cases.

The analysis performed allows one to believe that the reactions of zirconocene dichloride 1 and 2 with MAO at a varied Al_{MAO}/Zr molar ratio afford only three reaction products. The whole sequence of the spectra observed at $Al_{MAO}/Zr \ge 40$ mol mol⁻¹ can be presented by a linear combination of only the initial spectrum of zirconocene dichloride and three calculated spectra of the reaction products. Zirconocene dichloride is monoalkylated under the action of MAO at low Al_{MAO}/Zr molar ratios. The further increase in the Al_{MAO}/Zr molar ratio induces the

successive formation of a complex of monomethylated zirconocene with MAO and a cationic complex. The estimation of the effective equilibrium constants shows that the equilibrium reaction of formation of the monomethylated derivative proceeds with approximately the same efficiency for complexes 1 and 2 under the action of MAO. In the case of complex 2, intermediate complexes with MAO are formed at much higher equilibrium concentrations of the latter. The low values of the equilibrium constants K_2 and K_3 explain, possibly, why MAO should be taken in a high (10^3-10^4) excess for the efficient activation of zirconocene 2 in the polymerization of olefins.^{27,28}

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References

- 1. E. Y. Chen and T. J. Marks, Chem. Rev., 2000, 100, 1391.
- 2. D. Coevoet, H. Cramail, and A. Deffieux, *Macromol. Chem. Phys.*, 1998, **199**, 1451.
- 3. N. I. Makela, H. R. Knuuttila, M. Linnolahti, T. A. Pakkanen, and M. A. Leskella, *Macromolecules*, 2002, **35**, 3395.
- 4. U. Wieser, F. Schaper, H.-H. Brintzinger, N. I. Makela, H. R. Knuuttila, and M. A. Leskella, *Organometallics*, 2002, **21**, 541.
- 5. W.-M. Tsai and J. C. W. Chien, J. Polym. Sci. A: Polym. Chem., 1994, 32, 149.
- 6. W. Kaminsky and M. Arndt, Adv. Polym. Sci., 1997, 127, 143.
- Tritto, R. Donetti, M. C. Sacchi, P. Locatelli, and G. Zannoni, *Macromolecules*, 1997, 30, 1247.
- I. Tritto, D. Zucchi, M. Destro, M. C. Sacchi, T. Dall'Occo, and M. Galimberti, J. Mol. Catal. A: Chem., 2000, 160, 107.
- D. E. Babushkin, N. V. Semikolenova, V. A. Zakharov, and E. P. Talsi, *Macromol. Chem. Phys.*, 2000, 201, 558.
- M. Bochmann and S. Lancaster, Angew. Chem., Int. Ed. Engl., 1994, 33, 1634.
- Ziegler Catalysts: Recent Scientific Innovations and Technological Improvements, Eds G. Fink, R. Mulhaupt, and H. H. Brintzinger, Springer-Verlag, Berlin, 1995.

- D. Coevoet, H. Cramail, A. Deffieux, C. Mladenov, J. N. Pedeutour, and F. Peruch, *Polym. Int.*, 1999, 48, 257.
- S. S. Lalayan, E. A. Fushman, V. E. L'vovskii, I. E. Nifant'ev, and A. D. Margolin, J. Polym. Sci. A: Polym. Chem., 2000, 42, 961.
- 14. O. N. Babkina, O. M. Chukanova, E. E. Faingol'd, and N. M. Bravaya, *Izv. Akad. Nauk, Ser. Khim.*, 2004, 749 [*Russ. Chem. Bull., Int. Ed.*, 2004, **53**, 785].
- 15. E. Giannetti, G. M. Nicoletti, and R. Mazzocchi, J. Polym. Sci. Polym. Chem. Ed., 1985, 23, 2117.
- 16. V. Cavillot and B. Champagne, Chem. Phys. Lett., 2002, 354, 449.
- 17. N. Makela, H. R. Knuuttila, M. Linnolahti, and T. A. Pakkanen, J. Chem. Soc., Dalton Trans., 2001, 91.
- E. Samuel and M. D. Rausch, J. Am. Chem. Soc., 1973, 95, 6263.
- 19. C. L. Lawson and R. J. Hanson, *Solving Least Squares Problems*, Prentice Hall, Englewood Cliffs, 1974, 340 pp.
- G. E. Forsythe, M. A. Malcolm, and C. B. Moler, *Computer Methods for Mathematical Computations*, Prentice Hall, Englewood Cliffs, 1977, 259 pp.
- 21. M. L. Gribaudo, F. J. Knorr, and J. L. McHale, *Spectrochim. Acta*, 1985, **41A**, 419.
- E. N. Ushakov, S. P. Gromov, O. A. Fedorova, Y. V. Pershina, M. V. Alfimov, F. Barigelletti, L. Flamigni, and V. Balzani, *J. Phys. Chem. A*, 1999, **103**, 11188.
- I. T. Jolliff, Principal Component Analysis, Springer-Verlag, Berlin, 1986.
- E. R. Malinowski, *Factor Analysis in Chemistry*, 2 ed., J. Wiley and Sons, New York, 1991.
- A. G. Ryabenko, A. A. Ryabenko, and P. V. Fursikov, *Zh. Anal. Khim.*, 2000, 55, 342 [*Russ. J. Anal. Chem.*, 2000, 55 (Engl. Transl.)].
- 26. R. Hoffman, J. Chem. Phys., 1963, 39, 1397.
- W. Spaleck, M. Antberg, J. Rohrmann, J. Witner, B. Bachmann, P. Kiprof, J. Behm, and W. Herrmann, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1347.
- L. Resconi, L. Cavallo, A. Fait, and F. Piemontesi, *Chem. Rev.*, 2000, **100**, 1253.

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