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Ab Initio Molecular Dynamics Simulations of Methylaluminoxane (MAO) Synthesis by Hydrolysis of Trimethylaluminum

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AB INITIO MOLECULAR DYNAMICS SIMULATIONS OF METHYLALUMINOXANE (MAO) SYNTHESIS BY HYDROLYSIS OF TRIMETHYLALUMINUM

A Dissertation
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The Department of Chemistry

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VITA
ABSTRACT

MAO is the co-catalyst in the metallocene catalytic systems, which are widely used in single site olefin polymerization due to their high stereoselectivity. To date, the precise structure of MAO, the particular compound or compounds catalytically active in MAO, have eluded researchers. MAO, a white amorphous powder, is not a good sample for a direct spectroscopic characterization, and its NMR spectra are broad and almost featureless. Many structural models have been proposed but none are generally accepted. In the first part of this work the MAO formation mechanism was addressed. Molecular dynamics simulations at MP2 configuration interaction theory level have been carried out for elemental steps in MAO formation by trimethylaluminum hydrolysis. Methane production, in agreement with experiment, and intermediate species that are consistent with the known structural features of MAO and similar to those isolated and structurally characterized for other aluminoxanes were observed. \((CH_3)_3Al-OH_2\) species, containing a stable \(Al-O\) single bond, and for whose presence there is
spectroscopic evidence, emerged as the building block molecule and a cage was formed. Activation barriers for these processes were estimated. After the cage, in agreement with the multi-component nature of MAO, several distinct reaction channels were identified. It was concluded that MAO formation is a step polymerization through a bi-functional monomer, \([\text{Al}(\text{CH}_3) - \text{O}]\) is the structural unit, and a kinetic model was proposed. The emerged structures are in agreement with the crystallographic evidence for aluminoxanes, they support the experimental data regarding MAO chemical composition and explain its role in the metallocene activation, which is a failure of the previously proposed models. In the second part of this work, catalytically active MAO components were identified. In the third part, the species that were generated from the proposed mechanism were validated as suitable models for the commercial MAO structure and function by comparison of their IR and NMR parameters with experiment.
1.1 General Introduction

MAO activates the metallocene catalysts in homogenous single site polymerization of olefins, diolefins, and styrene. Metallocenes are organometallic compounds in which a group four metal, $\text{Zr}$, $\text{Ti}$ or $\text{Hf}$, is inserted between two cyclopentadienyl, $C_p$, ring structure ligands to form a sterically hindered site activated by MAO co-catalyst.

Metallocene/MAO systems are of great interest for industry since they are not only the most highly active catalytic systems for the polymerization of $\alpha$-olefins but they are also known for their high stereoselectivity and narrow molecular weight distribution of the polymer they produce, giving polymer producers unprecedented control over the architecture of their products and the way they make them. In the early 80’s, for the first time, using homogenous $Cp_2\text{ZrCl}_2/\text{MAO}$ system, it was able to produce polyethylene with molecular
weights up to 1 million g/mol and a narrow molecular weight distribution of approximate two, and propylene to a perfectly atactic polymer [1].

Discovered accidentally, MAO is typically prepared by the carefully controlled reaction of trimethylaluminum (TMA) and water, which is the source of oxygen. The reaction is strongly exothermic and difficult to control.

Since the discovery of the high catalytic activity of metallocenes, experimental and theoretical studies have focused on understanding, modifying, improving and extending this catalyst family. MAO is the most active co-catalyst for metallocene catalysts; however it is also most difficult to characterize. Despite an intense research effort, the MAO structure, the mechanism by which the co-catalyst activates the metallocene and the polymerization mechanism at the active site are not fully understood.

1.2 Proposed MAO Structural Models

The structure and function of MAO in metallocene single-site catalysts has been the subject of a large number of studies as reflected in recent reviews[1,2]. MAO, a white amorphous powder which is soluble in toluene and other aromatic solvents and highly reactive with air does not lend itself to a direct spectroscopic characterization. In the last few years, the advantages of faster computers and parallel computing made possible theoretical studies of MAO. Many structural models have been proposed by different groups [2] but there is not a generally accepted one.

In Figure 1.1 a series of the proposed models is presented. $^{27}\text{Al}$ and $^{17}\text{O}$ NMR investigations [4] and crystallographic structures for other alkylaluminoxanes [5] (please refer to Figure 1.2) have led to general
Figure 1.1 Proposed Models for MAO structure. *

Figure 1.2 Synthesized t-butylaluminoxanes, \([(\text{t-Bu})\text{Al}(\mu_3-O)]_n\), \(n = 6, 8, 9, 12\). *

*Reprinted from [3] with the permission from American Chemical Society, as documented on Letters of Permission.
agreement that MAO is a multi-component material with three-dimensional cage-like cluster structures, composed of square, hexagonal and/or octahedral faces, in which four-coordinate aluminum centers are bridged by three-coordinate oxygen atoms. Three and five-coordinate Al sites [4,6], as well as bridging methyl groups [7] in MAO structure must also be considered.

1.3 MAO Molecular Weight

The most commonly reported average molecular weight for MAO is in the range of 700 to 1200 g/mol, but molecular weights at about 400 and 3000 g/mol have also been reported [1,8-11].

1.4 Chemical Composition of MAO

MAO composition is often characterized by the methyl to aluminum ratio. The most commonly reported \( \frac{CH_3}{Al} \) ratio is in range of 1.4 to 1.5 [1]; values higher than 1.5 and lower than 1.4 have also been reported, and most importantly, it is always higher than 1. However, the most commonly proposed models for MAO structure [2] fail to explain its chemical composition, and a distinction has been made between “classic” \( \frac{CH_3}{Al} \) ratio 1:1), “pure” or TMA-free MAO and “real” or TMA-containing MAO. Considering that MAO and TMA behave like independent compounds, no evidence was found for a chemical reaction between TMA and TMA-free MAO and little or no free TMA is found in MAO [12], the above classification in “classic”, “real” or “pure” MAO is meaningless.
1.5 MAO Co-catalytic Activity

Despite its successful use over the past twenty years, along with its structure, important aspects of the mechanism by which MAO activates the metallocene are still under debate. IR and UV investigations have shown that the metallocene and MAO rapidly form a complex. There is a general agreement that the primarily role of MAO is to methylate the metallocene generating, at high excess of MAO, a cationic species with a vacant coordination site, \([Cp_2MCH_3]^+\) where \(M\) can be \(Zr\), \(Ti\), or \(Hf\), responsible for the catalytic activity of metallocene/MAO system [1]. This requires Lewis acidic sites in MAO. Since the general description of aluminoxanes is that of coordinatively saturated cage compounds, in order to explain MAO Lewis acidity Barron et al. [13] developed the concept of latent Lewis acidity involving the ring strain inherent in the cage compounds. Latent Lewis acidity is a consequence of the ring strain present in cluster assuming that four–coordinate aluminum atoms and three–coordinate oxygen atoms prefer tetrahedral and trigonal planar geometries, respectively. MAO itself isn’t exactly a Lewis acid, instead, according to latent Lewis acidity concept MAO becomes a Lewis acid when its cage structure opens in the presence of metallocene and for a given bond type the relative magnitude of the Lewis acidity is related to the relative strain present in the cage. Another possibility to generate three coordinate Al sites in MAO is by breaking bridging methyl groups, it has been investigated by Ystenes et al. [7], concluding that the bridging methyl groups in MAO are essential for the activation of the
metallocene. Part of our computational effort in elucidating MAO structure is to search for evidence of different bridging methyl groups.

Besides the methylation another important function of MAO lies in its large, three-dimensional structure which diffuses the anionic charge that previously was held tightly by chlorine on the metallocene. However, not totally clarified is the function of MAO during the polymerization and its necessity in such a high excess (typically ratios $\text{Al}/\text{Zr}$ higher than 200 are required for catalytic activity in metallocene/MAO systems).

In the first part of this work, from quantum molecular dynamics simulations and electronic structure calculations, a formation mechanism of polymethylaluminoxane (PMAO) or what at its discovery was named methylaluminoxane (MAO) [1], with a $\text{CH}_3/\text{Al}$ ratio higher than 1 and in the range of the experimental values, is proposed. In the proposed mechanism, MAO formation has all the characteristics of a step polymerization through a bi-functional monomer $((\text{CH}_3)_3\text{Al} - \text{OH}_2)$, $[(\text{CH}_3)\text{Al} - \text{O}]$ is the structural unit, and a kinetic model is presented.

In agreement with its multi-component nature, in the second part of this work, several reaction channels in MAO formation have been identified, and to validate the resulting structures their calculated NMR and IR properties are compared with experiment in the third part.
CHAPTER 2

METHODOLOGY AND THEORY

2.1 Molecular Dynamics Simulations

Molecular Dynamics Simulation is a deterministic method, in which successive configurations of the system are generated by integrating Newton’s equation of motion:

\[ F_i = m_i \cdot a_i \]

This equation describes the motion of a particle of mass \( m_i \), \( F_i \) being the force on the particle. The acceleration at each step is calculated from negative gradient of the overall potential:

\[ F_i = -\nabla V_i \]

The result is a trajectory that specifies how the positions and velocities of the particles in the system vary with time. Under the influence of a continuous potential the motions of all particles are coupled together, the many-body problem that can not be solved analytically and the equations of motion are integrated using a finite difference method.
2.1.1 Finite Difference Methods. The Verlet Algorithm

The essential idea of using finite difference techniques to generate molecular dynamics trajectories is that the integration is broken down into many small stages, each separated in time by a fixed time \( \delta t \). The total force on each particle in the configuration at a time \( t \) is calculated as the vector sum of its interactions with other particles. This assumes the potential energy is pairwise additive. From the force the accelerations of the particles can be determined, which are then combined with the positions and velocities at a time \( t \) to calculate the positions and velocities at time \( t + \delta t \). The force is assumed to be constant during the time step. The forces on the particles in their new positions are then determined, leading to new positions and velocities at time \( t + 2\delta t \), and so on.

There are many algorithms for integrating the equation of motion using finite difference methods. All the algorithms assume that the positions and dynamical properties (velocities, accelerations) can be approximated as Taylor series expansions:

\[
\begin{align*}
\mathbf{r}(t + \delta t) &= \mathbf{r}(t) + \mathbf{v}(t) \delta t + \frac{1}{2} \mathbf{a}(t) \delta t^2 \quad (2.1.1) \\
\mathbf{v}(t + \delta t) &= \mathbf{v}(t) + \mathbf{a}(t) \delta t + \frac{1}{2} \mathbf{a}(t) \delta t^2 \quad (2.1.2)
\end{align*}
\]

\( \mathbf{v} \) is the velocity (the first derivative of the position with respect to time), \( \mathbf{a} \) is the acceleration (the second derivative of the position with respect to time), and so on. The Verlet Algorithm [Verlet 1967] [14] is perhaps the most widely used method for integrating the equations of motion in molecular dynamics simulations and we use this algorithm in our simulations. It uses the positions and
accelerations at time $t$, and the positions from the previous step, $r(t - \delta t)$ to calculate the new positions at $t + \delta t$, $r(t + \delta t)$.

The equation for advancing the positions is:

$$r(t + \delta t) = 2r(t) - r(t - \delta t) + a(t)\delta t^2 (2.1.3)$$

The velocities do not appear at all; they have been eliminated by addition of the equations obtained by Taylor expansion about $r(t)$:

$$r(t + \delta t) = r(t) + v(t)\delta t + \frac{1}{2}a(t)\delta t^2 (2.3) + \ldots (2.1.4)$$

$$r(t - \delta t) = r(t) - v(t)\delta t + \frac{1}{2}a(t)\delta t^2 (2.3) - \ldots (2.1.5)$$

The velocities are not need to compute the trajectories, but they are useful for estimating the kinetic energy and they may be obtained by:

$$v(t) = \frac{[r(t + \delta t) - r(t - \delta t)]}{2\delta t} (2.1.6)$$

What makes this algorithm widely used is the fact that its implementation is straightforward and the storage requirements are modest, comprising two sets of positions $r(t)$ and $r(t - \delta t)$. $r(t - \delta t)$ and $r(t + \delta t)$ play a symmetric role in (2.1.3) making the algorithm exactly reversible in time, and the method has been shown to have excellent energy conservation properties even with long time steps.

One of its drawbacks is that the positions $r(t + \delta t)$ are obtained by adding a small term ($a(t)\delta t^2$) to the difference of two much larger terms, $2r(t)$ and $r(t - \delta t)$. This may lead to a loss of precision. Several variations on the Verlet algorithm have been developed, the leap-frog algorithm, the velocity Verlet method or Beeman’s algorithm are some of them. We used “velocity Verlet” method which
stores positions and velocities all at the same time $t$. In the “velocity Verlet” algorithm [15]:

$$r(t + \delta t) = r(t) + \delta v(t) + \frac{1}{2} \delta^2 a(t) (2.1.7)$$

$$v(t + \delta t) = v(t) + \frac{1}{2} \delta [a(t) + a(t + \delta t)] (2.1.8)$$

The algorithm only requires the storage of $r$, $v$, and $a$. Firstly, the new positions at time $t + \delta t$ are calculated using Eq.(2.7), and the velocities at mid-step are computed using:

$$v(t + \frac{1}{2} \delta t) = v(t) + \frac{1}{2} \delta a(t) (2.1.9)$$

The forces and accelerations at time $t$ are then computed, and the velocity at time $t + \delta t$ is given by:

$$v(t + \delta t) = v(t + \frac{1}{2} \delta t) + \frac{1}{2} \delta a(t + \delta t) (2.1.10)$$

At this point, the kinetic energy at time $t + \delta t$ is available. The potential energy at this time will have been evaluated in the force loop.

### 2.1.2 Choosing the Time Step

There are no hard and fast rules for calculating the most appropriate time step to use in molecular dynamics simulations; too small and the trajectory will cover only a limited portion of the phase space; too large and instabilities may arise in the integration algorithm due to high energy overlaps between atoms. A time step $\delta t = 20 \text{fs} \ (1 \text{fs} = 10^{-15} \text{s})$ seems to be appropriate for our simulations.
2.1.3 Setting Up and Running the Molecular Dynamics Simulations

First it is necessary to establish an initial configuration of the system. Assigning the initial velocities to atoms can be done by randomly selecting them from a Maxwell-Boltzmann distribution at the temperature of interest.

\[ p(v_{ix}) = \left( \frac{m_i}{2\pi k_B T} \right)^{1/2} \exp \left[ -\frac{1}{2} \frac{m_i v_{ix}^2}{k_B T} \right] \] (2.1.11)

The Maxwell-Boltzmann equation provides the probability than an atom of mass \( m_i \) has a velocity \( v_{ix} \) in the direction \( x \) at a temperature \( T \). For our system the temperature was in the range \( T=300-600 \) K. Initially we set all the velocities to zero and then rescale them after 20-40 passes to simulate constant temperature. Rescaling the velocities is done to keep the kinetic energy constant, and since the average kinetic energy is given by \( \langle K_x \rangle = \frac{3}{2} N kT \), where \( N \) is the number of particles in the system and \( k \) is the Boltzmann constant, keeping the kinetic energy constant means keeping the temperature constant. If the rescaling is done on every step, it alters the system dynamics but if it is done at certain intervals it adds some periodic perturbation to the system, which is in general undesirable, but it is a widely used method to simulate constant temperature and gives the same results as the rigorous methods [16].

At each step the force on each atom must be calculated by differentiating the potential function:
\[ F_i = -\nabla V_i = -\nabla V(r_1, r_2, r_3, \ldots, r_N) \] (2.1.12), where \( N \) is the number of particles in the system.

Our simulations were carried at Moller-Plesset MP2 theory level potential for reliable \textit{ab initio} electronic structure calculations. Having the forces on each atom, accelerations can be calculated. Solving the equations of motion for all the particles in the system (\textit{velocity Verlet} algorithm) over the time step \( \delta t \) provides the positions and velocities for the next step in simulation.

\begin{align*}
  r_i(t_n) &\rightarrow r_i(t_{n+1}) \quad (2.1.13) \\
  v_i(t_n) &\rightarrow v_i(t_{n+1}) \quad (2.1.14) \\
  t_{n+1} &= t_n + \delta t \quad (2.1.15)
\end{align*}

At each step derived physical quantities are calculated and data are written to trajectory file. For a complete simulation the last three steps are repeated for \( \approx 10^3 \text{-} 10^6 \) successive times (MD steps).

\section*{2.2 The Hartree-Fock Method}

In this work, the molecular dynamics simulations were carried at Moller-Plesset MP2 \textit{ab initio} theory level with double zeta basis set LANL2DZ. “Electron-deficient” bridging aluminum compounds were expected; this type of compounds have posed a challenge to computational chemistry methods in the past and electron correlation effects were found to be very important for describing them [17]. Proposed in 1934 by Moller and Plesset [18], MP2 method is a perturbation treatment to estimate the electron correlation energy in which the unperturbed wave function is the Hartree-Fock function.
The Hartree-Fock (H-F) method is typically used to solve the time-independent Schrödinger equation (2.2.1) for a multi-electron atom or molecule described in the fixed-nuclei Born-Oppenheimer approximation by the electronic molecular Hamiltonian. Because of the complexity of the differential equations for any but smallest systems, the problem is usually impossible to solve analytically, so that the numerical technique of iteration is used. In computational chemistry, the H-F calculation scheme is a self-consistent field (SCF) iterative variational procedure to calculate the Slater determinant for which the expectation value of the electronic Hamiltonian is minimum.

In the Hartree-Fock approach the many electron problem is replaced by a one electron problem in which the electron-electron repulsion is treated in an average way, all the electrons being independent. H–F is a mean field theory in which each electron has its own wave-function or orbital.

\[
\hat{H}_0 \, \psi_0 \rangle = E_0 \, \psi_0 \rangle \tag{2.2.1}
\]

The electronic state of the system is approximated by the wave function \( \psi_0 \), a Slater determinant of one-electron spin orbitals, \( \chi(x) \), where \( x \) indicates the position and spin of the electron, which is an anti-symmetric (the electrons are indistinguishable), and by construction satisfies the Pauli exclusion principle (goes to zero if any two wave-functions or two electrons are the same).

\[
\psi_0(x_1, x_2, \ldots, x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(x_1) & \chi_2(x_1) & \cdots & \chi_N(x_1) \\ \chi_1(x_2) & \chi_2(x_2) & \cdots & \chi_N(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(x_N) & \chi_2(x_N) & \cdots & \chi_N(x_N) \end{vmatrix} \tag{2.2.2}
\]

The electronic Hamiltonian for a multi-electron molecule is given by:
\[ \hat{H}_0 = \sum_i -\frac{1}{2} \nabla_i^2 - \sum_i \sum_a \frac{Z_a}{|\vec{r}_i - \vec{d}_a|} + \frac{1}{2} \sum_i \sum_{j \neq i} \frac{1}{|\vec{r}_i - \vec{r}_j|} + \frac{1}{2} \sum_a \sum_{b \neq a} \frac{Z_a Z_b}{|\vec{d}_a - \vec{d}_b|} (2.2.3). \]

Where \( \vec{r}_i \) is the vector position of electron \( i \), \( Z_a \) is the charge of fixed nucleus \( a \), and \( \vec{d}_a \) is the vector position of nucleus \( a \). The first term in Hamiltonian is the sum of the kinetic energy operators for each electron in the system. The second term is the sum of the electron-nucleus Coulombic attractions. The third term is the sum of the electron-electron Coulombic repulsions and the final term is the sum of the nucleus-nucleus Coulombic repulsions, known as nuclear repulsion energy.

In the Hartree-Fock approximation the Hamiltonian considers each electron in the average field of all other electrons in the molecule and \( \hat{H}_0 \) is replace with an effective one-electron operator called the Fock operator, \( \hat{F} \), in which all of the terms of the exact Hamiltonian except the nuclear-nuclear repulsion term are expressed as the sum of the one-electron operators:

\[ \hat{H}_0 = \sum_{i=1}^{N} \hat{F}_i = \sum_{i=1}^{N} \left[ \left( \frac{1}{2} \Delta - \sum_{j=1}^{N} Z_j r_{i,j} \right) + \sum_{j=1}^{N} (2 \hat{J}_i - \hat{K}_i) \right] (2.2.4) \]

\( \hat{J}_i \) is the Coulomb operator, defining the electron-electron repulsion energy due to the \( l \)-th electron and \( \hat{K}_i \) is the exchange operator defining the electron exchange energy.

Finding the Hartree-Fock one-electron wave-function is now equivalent to solving the Schrödinger equation in which the newly constructed Fock operator is used as the Hamiltonian. Solving the equation yields a new set of approximate one-electron orbitals. This new set of orbitals is then used to construct a new
Fock operator beginning the cycle again. The procedure is stopped when the change in the total electronic energy is negligible between two iterations. In this was, so-called self-consistent one-electron orbitals are calculated.

2.3 The MP2 Method

Moller-Plesset perturbation theory is a method to add excitations to the Hartree-Fock wave-function and therefore to include the effect of electron correlation. Following Born interpretation of wave-function, if \( P(r_1, r_2) \) is the probability density for finding electrons 1 and 2 in regions of space around \( r_1 \) and \( r_2 \) respectively then:

\[
P(r_1, r_2) = P(r_1) * P(r_2)
\]

The probability density for a given electron is independent of the positions of all the other electrons, in other words electron 1 has no knowledge of the instantaneous position of 2, only of its average value.

In reality the motions of electrons are more intimately correlated. Because of direct Coulomb repulsion of the electrons, the instantaneous position of electron 2 forms the center of a region in space which 1 will avoid. Hence, one must find a way to introduce the instantaneous electron correlation into the wave function. Different electron correlation methods have been developed.

Density Functional Theory (DFT) introduces the electron correlation by using exchange and correlation energies via Kohn-Sham approach [19].

Configuration Interaction Methods (CI) [20] are electron correlation methods in which one or more occupied orbital within Hartree-Fock determinant is replaced with a virtual orbital and form the wave function as a combination of
H-F determinant and all possible substituted determinants. CIS adds single excitations, CID adds double excitations, CISD adds single and double excitations, and CIDT adds double and triple excitations.

Møller–Plesset Perturbation theory (MP2, MP3, MP4) is a electron correlation method, and it has become one of the most widely used post-HF methods for the treatment of electronic correlation effects partly because is cheap computationally compared with CID methods. MP2 method treats the correlation part of the Hamiltonian as a perturbation on the Hartree-Fock part, and truncates the perturbation expansion at order 2.

\[ \hat{H} = \hat{H}_0 + \lambda \hat{V} \] (2.3.2), where \( \lambda \) is an arbitrary parameter.

If the perturbation is sufficiently small, then the resulting wave-function and the energy can be expressed as power series of \( \lambda \):

\[ \psi = \psi^{(0)} + \lambda \psi^{(1)} + \lambda^2 \psi^{(2)} + \lambda^3 \psi^{(3)} + \ldots (2.3.3) \]

\[ E = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \lambda^3 E^{(3)} + \ldots (2.3.4) \]

\( \psi^{(1)} \) is the first order wave-function correction and so on;

\( E^{(0)} \) is the sum of the orbital energies of electrons;

\( E^{(1)} \) is the first order energy correction to the ground state energy;

\( E^{(2)} \) is the second order energy correction;

The perturbed wave-function (2.3.3) and energy (2.3.4) into the Schrödinger equation give:

\[ (H_0 - E^{(0)})\psi^{(0)} = 0 \] (2.3.5)

\[ (H_0 - E^{(0)})\psi^{(1)} = (E^{(1)} - V)\psi^{(1)} \] (2.3.6)
\[(H_0 - E^{(0)})\psi^{(2)} = (E^{(1)} - V)\psi^{(1)} + E^{(2)}\psi^{(0)} \tag{2.3.7}\]

\(E^{(0)} + E^{(1)} = E_{H-F}\) is the Hartree-Fock energy and \(E^{(2)}\) is the first perturbation to Hartree-Fock energy, and it is a negative entity lowering the Hartree-Fock energy, which is what electron correlation should do.

### 2.4 Density Functional Theory Method

Density functional theory (DFT) is a quantum mechanical method used to investigate the electronic structure of many-body systems, in particular molecules and the condensed phases. In the last decade the DFT has been a successful approach for the description of the ground state properties for a large variety of compounds from metals and semiconductors to complex materials such as proteins and carbon nanotubes.

The main objective of DFT is to describe an interacting many-body system via its electronic density, \(\rho(r)\), and the external potential, \(\nu(r)\), replacing the complicated many-electron wave-function from traditional methods in electronic structure theory [19].

DFT method relays on Hohenberg-Kohn (HK) theorems [21]. The first theorem demonstrates the existence of a one-to-one mapping between the ground state electron density and the ground state wave-function of a many-particle system. The total electronic energy can be written as:

\[E[\rho] = T[\rho] + V_{ne}[\rho] + V_{ee}[\rho] = \int \rho(r)\nu(r)dr + F_{HK}[\rho] \tag{2.4.1}\]

where \(T[\rho]\) denotes the kinetic energy, \(V_{ne}\) and \(V_{ee}\) are the potential energies due to the nuclei-electron and electron-electron interactions, respectively, and \(F_{HK}[\rho]\) is given by:
\[ F_{HK}[\rho] = T[\rho] + V_{xc}[\rho] \] (2.4.2)

\( F_{HK} \) is defined independently of the external potential \( \nu(r) \), making it an universal functional of \( \rho(r) \).

The second HK theorem proves that the ground state density minimizes the total electronic energy of the system, and the minimization is done by using the variational principle. However, the explicit form of \( F_{HK} \) is hard to achieve and approximate forms are needed. An indirect approach had been given within Kohn-Sham method [22].

In Kohn-Sham DFT method the intractable many-body problem of interacting electrons in a static external potential is reduced to a tractable problem of non-interacting electrons moving in an effective potential. The non-interacting reference system has exactly the same electron density as the real system. The exact wave-function of the non-interacting system is given by a Slater determinant constituted from Kohn-Sham spin-orbitals, \( \psi_i(r) \).

Solving the Kohn-Sham equations of the non-interacting system (2.4.3) yields the orbitals \( \psi_i \) that reproduce the density \( \rho(r) \) of the original many-body system:

\[
-\frac{\hbar^2}{2m} \nabla^2 + V_s(r) \psi_i(r) = \varepsilon_i \psi_i(r) \] (2.4.3)

\[ \rho(r) \equiv \rho_s(r) = \sum |\psi_i(r)|^2 \] (2.4.4)

The effective potential, \( V_s \), is given by:

\[ V_s = V + \int \frac{e^2 \rho_s(r')}{|r-r'|} dr' + V_{xc}[\rho_s(r)] \] (2.4.5)
where the second term is the Hartree-Fock electron-electron Coulomb repulsion and the last term is the exchange-correlation potential. The solution of Kohn-Sham equations (2.4.3) is an iterative process and is done self-consistently. The major problem of DFT is that the exact functionals for the exchange and correlation are not known. However, there are approximations which permit the calculation of certain physico-chemical entities quite accurately. The most commonly used is the local density approximation (LDA) [22,23], where the functional depends only on the density at the coordinate where the functional is evaluated. The local spin-density approximation (LSDA) is a generalization of the LDA to include electron spin. Another category is the non-local or gradient-corrected approximation which includes the electron-spin densities and the gradients of the electron-spin densities and it is so-called generalized gradient approximation (GGA)[24].

In search for accurate results with the DFT methods many functionals have been developed both in physics and chemistry. Perhaps the most popular functional in quantum chemistry is B3LYP [25]. This is a combination of the LYP (Lee-Yang-Parr) GGA functional [26] for correlation with Becke’s three-parameter hybrid functional B3 [25] for exchange. B3 exchange functional includes a fraction of Hartree-Fock exchange into the DFT exchange functional (other mixtures are also possible). Formally, this might be considered a drawback, but in practice B3 has been proven to be the most successful exchange functional for chemical applications, particularly when combined with LYP GGA functional for correlation energy [27], and this is the DFT method used in this work.
2.5 The Basis Sets

The set of one-electron wave functions used to build molecular orbital wave functions is called basis set. In this work, for molecular dynamics simulations the electronic configurations of the systems were described by LANL2DZ basis set, which is a double zeta extended basis set developed by Los Alamos National Laboratory. In double zeta basis set each atomic orbital is expressed as sum of two Slater type orbitals (STOs, and which is the minimal basis set meaning that it has only as many atomic orbitals as needed to accommodate the electrons of the neutral atoms and retain spherical symmetry), the zeta ($\zeta$) value accounts for how diffuse (large) the orbital is and the constant $D$ determines how much each STO counts towards the final orbital.

In all the other structure calculations the electronic configurations of the molecular systems were described by a large split-valence polarized basis set, 6-31G** or 6-31G(d,p), which is the most popular basis set because of its compromise between computational efficiency and reasonable results. In the split-valence basis sets the valence atomic orbitals are split in two parts: an inner, compact orbital and an outer, a more diffuse one. The coefficients of these two kinds of orbitals can be varied independently during the construction of molecular orbitals, in response to changes in the molecular environment.

In 6-31G basis set, which has a single function for the core and two for the valence, the core orbital of each atom is described by a linear combination of six Gaussian primitives, and the two valence functions are modeled by a linear combination of three and one Gaussians, respectively.
Further improvement of the basis functions is achieved by adding $d$-orbitals to all heavy atoms and/or $p$-orbitals to H atoms. This allows a shift of the center of an orbital away from the position of the nucleus. According to Pople notation, in 6-31G** basis set the first asterisk implies the addition of a set of $d$-orbitals to each heavy atom in the previously described split-valence basis set, whereas the second asterisk stands for the addition of a set of $p$-orbitals to each hydrogen. The choice of the 6-31G** basis set for the MP2 and DFT calculations is supported by other successful MP2/6-31G** calculations on bridging aluminum compounds [17,28].
CHAPTER 3

COMPUTATIONAL DETAILS

All the calculations were performed on Beowulf-class 512 dual Intel Pentium IV Xenon parallel cluster at Center for Computation and Technology at Louisiana State University.

3.1 Molecular Dynamics Simulations

NWChem 4.5 [29] computational package has been used to obtain the forces in a gas phase molecular dynamics (MD) setup under the Moller-Plesset second order energy correction (MP2) [30] configuration interactions method and the Los Alamos National Laboratory two-double-zeta (LANL2DZ) basis set [31] chemistry model. MD simulations have been carried out for the elemental steps in MAO formation, until the cage was formed. Ab initio molecular dynamics simulation of these reaction systems requires a long computational time to overcome the activation barrier. To reduce this time, we defined Al-O and C-H attractive forces that turn on only in the distance region where the activation barrier exists. These attractive forces reduce the activation barrier needed for the system to react.
Define $r_L$ as the lower limit and $r_U$ as the upper limit of that distance region, with $d = r_U - r_L$ being the distance region where the attractive forces act.

Attractive forces described by a cubic potential are given by:

$$V(r) = \frac{3\Delta E}{d^2} \beta \left[ (r - r_L)^2 - \frac{2}{3} \frac{(r - r_L)^3}{d} \right] \quad (3.1.1)$$

$\Delta E$ is the amount of energy by which the barrier is reduced, and is dimensionless in (3.1.1). $\beta = \frac{1}{kT} \quad (3.1.2)$

The forces are zero at the boundaries of the defined region, so that a molecule entering or leaving this region would not experience a sudden force.

---

![Al-O, C-H Attractive Potentials](image)

**Figure 3.1.1** Al-O and C-H attractive potentials for $\beta = 1000$ and $\Delta E = 5, 10, 30, 40 \text{ and } 60$ respectively.
3.2 Energy Optimization. Transition State

The concepts of energy surface for molecular motion, equilibrium geometries, transition structures and reaction paths depend on the Born-Oppenheimer approximation to treat the motion of the nuclei separately from the motion of the electrons. For a N atom molecule, there are 3N-6 (or 3N-5 for a linear molecule) internal coordinates (bonds, angles, torsional angles, etc.). The energy of a molecule, due to the interactions of electrons and nuclei, it is a function of all of these coordinates and corresponds to a surface in a multi-dimensional space. The potential energy surface (PES) has as many dimensions as there are degrees of freedom, and each point on the potential energy surface represents a particular molecular structure.

The energy optimization or minimization is the process to determine the geometry of minimum energy by adjusting bond angles and lengths. It is an iterative process that starts with a guessed geometry and ends up with an optimized geometry. Except for in very simple cases the potential energy surface can not be obtained from experiment. Electrons are too small and too light to be described by classical mechanics, and quantum mechanics must be used to calculate the energy of a molecule as a function of the position of the nuclei.

Geometry optimization usually attempt to locate minima on the potential energy surface, predicting equilibrium structures of the molecular systems or locate peaks and ridges on the PES, particularly to locate the transition structure for a chemical reaction which is a local maximum along one and only one direction while being a local minima in all other orthogonal directions. Maxima, minima and saddle points can be characterized by their first and second
derivatives. For a function of several variables, the first derivatives with respect to each of the variables form a vector called the gradient. The second derivatives form a matrix called the Hessian. In classical mechanics, the first derivative of the potential energy with respect to the coordinates for a particle is the negative of the force on the particle, and the second derivative is the force constant. At both minima and saddle points the first derivative of the energy is zero. Since the gradient is the negative of the force, all the forces on the atoms in a molecular system must be zero at such a point, and on the PES, such a point is called a stationary point. The nature of the stationary point can be determined from the second derivatives. In one dimension, the second derivative is positive for a minimum, negative for a maximum and zero for a point of inflection. In more than one dimension, the eigenvalues of the second derivative matrix, rather than individual elements of the matrix, determine the characteristics of the stationary point. If all the eigenvalues are positive, the point is a local minimum; if all are negative is a local maximum. A transition structure, which corresponds to the highest point on a minimum energy reaction path, is a first order saddle point on the potential energy surface. Such point has one negative eigenvalue and all the rest are positive, which means it is a maximum in one direction and a minimum in all perpendicular directions. An n-th order saddle point has n negative eigenvalues, which means is a maximum with respect to n mutually perpendicular directions. Transition states and second order saddle points on a PES are depicted in Figure 3.2.1[32]. Several strategies exist to locate the stationary points on the energy hypersurface [33].
The gradient methods that rely on analytical calculation of the first derivatives of the potential energy with respect to the nuclear positions (gradient) have become practical and efficient for ab initio methods [34]. The gradient is a vector that points to the direction along the potential surface in which the energy decreases most rapidly from the current point as well as the steepness of that slope. Since the target of an optimization is energy minima, the coordinates are changed in the direction of the negative gradient to generate a new nuclear geometry. At the new geometry, the cycle is repeated until the geometry stops changing. The second derivative of the energy with respect to the molecular coordinates generates the matrix of force constants. These force constants specify the

Figure 3.2.1 Potential Energy Surface (PES).
curvature of the surface at that point, providing additional information for determining the next step, which are essential in locating the transition states.

In this work the optimization of the equilibrium geometries and transition states was carried out using a modified conjugate gradient algorithm proposed by Schlegel [34], so-called Berny algorithm, as implemented in Gaussian98 and Gaussian03 [35]. This optimization scheme evaluates the gradients each time the energy is computed and the second derivative matrix is updated employing the gradients. At each step, a one dimensional minimization using a quadratic polynomial is carried out, followed by a n-dimensional search using the Hessian matrix. Zero-point energy corrections to electronic energies were calculated from the vibrational frequencies and used unscaled. In the case of alkyl aluminum compounds (\(TMA\) and \(TMA_2\)), as already documented [17], MP2 level of theory is required for accuracy. It was found that in electronic structure calculations for alkylaluminoxane compounds, the B3LYP and MP2 methods gave similar results, in agreement with previous studies [2].

Computationally, to locate the transition states is often problematic since the starting structure must be very close to the actual transition state. In all the cases, in order to verify the nature of the transition state, the Hessian needs to display the required number of negative eigenvalues, which were checked through frequency calculations. Aside from this local criterion, in all the cases, the intrinsic reaction calculations (\(IRC\)) using Gonzalez-Schlegel method were performed in order to verify the minima connected through the transition state. \(IRC\) is defined as the minimum energy reaction pathway in mass-weighted Cartesian coordinates between the transition state of a reaction and its reactants.
and products. In this work, minimum energy structures, activation energies and thermodynamic data have been calculated at B3LYP density functional hybrid theory level and in some cases at MP2 level in frozen core approximation, with 6-31g** [36] polarized basis sets. All the calculations are at the room temperature.

3.3 The Solvent Effect

MAO synthesis is preferably taking place in toluene [37,38]. Given the non-polar nature of the solvent, it is expected the solvent effect to be small, and this has been seen previously [39]. Therefore, the solvent effect is not included in the calculations.

3.4 IR Vibrational Analysis

From previous studies [40,41], the DFT methods, with the hybrid functionals having superiority, can provide vibrational frequencies which are consistently closer to the experiment than those obtained with Hartree-Fock and MP2 theories, requiring the application of either small or no scaling factors.

On the other hand, the calculations of IR intensities has been shown to require the use of large basis set with diffuse and polarization functions for the theoretical data to accurately correlate with experiment [42].

In this work, using analytical gradient techniques as implemented in Gaussian98 and Gaussian03, vibrational frequencies have been calculated at B3LYP [25] density functional hybrid level of theory with 6-31g** [36] split valence polarized basis sets on all atoms. For comparison with experiment, the theoretical vibrational frequencies from tight geometries have been scaled with a factor recommended for the above considered level of theory [40].
3.5 NMR Parameters

NMR parameters such as chemical shift, indirect spin-spin coupling constant and direct dipole-dipole coupling constant are quantities determined by the electronic structure in a molecular system. The molecular properties responsible for the generation of NMR spectra were identified and analyzed in terms of perturbation theory more than fifty years ago by Ramsey [43]. The development of special methods for the calculation of NMR properties, as well as a general improvement in \textit{ab initio} techniques and computational technology made the calculation of NMR parameters a useful and popular tool of computational quantum chemistry.

In this work chemical shift, $\delta$, for $^{27}$Al and $^1$H, and the quadrupolar coupling constant, $C_q$, and the asymmetry parameter, $\eta$, for $^{27}$Al were calculated for comparison with experiment. In an NMR experiment, the magnetic field $B$ at the nucleus differs from the applied magnetic field $B_0$, due mainly to the shielding of the nucleus by the electrons in the molecule. Consequently, the chemical shielding of a nucleus is sensitive to its electronic environment. The relationship between $B$ and $B_0$ is given by: $B = (1 - \sigma)B_0$ where $\sigma$ is the chemical shielding tensor. The chemical shift $\delta_x$ of a nucleus X with respect to a given standard is expressed by: $\delta_x = \sigma_{std} - \sigma_x$, according to which an increase in shielding corresponds to a decrease in chemical shift and the vice versa [44].

To evaluate the NMR chemical shieldings the gauge-independent atomic orbital (GAIO) method as implemented in Gaussian03 has been employed. GAIO is a quantum mechanical technique for the calculation of magnetic properties of
chemical systems. It is one of the main methods to solve the so-called gauge problem which in its simplest form is the unphysical dependence of the calculated results on the arbitrary gauge of the vector potential, in particular, the dependence on the position of the molecule if magnetic fields are present [45]. In the GIAO method the atomic basis functions depend explicitly on the magnetic field by inclusion of a complex exponential phase factor (gauge factor) that depends on the magnetic field, as well as on the center coordinates of the atomic orbital and the Cartesian coordinates of the electron. Such orbitals are known as Gauge Included Atomic Orbitals and their matrix elements only contain a difference in the vector potentials, completely removing the reference to an absolute gauge origin [20].

An important factor in the accuracy of quantum calculated chemical shifts from isotropic magnetic shielding tensors, for comparison with experiment, is a good quality geometry. Also, like in any other \textit{ab initio} calculation, the choice of the atomic basis set is crucial. In this respect, systematic investigation of the basis set convergence of nuclear shieldings at the SCF level using GIAO method shows that for an accurate calculation a basis set of at least valence triple-$\zeta$ quality and with at least one set of polarization functions is needed [46].

In this work, nuclear shieldings have been calculated at Hartree-Fock level of theory for the B3LYP exchange-correlation functional optimized geometries using polarized split-valence 6-31g** basis sets on all the atoms. From previous studies the method proved to accurately describe aluminoxanes spectra [47].

The other NMR spectral parameters of interest, nuclear quadrupole coupling constant (Cq) and the asymmetry parameter $\eta$, have been calculated
from the electric field gradient (EFG) tensor. The EFG tensor is the second
derivative of the electrostatic potential at the atomic position and contains the
interaction between the nuclear-electric-quadrupole moment, which arises from
the charge distribution within the nucleus, and the electric field gradient created
by charge distribution outside of the nucleus of interest, which contain electrons
and protons from other nuclei [48]. The EFG tensor has nine components (of
which, however, only six are distinct), it is diagonalizable into the principal axis
system and it is traceless:

$$\frac{\partial^2 V}{\partial x\partial x} + \frac{\partial^2 V}{\partial y\partial y} + \frac{\partial^2 V}{\partial z\partial z} = 0$$ (3.1.3)

By convention the three remaining components are ordered by absolute
magnitude and denoted:

$$q_{xx} = \frac{\partial^2 V}{\partial x\partial x} \leq q_{yy} = \frac{\partial^2 V}{\partial y\partial y} \leq q_{zz} = \frac{\partial^2 V}{\partial z\partial z}$$ (3.1.4)

The largest component, \(q_{zz}\), is also denoted by \(q\). Since the EFG tensor
is traceless, it can be characterized by only two independent parameters and
those are usually chosen to be the quadrupolar coupling constant (Cq) and the
asymmetry parameter, \(\eta\) which are defined as following:

$$Cq = \frac{e^2 q Q}{h}$$ (3.1.5) where \(e\) is the electron charge, \(q\) is the largest component of
the EFG tensor, \(Q\) is the nuclear-electric-quadrupole moment and \(h\) is the
Planck’s constant.

In this work the nuclear quadrupole constant and the asymmetry
parameter have been calculated for \(^{27}\text{Al}\). In order to do so, besides the EFG
tensor calculated with Gaussian03, the nuclear-electric-quadrupole moments (Q) of the nucleus must be specified in (3.1.5), and this is 146.6(1.0)x10^{-31}m^2 [49] for the $^{27}$Al; the S.I. unit for the nuclear-electric-quadrupole moment is barn (1barn=10^{-28}m^2). Gaussian reports EGF tensor eigenvalues in atomic units and the S.I. unit for Cq is MHz; a conversion factor (see 3.1.5) of -34.446 for $^{27}$Al [48] has been used.

The asymmetry parameter, $\eta$, describes the distortion of the EFG from the axial symmetry and it is given by:

$$\eta = \frac{q_{xx} - q_{yy}}{q_{zz}}$$  \hspace{1cm} (3.1.6), \hspace{1cm} $\eta \in [0,1]$. \hspace{1cm} $\eta = 0$ means three-fold symmetry (rotational symmetry of order three, $C_3$, and which is lower than a 3D rotational symmetry with respect to any angle, the so-called cylindrical symmetry), while $\eta = 1$ means very asymmetric.
CHAPTER 4

RESULTS AND DISCUSSION

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This chapter is organized in three sections. In the first part, from quantum molecular dynamics simulation and structure calculations, possible steps in MAO formation by TMA hydrolysis are presented, and the emerged structures are compared with the isolated aluminoxane species. At the end of the first section a kinetic model of the proposed mechanism is described.

In the second section, based on the proposed MAO formation mechanism and employing electronic structure calculations, several reaction channels in MAO formation are identified. Among the proposed MAO structural models catalytically active components are considered.

In the third part of this chapter, to evaluate the proposed MAO structural models, their calculated IR and NMR spectra are compared with experiment.
4.1 MAO Polymerization Mechanism from Quantum Molecular Dynamics and Electronic Structure Calculations

Methylaluminoxane (MAO) is usually prepared by the carefully controlled reaction of trimethylaluminum and water, which is the source of oxygen. The reaction is strongly exothermic and at high water levels explosions could happen. Based on the way water is introduced in the preparation, there are direct hydrolysis methods, such as the Kaminsky’s method in which ice is the source of water and the reaction conditions are quite difficult to control, or crystallized water methods in which salt hydrates such as $CuSO_4 \cdot 5H_2O$ or $Al_2(SO_4)_3 \cdot 18H_2O$ are the source of water, allowing a more accurate control of the quantity of water in the reaction system. High catalytic activity is reached when the ratio of water to trimethylaluminum is equimolar [1]. Non-hydrolytic approaches have been reported [50], but they have not replaced the hydrolytic process for producing industrial-scale quantities of MAO for use in single-site catalytic systems.

4.1.1 The Initiation Process

Trimethylaluminum ($TMA$) is known to be a dimer even in gas phase, with an experimental gas-phase association enthalpy of $-20.40\pm0.34\text{ kcal/mol}$ [51].

From previous studies, MP2 calculations for $TMA$ dimerization are consistent with the experimental value for enthalpy as well as $TMA_2$ electron diffraction geometry [17].

As expected, the gas phase calculated reaction path for $TMA$ dimerization (please see Figure 4.1.1 for the activation energies of the direct and reverse
process, as well as for the geometry of the transition state) using the *ab initio* MP2 method favors the dimerization over the monomer formation, and we started the gas phase simulations with *TMA* as a dimer. When water is added to the system, *TMA*₂ easily dissociates (Figure 4.1.2), the activation energy for the direct reaction is more than two times lower than the activation energy for the

![Figure 4.1.1](image1.png)

**Figure 4.1.1** Calculated reaction path for *TMA* dimerization under MP2/6-31g** chemistry model.

![Figure 4.1.2](image2.png)

**Figure 4.1.2** Calculated reaction path for *TMA*₂ dissociation when water is added to the system, under B3LYP/6-31g** chemistry model.
reverse reaction, forming free TMA and a species with a stable Al–O bond, TMA–OH₂. The formation of TMA in the first steps of the MAO synthesis was proved experimentally [52] and ¹H NMR spectroscopic evidence for TMA–OH₂ existence in a polar solvent (diethyl ether) was reported by Boleslawski et al. [53]. Natural bond orbital analysis [35] of the latter, at B3LYP/6-31g** level, shows an Al–O sigma bond with more than 95% contribution from the oxygen in building the bonding orbital and a total dipole moment of 4.04 Debye (D). The length of the Al–O bond in the TMA–OH₂ optimized geometry for both MP2 and B3LYP methods with 6-31g** basis sets is 2.09Å, in the range of typical Al–O single bond [54].

4.1.2 The Dimer Formation

From quantum dynamics simulations it was seen that, once in the system, the new TMA–OH₂ species may further react with free TMA, as in Figure 4.1.3,

Figure 4.1.3 Calculated reaction path for TMA–OH₂ / TMA system under B3LYP/6-31g** chemistry model.

![Figure 4.1.3](image)

Figure 4.1.4 Calculated reaction path for methyl bridge displacement by water under B3LYP/6-31g** chemistry model.

![Figure 4.1.4](image)
forming a four atom ring that includes a bridging methyl ($M_2^+$, please refer to Note 1 on page 51 regarding the terminology used to define the species developed along the proposed mechanism), or react with itself forming a four-membered $Al_2O_2$ ring ($M_2^{2+}$ in Figure 4.1.5) as proposed in other initial reaction schemes [53,55], but without further indications regarding the mechanism.

![Calculated reaction path for TMA–OH₂ dimerization under B3LYP/6-31g** chemistry model.](image)

**Figure 4.1.5** Calculated reaction path for $TMA – OH_2$ dimerization under B3LYP/6-31g** chemistry model.

Even though the activation energy for the first process is lower, thermodynamically, and the entropy increase is the driving force, $TMA – OH_2$ dimerization is preferred; in Table 4.1.1 $\Delta G$ for the dimer formation, $M_2^{2+}$, is 57.55 kcal/mol more negative than $\Delta G$ for $M_2^+$ formation. For a low reaction barrier, the bridging methyl in the partially hydrolyzed $M_2^+$ species reacts with a water molecule (please see Figure 4.1.4), forming, again, the dimer. A similar dimeric hydroxide, $[(’Bu)_2Al(\mu-OH)]_2$, has been isolated by Barron and co-workers [5]
by hydrolysis of $Al('Bu)_3$ in toluene using a hydrated salt, $Al_2(SO_4)_3 \cdot 14H_2O$, or by the addition of water to a refluxing toluene solution of $Al('Bu)_3$. The same authors consider this dimeric hydroxide remarkably stable to thermolysis and it converts slowly to a mixture of aluminoxane species, $[('Bu)_2Al(\mu_3-O)]_n$ (n=6-12). In agreement with experiment, our quantum molecular dynamics simulations show the conversion of the hydroxylic methylaluminum dimer to trimer, tetramer, and so on, forming the aluminoxane species in the termination step of a process that has all the characteristics of a step polymerization through a bi-functional monomer ($TMA-OH_2$). In a step-polymerization the growth proceeds slowly from dimer to trimer, tetramer, and so on, any two species can be coupled. Polymers synthesized by step-polymerization often have lower molecular weights and high dispersity in molecular weight distribution. PMAO (polymethylaluminoxane) is considered a mixture of oligomers with a very wide molecular weight distribution [37], and thirty hours of reaction time are needed to isolate 19.7 g methylaluminoxane [38].

4.1.3 Trimer and Tetramers

In Figure 4.1.6 the growth of the dimer to trimer, two fused four-membred $Al_2O_2$ rings, is presented. For each monomer added, two $CH_4$ molecules are eliminated, and the overall activation energy which is considered the activation energy for the rate-determining step, slightly increases in the dimer to trimer growing process by comparison with the dimerization process.

The tetramer formation from the trimer is a bifurcation point; it can be a ladder-like structure (please see Figure 4.1.7) or a cage-like structure (see the
reactant in Figure 4.1.8). Thermodynamically, the cage-like structure is 2.2 kcal/mol more stable than ladder-like structure \( M_4^+ \) formation in Table 4.1.1).

**Figure 4.1.6** Calculated reaction path for the trimer formation under B3LYP/6-31g** chemistry model.

**Figure 4.1.7** Calculated reaction path for ladder-like tetramer (three fused four-membered \( Al_2O_2 \) rings) formation from the trimer under B3LYP/6-31g** chemistry model.
4.1.4 Pentamers, Hexamers and the Hexameric Cage

The next step in MAO polymerization is the pentamer formation via either by dimer - trimer coupling, or by monomer and tetramer reaction as shown in Figure 4.1.8. Several geometries are proposed for the pentamer, and the cage-
like structure ($M_5^{3^+}$) is not the most stable in this case. The molecular structure of $M_5^{3^+}$, one possibility of dimer-trimer coupling, is similar to the isolated pentameric aluminoxane [5], and is 17.39 kcal/mol more stable than the cage-like pentamer and 15.46 kcal/mol than the ladder-like structure ($M_5^{2^-}$).

The latter finding suggests as possible the presence of small size ladder-like structures in MAO.

By the addition of another monomer to the pentamers, the hexameric cage, $[(CH_3)AlO]_6$, is formed. This is incontestably the most thermodynamically stable structure so far (please see $M_6^6$ formation in Table 4.1.1). A well known similar cage for t-butylaluminoxane has been isolated and structurally characterized by X-ray crystallography [5]. In the same study, a structure consisting of an $Al_3O_3$ ladder core, as in the above trimer (Figure 4.1.6), has been isolated and considered the direct precursor to the isolated hexameric aluminoxane. That structure is analogous to the above $M_6^{6^-} - 2$ methylaluminoxane and the present mechanism explains its formation either by reaction of two trimers ($M_3^{3^+}$), which is thermodynamically favored (please see Table 4.1.1), or by a dimer ($M_2^{2^+}$) – ladder-like tetramer ($M_4^{2^-}$ – 2) coupling.

Based on the geometries of the species involved in the above discussed propagation steps, one can notice not only that aluminoxane species similar to the most stable configurations were isolated, but also that the monomer concentration may be already low at this step of the reaction, which is not uncommon since step polymerizations are characterized by the disappearance of
the monomer very early in the reaction. Typically, less than 1% of the original monomer remains in the system at the reaction point where the average polymer chain contains ~ 10 monomer units ([56], page 42).

On the other hand, following the ladder-like structures in this development, the $M_6^{6-} \cdot 2$ hexameric hydroxide is much more stable (30.27 kcal/mol) than the ladder-like hexamer ($M_6^{6-} \cdot 1$), suggesting that the presence of the ladder-like structures after the cage is very unlikely.

4.1.5 Beyond the Hexameric Cage

The insertion of the monomer at the cage can be done in two different ways: breaking a square-square $Al-O$ bond, when structure $M_7^{-} \cdot 1$ is formed, or an axial approach by breaking a square-hexagonal $Al-O$ bond forming structure $M_7^{-} \cdot 3$. The square-square $Al-O$ bond denotes the bond shared by two adjacent four-membered rings, while the square-hexagonal $Al-O$ bond stands for the bond shared by two adjacent four and six membered rings.

![Scheme 4.1.3 $M_7^{-} \cdot 1$](image1)

![Scheme 4.1.4 $M_7^{-} \cdot 2$](image2)

![Scheme 4.1.5 $M_7^{-} \cdot 3$](image3)
Thermodynamically, compound $M_i^{-1}$ is much more stable making the first above described approach of monomer insertion at the cage the main reaction channel; its $\Delta G$ formation from the cage is 28.91 kcal/mol more exothermic than in the case of $M_i^{-2}$, and 6.85 kcal/mol more than in the case of $M_i^{-3}$ formation (please see Table 4.2.1).

Following the axial approach, consistent patterns couldn’t be identified, but several structures have been proposed and will be discussed in detail in the second section of this chapter. However, one of the structures developed in this approach, by breaking two opposite square-hexagonal $Al-O$ bonds in the cage followed by one of the scenarios: reaction of a monomer at each of the opened sites and addition of a third monomer, reaction of a dimer at one of the opened sites and of a monomer at the other site, or insertion of a trimer between the two opened sites, turned out to be analogous to the isolated aluminoxane nonamer [6].

![Scheme 4.1.6 $M_{8}^{\pm} - 11$](image1)

![Scheme 4.1.7 $M_{8}^{\pm} - 12$](image2)
The focus for now is on compound $M_7^T - 1$. Notice that from this point on the hydrogen atoms will be omitted in the species structure displays. Adding the monomer to it is again a bifurcation point since it can be done in two very different ways. One way is by breaking another $Al - O$ bond at the cage, and a new four-membered $Al_2O_2$ ring forms within the cage, as in $M_8^S - 11$ (for the description of the terminology used to designate the growing and termination species resulting form different growing and termination patterns after the hexameric cage please see Note 2 on page 51). In $M_8^S - 12$ a four-membered $Al_2O_2$ ring is formed outside the cage and this option is thermodynamically less favorable; its $\Delta G$ formation from $M_7^T - 1$ is 13.31 kcal/mol less negative than in the case of $M_8^S - 11$ formation, please see the energetics of these reactions in Table 4.1.1. From the cage, as seen in $M_8^S - 11$, the growth can be done at two identical sites, while the monomer insertion as in $M_8^S - 12$ allows a three-directional growth.

$M_8^S - 11$ can also been seen as the product of the reaction between the cage $M_6^6$ and the dimer $M_2^{2^2}$ when a methane molecule is eliminated. On the other hand, considering an intra-molecular elimination of methane from $M_8^S - 11$, involving the hydrogen from O13 and a methyl group from Al20, $M_8^S$ structure is formed. However, $M_8^S$ structure ($E^0 = -2861.593721\ a.u.$) is much less stable (25362.8 kcal/mol less negative) than $M_8^S - 11$ ($E^0 = -2902.011900\ a.u.$); therefore this reaction route is not favored.
In addition, this reaction route is not thermodynamically favored over the monomeric growth at $M_{8}^{8'} - 11$ to form $M_{9}^{9'} - 11$ ($\Delta G$ of the former formation is almost three times more negative than $\Delta G$ formation of the latter from $M_{8}^{8'} - 11$, please see these reactions in Table 4.1.1). A similar structure has been synthesized in the case of t-butylaluminoxane as the minor product by reaction of $[(\text{'Bu})_{2} \text{Ga}(\mu-OH)]_{3}$ with $\text{Al('Bu)}_{3}$ [5].

The above discussion suggests that in the case of t-butylaluminoxane, the only aluminoxane for which crystalline species have been isolated, hydroxide species like $M_{8}^{8'} - 11$, due to the steric effect, stabilizes through intra-elimination of an alkyl molecule, forming closed cages like $M_{8}^{8}$. Similar models have been proposed for MAO [5], but as shown above, their formation is not a favored reaction route, and more than that, they cannot explain MAO composition.
4.1.6 The Termination

As mentioned above, during MAO synthesis by TMA hydrolysis, species with one or more $-OH$ functional groups, similar to the isolated t-butylaluminoxane hydroxides [5], have been identified. However, traces or no $-OH$ [10] are present in the final MAO.

In situ FTIR spectroscopy studies [12] show no evidence of chemical reaction between MAO and TMA. TMA and MAO behave as independent compounds and MAO samples contain little or no free TMA. Considering the initiation scheme (Table 4.1.1), and answering to the above experimental evidences, TMA does the termination in MAO polymerization. It reacts with $-OH$ functional releasing $CH_4$ and the excess of it is the free TMA in MAO solutions.

Ab initio molecular dynamics simulations of such reactions, Figures 4.1.9 and 4.1.10, investigated at the beginning of this work when we had little or no direction regarding the mechanism, show the possibility of TMA to react with the hydroxyl group(s) at the growing species. The resulting species are not only similar to some of the isolated aluminoxanes ($M_4^\beta$ [5] and $M_4^\delta$ [6]), but also they introduce three-coordinate aluminum centers, which has been suggested by NMR studies [47] as being present in MAO, and for larger species (after the hexameric cage) bridging methyl groups, that has been proven to be essential for MAO co-catalytic activity [7].

Since the calculated activation barriers for termination reactions before the cage are very low (less than 1 kcal/mol), it may be concluded that terminated
species are formed before the cage. This is an answer to the very broad reported molecular weight distribution in MAO, a 400 - 3000 g/mol range [57].

**Figure 4.1.9** Calculated path for the reaction of TMA and partially hydrolyzed TMA$_2$ forming $M_3^1$, under B3LYP/6-31g** chemistry model.

**Figure 4.1.10** Calculated path for $M_4^3$ formation by partial termination reaction of the trimer, under B3LYP/6-31g** chemistry model.
Interestingly enough, species similar to $M_8^{7}$ have been isolated for t-butylaluminoxane [5], supporting this MAO formation mechanism. After the cage, structure $M_8^{7} - 1$ termination can be done in three different ways, as see in $M_8^{7} - 11$, $M_8^{7} - 12$ and $M_8^{7} - 13$.

The termination of the growing species by reaction of $-OH$ functional with $TMA$ in the $M_8^{7} - 11$ case involves the breaking of an adjacent square-square $\text{Al} - \text{O}$ bond at the cage with the formation of a four-membered $\text{Al}_2\text{O}_2$ ring and of a six-membered ring through a bridging methyl within the new cage. A four-membered ring through a bridging methyl is formed outside the cage in the $M_8^{7} - 12$ case, while in $M_8^{7} - 13$, bridging methyl structural motif is missing. In all the cases a methane molecule is eliminated.

Another possibility for termination after the cage can be the following: the insertion of $TMA$ by breaking a square-square $\text{Al} - \text{O}$ bond, that is known to be much more strained than a square-hexagonal bond [39], in structures like $M_8^{8}$. 
The outcome of such an approach on the latter is \( M_9^8 \) structure, which in this case is not a new termination motif, but it leads to new structures in other cases. Thermodynamically the decrease in enthalpy is the driving the driving force of such a process (please see \( M_9^8 \) formation in Table 4.1.1).

It is now generally accepted that the active species in the metalloocene catalyst is a coordinatively unsaturated transition metal cation and that the role of MAO is thus to methylate the metalloocene, activate the methylated complex and stabilize the resulting active cationic complex [1]. The presence of bridging methyl groups in MAO has been proven by IR studies (it was determined to be 15-20% of the methyl groups), and this structural motif is considered fundamental for MAO co-catalytic activity [7]. After the building mechanism was established, the focus of this project was to identify consistent patterns in building methyl bridged structures.
<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta E^0$</th>
<th>$\Delta H$</th>
<th>$\Delta G$</th>
<th>Theory</th>
</tr>
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<tr>
<td>$TMA_2 + H_2O \xrightleftharpoons[k_{-1}]{k_1} TMA + TMA - OH_2$</td>
<td>-7.79</td>
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<td>$TMA + TMA \xrightarrow{k_2} TMA_2$</td>
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<td>-80.86</td>
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<td>-78.24</td>
<td>-84.88</td>
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<td>$M_{5}^{5\nu} - 2 + TMA - OH_2 \xrightarrow{k_p} M_{6}^{6\pi} - 1 + 2CH_4$</td>
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<td>-79.85</td>
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<td>$M_{2}^{2\pi} + M_{4}^{4\pi} - 2 \xrightarrow{k_p} M_{5}^{5\nu} - 2 + 2CH_4$</td>
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<tr>
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<td>$M_{8}^{8\pi} - 11 \xrightarrow{} M_{8}^{8\pi} + CH_4$</td>
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<td>$M_{8}^{8\pi} - 11 + TMA - OH_2 \xrightarrow{k_p} M_{9}^{9\nu} - 11 + 2CH_4$</td>
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<td>$TMA - OH_2 \xrightarrow{} (CH_3)_2 AlOH + CH_4$</td>
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<tr>
<td>$TMA - OH_2 + TMA \xrightarrow{k_p} M_{2}^{2\iota} + CH_4$</td>
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<td>-54.05</td>
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Table cont.
Table cont.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Energy</th>
<th>Energy</th>
<th>Energy</th>
<th>Method</th>
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<tbody>
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<tr>
<td>$M_3^{3+} + TMA \rightarrow M_4^{3+} + CH_4$</td>
<td>-39.96</td>
<td>-38.03</td>
<td>-38.42</td>
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</tr>
<tr>
<td>$M_7^{7-} + TMA \rightarrow M_8^{7-} + CH_4$</td>
<td>1 -40.03</td>
<td>-40.11</td>
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<td>B3LYP</td>
</tr>
<tr>
<td>$M_7^{7-} + TMA \rightarrow M_8^{7-} + CH_4$</td>
<td>2 -38.21</td>
<td>-37.96</td>
<td>-34.25</td>
<td>B3LYP</td>
</tr>
<tr>
<td>$M_7^{7-} + TMA \rightarrow M_8^{7-} + CH_4$</td>
<td>3 -37.86</td>
<td>-37.80</td>
<td>-35.57</td>
<td>B3LYP</td>
</tr>
<tr>
<td>$M_8^{8-} + TMA \rightarrow M_9^{8-} + 11$</td>
<td>-10.08</td>
<td>-10.72</td>
<td>5.92</td>
<td>B3LYP</td>
</tr>
</tbody>
</table>

Note 1: In $M_i^{j;"or"}i$ stands for the total number of Al atoms, $j$ for the total number of oxygen atoms, and ‘1’, ‘2’ and ‘3’ accounts for one, two and three $-OH$ functional groups, respectively. For example, $M_3^{3+}$ is a species that contains three Al atoms, and three O atoms, among which two of them are part of hydroxyl functional groups. In addition, to designate different isomers a dash (−) followed by a number (1, 2 or 3) is added to the previously described notation scheme. $M_4^{4-}1$ is for the tetramer cage-like geometry while $M_4^{4-}2$ is for the ladder-like geometry. $M_5^{5-}1$ is for the pentamer cage-like geometry, $M_5^{5-}2$ is for ladder-like geometry, and $M_5^{5-}3$ is for the geometry analogous to isolated t-buty l pentameric hydroxide. $M_6^{6-}1$ stands for the ladder-like hexameric hydroxyde, while the geometry of $M_6^{6-}2$ is analogous to the Harlan et al. characterized hexameric hydroxyde.

Note 2: After the hexameric cage, to designate isomeric species resulting from different growing or termination patterns a second number is added to the notation scheme described in Note 1. That second number should be seen as connected with the first number, and should be read, for example $M_8^{8-}11$, as “m eight seven one one”. It denotes, in Table 4.1.1, the termination motif 1 (small box) from the reaction of $TMA$ with $M_7^{7-}1$.

4.1.7 The Kinetic Model for MAO Polymerization

Based on molecular dynamics and structural information from $ab$ $initio$ simulations and respectively, electronic structure calculations in this study, corroborated with structural information for the few alkylaluminoxane isolated
species (t-butylaluminoxane), polymethylaluminoxane formation emerges as a step polymerization through a bifunctional monomer.

4.1.7.1 The Initiation

The initiation process, corresponding to the monomer \((TMA - OH_2)\) formation, is completely described thermodynamically and kinetically by the following linearly independent set of reactions:

\[
TMA_2 + H_2O \xleftrightarrow[k_1]{k_{-1}} TMA + TMA - OH_2 \quad (4.1.1)
\]

\[
TMA + TMA \xleftrightarrow[k_2]{k_{-2}} TMA_2 \quad (4.1.2)
\]

The equilibrium constant for reaction (4.1.1) is given by:

\[
K_1 = \frac{k_1}{k_{-1}} = \frac{[TMA][TMA - OH_2]}{[TMA_2][H_2O]} \quad (4.1.3).
\]

The equilibrium constant for \(TMA\) dimerization can be written as:

\[
K_2 = \frac{k_2}{k_{-2}} = \frac{[TMA_2]^2}{[TMA]^3} \quad (4.1.4).
\]

4.1.7.2 The Propagation

Once the polymerization starts, any of the species can react with each other and the process proceeds by a relatively slow increase of the polymer weight, which is a step polymerization characteristic.

\[
TMA - OH_2 + TMA - OH_2 \xrightarrow{kp} M_2^2 + 2CH_4 \quad (4.1.5)
\]

\[
M_2^2 + TMA - OH_2 \xrightarrow{kp} M_3^3 + 2CH_4 \quad (4.1.6)
\]

\[
M_3^3 + TMA - OH_2 \xrightarrow{kp} M_4^4 + 2CH_4 \quad (4.1.7)
\]
\[ M_2^{x^c} + M_2^{x^c} \rightarrow_{kp} M_4^{x^c} + 2CH_4 \quad (4.1.8) \]
\[ M_4^{x^c} + TMA - OH_2 \rightarrow_{kp} M_5^{x^c} + 2CH_4 \quad (4.1.9) \]
\[ M_3^{x^c} + M_2^{x^c} \rightarrow_{kp} M_5^{x^c} + 2CH_4 \quad (4.1.10) \]
\[ M_5^{x^c} + TMA - OH_2 \rightarrow_{kp} M_6^{x^c} + 2CH_4 \quad (4.1.11) \]
\[ M_5^{x^c} + TMA - OH_2 \rightarrow_{kp} M_6^{x^c} + 4CH_4 \quad (4.1.12) \]
\[ M_7^{x^c} - 1 + TMA - OH_2 \rightarrow_{kp} M_8^{x^c} - 11 + 2CH_4 \quad (4.1.13) \]
\[ M_7^{x^c} - 1 + TMA - OH_2 \rightarrow_{kp} M_8^{x^c} - 12 + 2CH_4 \quad (4.1.14) \]

\( M_6^c \) is the cage and \( M_6^{x^c} \) is the ladder-like hexamer. After the cage, a bi-directional growth is seen, as in (4.1.13) for one direction, when the general formula of the generated mers is \( HO - [Al(CH_3) - O]_n - OH \), where \( n \) is the degree of polymerization, and a three-directional growth as in (4.1.14) when the general formula of the growing species is \( [Al(CH_3) - O]_n - (OH)_3 \), where \( n \) is the degree of polymerization. See above structural details for \( M_8^{x^c} - 11 \) and \( M_8^{x^c} - 12 \).

### 4.1.7.3 The Termination

It is generally accepted that MAO is a multi-component material. As discussed above, the termination process is done by reaction of \( TMA \) or already partially terminated species with \( -OH \) functional of the growing mers. The final MAO structures comply with the following general formulas:

- \( (CH_3)_{3}Al - [Al(CH_3) - O]_{n} - Al(CH_3)_{3} \), \( n = 2k \), \( n > 6 \) (i) for the bidirectional growth,
- \( [-Al(CH_3) - O]_{n} - 3Al(CH_3)_{3} \), \( n = 3k \), \( n > 6 \) (ii) for the three-directional growth,
- and a particular case of the latter when the growth is followed by...
termination at each step, \([-Al(CH_3) - O-]_n + \text{Al}(CH_3)_3 n=3k n>1\) (iii), where \(n\) is the number of monomeric growing steps after the cage and \(k\) is an integer, \(k=1, 2, 3,\) etc. \([Al(CH_3) – O]\) is the monomer unit.

The rate of step polymerization is the sum of the rates of reaction between molecules of various sizes, and it can be conveniently expressed in terms of the concentrations of the reacting functional groups \(-OH\) and \(-Al(CH_3)\). Under the concept of equal reactivity of functional groups [56], the rate of polymerization can then be expressed as the rate of disappearance of the monomer \((TMA – OH_2)\) and it is given by:

\[
R_p = \frac{d[TMA – OH_2]}{dt} = k_p[TMA – OH_2]^2 (4.1.15),
\]

where \(k_p\) is the propagation rate constant.

From (4.1.3): \([TMA – OH_2] = K_1 \frac{[TMA_2][H_2O]}{[TMA]} (4.1.16)\). From (4.1.4): \([TMA_2] = K_2[TMA]^2 (4.1.17)\). Using (4.1.16) and (4.1.17) in (4.1.15), for \(TMA_2 / H_2O\) reactive system, the rate of polymerization can be expressed as:

\[
R_p = \frac{k_pK_1^2}{K_2}[TMA_2][H_2O]^2 = K[TMA_2][H_2O]^2 (4.1.18).
\]

The concept of equal reactivity of functional groups of a bi-functional monomer simplifies the kinetic analysis assuming that the reactivity of both functional groups are the same, the reactivity of one of the functional group is the same irrespective of whether the other functional group has reacted, and that the reactivity of a functional group is independent of the size of the molecule to which it is attached. Interestingly enough, the structure calculations for the proposed models support this concept considering that the analyzing step by step one of the growing patterns after the
hexameric cage (please see Table 4.2.2, as well as Figure 4.2.3 in the next section). The changes in free Gibbs energy, as well as the enthalpy and the electronic energy, are very small from one step to the other in the propagation process; notice that the increase in the entropy is the driving force, and $\Delta G$ formation of these species is $-96.41 \pm 4.5\, \text{kcal/mol}$.

In (4.1.18), for a stoichiometric concentration of the reactant system, the rate of polymerization is given by: $R_p = -\frac{d[M]}{dt} = K[M]^3$ (4.1.19). Integration of equation (4.1.19) yields: $2Kt = \frac{1}{[M]^3} - \frac{1}{[M_0]^3}$ (4.1.20), where $[M_0]$ is the initial (at $t=0$) concentration of $-\text{OH}$ or $-\text{Al(CH}_3\text{)}_2$ functional groups. In terms of the extent or fraction of reaction $p$, the concentration $[M]$ at time $t$ of either of the functional groups is given by: $[M] = [M]_0 - [M]_0 p = [M]_0 (1-p)$ (4.1.21). The extent of reaction is related to the degree of polymerization by Carothers’s equation [59], $\overline{X}_n = \frac{1}{1-p}$, which combined with (4.1.20) and (4.1.21) yields: $\frac{1}{(1-p)^2} = (\overline{X}_n)^2 = 2[M]_0^3 Kt + 1$ (4.1.22), where $\overline{X}_n$ is the number-average degree of polymerization.

Describing the discovery of metallocene catalysts, Kaminsky reports that their catalytic activity depends on the amount of water used in the co-catalyst (MAO) synthesis. It reaches a maximum when the ratio of water to $\text{TMA}$ is equimolar [1]. Considering it, (4.1.15) can be reformulated as: $R_p = k_p K_1^2 K_2^2 [\text{TMA}]^2 [H_2O]^2 = K'[\text{TMA}]^2 [H_2O]^2$ (4.1.23). Again, assuming that the
concentration of the functional groups is the same at \( t=0 \) as well as throughout the entire kinetic measurements, the reaction rate is given by:

\[
R_p = -\frac{d[M]}{dt} = K \cdot [M]^4 (4.1.24),
\]

which after the integration becomes:

\[
\frac{1}{(1-p)^3} = (\overline{X}_n)^3 = 3[M]_0 K t + 1 (4.1.25).
\]

Considering either third-order or fourth-order kinetic dependencies (Eqs.4.1.22 and 4.1.25), a linear increase of the polymerization degree with time is expected. In fact, the available experimental data for step polymerization processes exhibit deviation from linearity, presenting an increased effect in the low conversion region and opposite effect in the high conversion region [56].

The number-average molecular weight \( \overline{M}_n \), defined as the total weight of a polymer sample divided by the total number of moles [56], is given by:

\[
\overline{M}_n = M_0 \overline{X}_n + n^* M_i (4.1.26),
\]

where \( M_0 \) is the mass of the monomer unit, \( n \) is the number of the terminal groups and \( M_i \) is the molecular weight of the terminal groups (TMA). Commonly, an average degree of polymerization of about 16 is reported [38]. With regard to this, the fraction of reaction \( p \) is approximately 0.93, suggesting that 7% of the initial TMA is free in the MAO solution. Considering (26), the number-average molecular weight is 1072 g/mol for the bi-directional growth (i), 1144 g/mol for the three-directional growth (ii) and 1360 g/mol for the special case of the three-directional growth (iii), yielding an average of 1192 g/mol which is in very good agreement with the experiment considering that the most commonly reported average molecular weight for MAO is 1200 g/mol [57].
4.1.8 Conclusions

- Based on quantum molecular dynamics simulations and reaction path calculations, corroborated with experimental structural evidences for aluminoxanes, MAO formation is a step polymerization through a bifunctional monomer, \( TMA-OH \).

- All isolated aluminoxane species can be explained though the proposed mechanism. For the large majority of the proposed structures the presence of the dimeric hydroxide (\( M_2^{2+} \)), little monomer and \( TMA \) is enough to explain their formation though the proposed mechanism.

- The fact that in large scale experiments, the dimeric hydroxide have been isolated after main components like \( [(^{t}Bu)Al(\mu_3-O)]_6 \), \( [(^{t}Bu)Al(\mu_3-O)]_9 \) and \( [(^{t}Bu)Al(\mu_3-O)]_{12} \) [5], along with the consideration that for the most step polymerizations there is less than 1% of the original monomer remaining at the reaction point where the average polymer chain contains \(~ 10\) monomer units, are held as strong arguments supporting the proposed mechanism.

- The dynamics of the reactant system presented in Figure 4.1.4 reveals an interesting insight: that the methyl bridges can be replaced by \(-OH\) groups. Based on experimental observations, speculations regarding the replacement of MAO methyl bridges by \(-OH\) groups from water, at the MAO cage surface have been done by Ystenes et al. [7].
4.2 Reaction Channels in MAO Polymerization from Quantum Structure Calculations

In the first part of the results chapter, based on quantum molecular dynamics simulations of the elemental steps and electronic structure calculations, it was concluded that MAO formation is a step polymerization through a bifunctional monomer, $TMA – OH_2$, and a mechanism of reaction was presented.

It is generally accepted that MAO is a multi-component material; thereby the search for multiple reaction channels is justified. In the second part of this chapter, from quantum structure calculations, several reaction channels in MAO formation are identified and possible catalytically active MAO components are considered.

The formation of the hexameric cage, $(CH_3AlO)_6$, which as mentioned before is similar to one of the few characterized alumininoxane species, was an important point in the proposed MAO formation mechanism. On the other hand, following the ladder-like structures during the mechanism development, it have been shown that the $M_6^{6+} – 2$ hexameric hydroxide, which is considered the direct precursor of the cage [6], is much more stable (30.27 kcal/mol) than the ladder-like hexamer ($M_6^{6+} – 1$). This suggests that the presence of the ladder-like structures after the hexameric cage is very unlikely.

To discuss the growth after the hexameric cage, the possible active species present in the system at this reaction step have to be considered. $M_6^{6+} – 2$ is considered the direct precursor of the hexameric cage. It has been shown that the pentamer, tetramer and trimer would consume forming this
species. As already mentioned, controlling the water release is very critical for this reactant system, so that can be considered that fresh monomer and dimer are present in the system at this step of the reaction. In fact, in large scale experiments, the dimeric hydroxide have been found present along with large components like \([('Bu)Al(\mu_{3}-O)]_6\), \([(Bu)Al(\mu_{3}-O)]_9\) and \([(Bu)Al(\mu_{3}-O)]_{12}\) [5].

Taking into account these observations, the growth from the hexamer cage by reaction of it with the monomer and the dimer is considered.

The insertion of the monomer at the cage can be done in two different ways: breaking a square-square \(Al-O\) bond, when structure \(M_{\gamma}^T-1\) is formed, or an axial approach when structures \(M_{\gamma}^T-2\) and \(M_{\gamma}^T-3\) are formed. Thermodynamically, the structure developed from the perpendicular approach (\(M_{\gamma}^T-1\)) is the most stable making it the main reaction channel after the cage; its \(\Delta G\) formation from the cage is with 28.91 kcal/mol more exothermic than in the case of \(M_{\gamma}^T-2\) and with 6.85 kcal/mol more than in the case of \(M_{\gamma}^T-3\) formation (please see Table 4.2.1).
The focus for now will be on patterns for growth and termination from $M_7^{77} - 1$ and the other reaction channels will be discussed later.

4.2.1 The Growth Motifs from Structure $M_7^{77} - 1$

Adding the monomer to $M_7^{77} - 1$ is, again, a bifurcation point since it can be done in two very different ways. One way is by breaking another square-square $\text{Al} - \text{O}$ bond, three hexagonal rings are formed and the cage extends with a new four-membered $\text{Al}_2\text{O}_2$ ring, as in $M_8^{\text{X} \text{} - 11}$. The other option is to insert the monomer without breaking another $\text{Al} - \text{O}$ bond in the cage, as in $M_8^{\text{Y} \text{} - 12}$, when

Scheme 4.2.3 $M_7^{77} - 3$

Scheme 4.2.4 $M_8^{\text{X} \text{} - 11}$

Scheme 4.2.5 $M_8^{\text{Y} \text{} - 12}$
a four-membered $Al_2O_2$ ring forms outside the cage. The growth as in $M_8^k - 11$ can be done at two identical sites, while the monomer insertion as in $M_8^k - 12$ allows a three-directional growth from the hexameric cage. Again, for details regarding these species notation scheme please refer to Note 1 and Note 2 on page 51.

### 4.2.2 The Termination Motifs from Structure $M_8^7 - 1$

Again, TMA does the termination reacting with $-OH$ functional group releasing methane. It can be done in different ways, as seen in structures $M_8^7 - 11$, $M_8^7 - 12$ and $M_8^7 - 13$.

---

Scheme 4.2.6 $M_8^7 - 11$

Scheme 4.2.7 $M_8^7 - 12$

Scheme 4.2.8 $M_8^7 - 13$
In the $M_{8}^{7} - 11$ case, just like in $M_{8}^{8} - 11$ bi-directional growth, an adjacent square-square $Al-O$ bond at the cage is broken with the formation of a four-membered $Al_{2}O_{2}$ ring and of a six-membered ring through a bridging methyl within the new rod-like cage. This termination motif coupled with the $M_{8}^{8} - 11$ growth motif in a bi-directional growth after the hexameric cage is considered a distinctive reaction channel and it has been chosen to refer to it as the $M_{8}^{8} - 11 / M_{8}^{7} - 11$ channel.

By comparison, in structures $M_{8}^{7} - 12$ and $M_{8}^{7} - 13$ the termination by TMA is done without breaking another $Al-O$ bond at the cage. In the former, a bridging methyl is formed in a tilted four-membered $Al_{2}O_{2}$ ring, and this termination motif coupled with the $M_{8}^{8} - 12$ growth is considered another distinctive reaction channel which allows a tri-directional growth and it is called the $M_{8}^{8} - 12 / M_{8}^{7} - 12$ reaction channel; in the latter, no bridging methyl in present and this termination motif associated with the $M_{8}^{8} - 12$ growth path is considered the $M_{8}^{8} - 12 / M_{8}^{7} - 13$ reaction channel, which again allows a tri-directional growth. As it will be discussed later, due to the lack of bridging methyl, the species developed following this reaction path are not considered catalytically active.

Thermodynamically, first of all should be noticed that the growth is overwhelmingly favored over the termination, at least at this point of reaction, and secondly, that considering the free Gibbs energy $M_{8}^{8} - 11 / M_{8}^{7} - 11$ channel is the preferred reaction channel (please see Table 4.2.1).
Another possibility for the termination, when $TMA$ is inserted at the cage by breaking a square-square $Al-O$ bond will be addressed later.

Table 4.2.1. Reaction channels in MAO formation after the hexameric cage. Thermodynamic data calculated under B3LYP/6-31g** chemistry model

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta E^0$</th>
<th>$\Delta H$</th>
<th>$\Delta G$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_6^6 + TMA - OH_2 \rightarrow^{kp} M_7^7 + CH_4$</td>
<td>1 -68.44</td>
<td>-68.76</td>
<td>-63.14</td>
</tr>
<tr>
<td></td>
<td>2 -36.75</td>
<td>-36.40</td>
<td>-34.23</td>
</tr>
<tr>
<td></td>
<td>3 -60.25</td>
<td>-60.15</td>
<td>-56.29</td>
</tr>
<tr>
<td>$M_7^7 - 1 + TMA - OH_2 \rightarrow^{kp} M_8^8 - 1 + 2CH_4$</td>
<td>-98.16</td>
<td>-97.93</td>
<td>-104.16</td>
</tr>
<tr>
<td></td>
<td>-84.05</td>
<td>-83.65</td>
<td>-90.85</td>
</tr>
<tr>
<td>$M_7^7 - 1 + TMA \rightarrow^{kt} M_8^8 - 1 + CH_4$</td>
<td>1 -40.03</td>
<td>-40.11</td>
<td>-34.89</td>
</tr>
<tr>
<td></td>
<td>2 -38.21</td>
<td>-37.96</td>
<td>-34.25</td>
</tr>
<tr>
<td></td>
<td>3 -37.86</td>
<td>-37.80</td>
<td>-35.57</td>
</tr>
<tr>
<td>$M_6^6 + TMA - OH_2 + TMA \rightarrow M_8^7 - 1 + 2CH_4$</td>
<td>1 -108.47</td>
<td>-108.87</td>
<td>-98.03</td>
</tr>
<tr>
<td></td>
<td>2 -106.65</td>
<td>-106.72</td>
<td>-97.14</td>
</tr>
<tr>
<td></td>
<td>3 -106.30</td>
<td>-106.56</td>
<td>-98.71</td>
</tr>
</tbody>
</table>

4.2.3 $M_8^8 - 11 / M_8^7 - 11$ Reaction Channel. The Rod-Like Structures

In the first part of this section some the structures developed from the hexameric cage following $M_8^8 - 11 / M_8^7 - 11$ reaction path at one site will be presented and the energetics of their formation reactions will be discussed.

Two different types of bridging methyl groups corresponding to two different series of structures will be identified. The reaction of the dimer ($M_2^2$) with the hexameric cage will also be examined.
In the second part, the structures developed considering the growth at the two identical sites will be considered, and structural elements such as \( CH_3 / Al \) ratio, \( Al / O \) ratio, and percentage of bridging methyl will be compared with commercial MAO.

Two consecutive growing species along with the corresponding termination structures formed as a result of \(-OH\) functional groups reacting with \( TMA \), \( M_8^{8/11} / M_9^{9/11} \), and \( M_9^{9/11} / M_{10}^{9/11} \) respectively, will be considered. In \( M_8^{8/11} \) the \(-OH\) functional connects two identical aluminum sites, while the bridging methyl in \( M_9^{8/11} \) connects two asymmetrical aluminum sites. On the other hand, in \( M_9^{9/11} \) the \(-OH\) connects two asymmetrical aluminum sites, while the bridging methyl in \( M_{10}^{9/11} \) connects two identical aluminum sites. It can be concluded that two series of distinct species are formed in this reaction channel, and two different types of bridging methyl groups connecting aluminum sites in six-membered rings, type I and type II, can be

\begin{align*}
\text{Scheme 4.2.9} & \quad M_8^{8/11} \\
\text{Scheme 4.2.10} & \quad M_9^{8/11}
\end{align*}
identified. In each final structure of these series there are two bridging methyl groups of one type. The reaction of the dimer with the hexameric cage will be discussed next.

$M^6_{9} - 11$ can also be seen as the product of the reaction between the $M^6_{6}$ cage and the dimer ($M^2_{2}$) when a methane molecule is eliminated. Considering an intra-molecular elimination of another methane from $M^6_{9} - 11$, involving the

**Scheme 4.2.11** $M^9_{9} - 11$

**Scheme 4.2.12** $M^9_{10} - 11$

**Figure 4.2.1** Type I, a symmetrical bridging methyl, connecting 2 AlCO$_2$ sites

**Figure 4.2.2** Type II, an asymmetrical bridging methyl, connecting AlCO$_2$ and AlC$_2$O sites
hydrogen from O13 and a methyl group from Al20, structure $M_8^{s}$ is formed. However, $M_8^{s}$ structure ($E^0 = -2861.593721 \text{a.u.}$) is much less stable (its electronic energy is 25362.8 kcal/mol less negative) than $M_8^{s} - 11$ ($E^0 = -2902.011900 \text{a.u.}$); therefore this reaction route is not favored. In addition, this reaction route is not thermodynamically favored over the monomeric growth at $M_8^{s} - 11$ to form $M_8^{o} - 11$; in Table 4.2.2 the $\Delta G$ formation of the latter is almost three times more negative than the $\Delta G$ formation of $M_8^{s}$ from $M_8^{s} - 11$. A similar octameric cage has been synthesized in the case of t-butylaluminoxane, as the minor product by reaction of [(‘Bu)$_2$Ga(μ-OH)], with Al(‘Bu)$_3$ [5].

Scheme 4.2.13 $M_8^{s}$

This suggests that in the case of t-butylaluminoxane, the only aluminoxane for which crystalline species have been isolated, hydroxide species like $M_8^{s} - 11$, due to the steric effect, stabilizes through intra-elimination of an
alkyl molecule, forming closed cages like $M_8^8$. Similar models have been proposed for MAO [5], but as shown above, their formation is not a favored reaction channel. Calculated thermodynamic data for initiation, growth and termination at one site under B3LYP/6-31g** chemistry model

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta E^0$</th>
<th>$\Delta H$</th>
<th>$\Delta G$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Initiation</strong></td>
<td>$M_6^6 + TMA - OH_2 \rightarrow M_7^7 - 1 + CH_4$</td>
<td>-68.44</td>
<td>-68.76</td>
</tr>
<tr>
<td><strong>Growth</strong></td>
<td>$M_7^7 - 1 + TMA - OH_2 \rightarrow M_8^8 - 11 + 2CH_4$</td>
<td>-98.16</td>
<td>-97.92</td>
</tr>
<tr>
<td><strong>Growth</strong></td>
<td>$M_8^8 - 11 + TMA - OH_2 \rightarrow M_9^9 - 11 + 2CH_4$</td>
<td>-89.92</td>
<td>-90.06</td>
</tr>
<tr>
<td><strong>Growth</strong></td>
<td>$M_6^6 + M_2^{2'} \rightarrow M_8^8 - 11 + CH_4$</td>
<td>-68.42</td>
<td>-68.38</td>
</tr>
<tr>
<td><strong>Growth</strong></td>
<td>$M_8^8 - 11 \rightarrow M_8^8 + CH_4$</td>
<td>-24.50</td>
<td>-24.33</td>
</tr>
<tr>
<td><strong>Growth</strong></td>
<td>$M_6^6 + M_2^{2'} \rightarrow M_8^8 + 2CH_4$</td>
<td>-92.92</td>
<td>-92.71</td>
</tr>
<tr>
<td><strong>Growth</strong></td>
<td>$M_9^9 - 11 + TMA - OH_2 \rightarrow M_{10}^{10} - 11 + 2CH_4$</td>
<td>-87.95</td>
<td>-87.76</td>
</tr>
<tr>
<td><strong>Growth</strong></td>
<td>$M_{10}^{10} - 11 + TMA - OH_2 \rightarrow M_{11}^{11} - 11 + 2CH_4$</td>
<td>-88.95</td>
<td>-88.60</td>
</tr>
<tr>
<td><strong>Termination</strong></td>
<td>$M_7^7 - 11 + TMA \rightarrow M_8^8 - 11 + CH_4$</td>
<td>-40.03</td>
<td>-40.11</td>
</tr>
<tr>
<td><strong>Termination</strong></td>
<td>$M_8^8 - 11 + TMA \rightarrow M_9^9 - 11 + CH_4$</td>
<td>-34.60</td>
<td>-35.05</td>
</tr>
<tr>
<td><strong>Termination</strong></td>
<td>$M_8^8 + TMA \rightarrow M_9^9 - 11$</td>
<td>-10.08</td>
<td>-10.72</td>
</tr>
<tr>
<td><strong>Termination</strong></td>
<td>$M_9^9 - 11 + TMA \rightarrow M_{10}^{10} - 11 + CH_4$</td>
<td>-29.65</td>
<td>-30.23</td>
</tr>
<tr>
<td><strong>Termination</strong></td>
<td>$M_{10}^{10} - 11 + TMA \rightarrow M_{11}^{11} - 11 + CH_4$</td>
<td>-33.58</td>
<td>-34.98</td>
</tr>
<tr>
<td><strong>Termination</strong></td>
<td>$M_{11}^{11} - 11 + TMA \rightarrow M_{12}^{12} - 11 + CH_4$</td>
<td>-32.5</td>
<td>-33.63</td>
</tr>
</tbody>
</table>

reaction route, and, as it will be shown later, they cannot explain MAO composition. Due to species like $M_8^8$, another possibility for termination after the
cage should be considered: the insertion of TMA by breaking a square-square bond, that is known to be much more strained than a square-hexagonal bond [39] in such structures. The outcome of such an approach on $M_{8}^{8}$ is structure $M_{8}^{8} - 11$, which in this case is not a new termination motive, but this type of termination approach can lead to new structures in other cases. Thermodynamically, the decrease in enthalpy is the driving of such a process (please see $M_{8}^{8} - 11$ formation in Table 4.2.1).

In Figures 4.2.3 and 4.2.4 the energetics for the one site monomeric growth and termination reactions, respectively, in the $M_{8}^{8} - 11/M_{8}^{7} - 11$ reaction channel are given.

![Figure 4.2.3 Energetics for the propagation process, steps 7 to 10 corresponding to the growth in Table 4.2.2, in $M_{8}^{8} - 11/M_{8}^{7} - 11$ reaction channel under B3LYP/6-31g** chemistry model](image)

Figure 4.2.3 Energetics for the propagation process, steps 7 to 10 corresponding to the growth in Table 4.2.2, in $M_{8}^{8} - 11/M_{8}^{7} - 11$ reaction channel under B3LYP/6-31g** chemistry model

Notice that the decrease in the enthalpy is the driving force for the termination process, while the entropy increase is the driving force for the
propagation process in this reaction channel. The explanation for this statement resides in the following: \( \Delta G = \Delta H - T \Delta S \), all the calculations are at room temperature, and in Table 4.2.2, in the growing process \( \Delta G \) is more negative than \( \Delta H \), while in the termination process is the opposite.

![Figure 4.2.4](image)

**Figure 4.2.4** Energetics for the termination process, steps 7 to 11 corresponding to the termination in Table 4.2.2, for \( M_8^S - 11/M_8^S - 11 \) reaction channel under B3LYP/6-31g** chemistry model.

The complete process of growth and termination at each step at the two identical sites in the \( M_8^S - 11/M_8^S - 11 \) reaction channel generates structures that obey the following general formula: \((CH_3)_3 Al - [ - Al(CH_3 - O)]_n - Al(CH_3)_3\), where \( n \) is the degree of polymerization, and it is an even number \( (n = 2k) \), with \( n > 6 \).

\[ n = 8 \]

![Scheme 4.2.14](image)
$n = 10$

Scheme 4.2.15 $M_{12}^{10}$

$n = 12$

Scheme 4.2.16 $M_{12}^{14}$

$n = 14$

Scheme 4.2.17 $M_{16}^{14}$
$n = 16$

![Diagram of Scheme 4.2.18 $M_{18}^{16}$](image)

$n = 18$

![Diagram of Scheme 4.2.19 $M_{20}^{18}$, no bridging methyl groups](image)

$n = 20$

![Diagram of Scheme 4.2.20 $M_{22}^{20}$](image)
From previous studies in our group it is known that keeping the bridging methyl groups during the optimization is a quite difficult task. In this work, there were no issues keeping the bridges in all the structures with type I (symmetrical) bridging methyl groups, while in the other series, with type II (asymmetrical) bridging methyl groups, the molecules started to bend with increasing \( n \) and for the most part the bridges couldn’t be kept, generating three coordinate Al sites \(( n = 18, n = 22 \)).

In Table 4.2.3 the molecular weight, \( CH_3/Al \) and \( Al/O \) ratios, and the content of the bridging methyl groups in the proposed structures from the \( M_8^{8'} -11/M_8^{7} -11 \) reaction channel, and MAO and two popular models analogous to isolated aluminoxane species, which it have been shown above can be included in this reaction path, are compared. The molecular weights for the species emerged in this reaction channel are in the range of the most commonly reported molecular weight for MAO, 700-1200 g/mol [1].
One of the major drawbacks of the popular models for MAO, as well as many others proposed by different groups [2], is the failure to explain MAO chemical composition. MAO composition is often expressed as the methyl to aluminum ratio and the oxygen content is determined from the valence balance. The most commonly reported $CH_3/Al$ ratio is in range of 1.4 to 1.5 [1]; values higher than 1.5 and lower than 1.4 have also been reported, and most importantly, it is always higher than 1.

MAO has been named “classic” for $CH_3/Al$ ratio 1:1, “pure” or TMA-free MAO and “real” or TMA-containing MAO. Considering that MAO and TMA behave like independent compounds, no evidence was found for a chemical reaction between TMA and TMA-free MAO and little or no free TMA is found in MAO [12], there is no base for the above classification in “classic”, “real” or “pure” MAO.

In Table 4.2.3, $CH_3/Al$ and $Al/O$ ratios in the structures emerged from $M_8^{8-}/M_8^{7-}$ reaction channel are in the range of experimental MAO stoichiometry, while in the popular models $M_6^6$ and $M_8^8$ are not.

It is now generally accepted that the active species in the metallocene catalyst is a coordinatively unsaturated transition metal cation and that the role of MAO is thus to methylate the metallocene, activate the methylated complex and stabilize the resulting active cationic complex [1]. The presence of bridging methyl groups in MAO has been proven by in situ FTIR spectroscopic studies, and this structural motif is considered fundamental for MAO co-catalytic activity [7]. Through the same studies, the fraction of bridging methyl groups in MAO was
determined, 15-20%, by selective exchange (the terminal groups are inert) of these groups with chlorine on addition of dimethylaluminum chloride (DMAC)[7].

**Table 4.2.3** Summary of structural data for the models developed in $M_8^{\alpha} - 11/M_8^{\beta} - 11$ reaction channel and their comparison with MAO

<table>
<thead>
<tr>
<th>MF</th>
<th>MW [g/mol]</th>
<th>CH$_3$:Al:O</th>
<th>%CH$_3$ br</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_{10}^{6}$</td>
<td>(CH$<em>3$</em>)$<em>4$Al$</em>{10}$O$_6$</td>
<td>608</td>
<td>1.4:1:0.8</td>
</tr>
<tr>
<td>$M_{12}^{10}$</td>
<td>(CH$<em>3$</em>)$<em>6$Al$</em>{12}$O$_{10}$</td>
<td>724</td>
<td>1.3:1:0.83</td>
</tr>
<tr>
<td>$M_{14}^{12}$</td>
<td>(CH$<em>3$</em>)$<em>8$Al$</em>{14}$O$_{12}$</td>
<td>840</td>
<td>1.29:1:0.86</td>
</tr>
<tr>
<td>$M_{16}^{14}$</td>
<td>(CH$<em>3$</em>)$<em>{14}$Al$</em>{16}$O$_{14}$</td>
<td>956</td>
<td>1.25:1:0.87</td>
</tr>
<tr>
<td>$M_{18}^{16}$</td>
<td>(CH$<em>3$</em>)$<em>{20}$Al$</em>{18}$O$_{16}$</td>
<td>1072</td>
<td>1.22:1:0.88</td>
</tr>
<tr>
<td>$M_{20}^{18}$</td>
<td>(CH$<em>3$</em>)$<em>{24}$Al$</em>{20}$O$_{18}$</td>
<td>1188</td>
<td>1.2:1:0.9</td>
</tr>
<tr>
<td>$M_{22}^{20}$</td>
<td>(CH$<em>3$</em>)$<em>{28}$Al$</em>{22}$O$_{20}$</td>
<td>1304</td>
<td>1.18:1:0.91</td>
</tr>
<tr>
<td>$M_{24}^{22}$</td>
<td>(CH$<em>3$</em>)$<em>{30}$Al$</em>{24}$O$_{22}$</td>
<td>1420</td>
<td>1.15:1:0.92</td>
</tr>
<tr>
<td>MAO</td>
<td>-[(CH$<em>3$</em>)$<em>{1.3-1.5}$AlO$</em>{0.7-0.8}$]-n</td>
<td>700-1200</td>
<td>1.3-1.5:1:0.7-0.8</td>
</tr>
<tr>
<td>$M_{6}^{6}$</td>
<td>(CH$<em>3$</em>)$_6$Al$_6$O$_6$</td>
<td>348</td>
<td>1:1:1</td>
</tr>
<tr>
<td>$M_{8}^{8}$</td>
<td>(CH$<em>3$</em>)$_8$Al$_8$O$_8$</td>
<td>464</td>
<td>1:1:1</td>
</tr>
</tbody>
</table>

In the above discussed structures the highest value for the bridging methyl percent is 14 and it decreases with the increase of molecular weight. However, since MAO is not only a polymeric, but also a multi-component material, structures with bridging methyl percentage lower that 15 and higher than 20 are
expected. Contrary to the previously proposed models for MAO, the structures resulting from the $M_{8}^{8} - 11 / M_{8}^{7} - 11$ reaction channel have the molecular weights, $\text{CH}_{3} / \text{Al}$ and $\text{Al} / \text{O}$ ratios in the range of experimental MAO values.

To finish this section, it should be mentioned that besides the fact that with the increase of the molecular weight the type II molecules started to bend, there are no steric or coordinative limitations in this reaction pathway in building “indefinitely” keeping Al four coordinate and O three coordinate in neutral structures. The energetics in Table 4.2.5 just prove it; it shows a linear increase of the electronic energy with the molecular weight or the polymerization step.

**Table 4.2.4** $M_{8}^{8} - 11 / M_{8}^{7} - 11$ reaction channel. Thermodynamic data, in kcal/mol, for the formation of the proposed structures from the hexameric cage

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta E$</th>
<th>$\Delta E^0$</th>
<th>$\Delta H$</th>
<th>$\Delta G$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_{6}^{6} + 2\text{TMA} - \text{OH} + 2\text{TMA} \rightarrow M_{10}^{6} + 4\text{CH}_{4}$</td>
<td>-209.56</td>
<td>-205.06</td>
<td>-206.01</td>
<td>-184.04</td>
</tr>
<tr>
<td>$M_{6}^{6} + 4\text{TMA} - \text{OH} + 2\text{TMA} \rightarrow M_{12}^{10} + 8\text{CH}_{4}$</td>
<td>-394.61</td>
<td>-389.47</td>
<td>-391.89</td>
<td>-376.76</td>
</tr>
<tr>
<td>$M_{6}^{6} + 6\text{TMA} - \text{OH} + 2\text{TMA} \rightarrow M_{14}^{12} + 12\text{CH}_{4}$</td>
<td>-567.75</td>
<td>-560.80</td>
<td>-562.26</td>
<td>-558.27</td>
</tr>
<tr>
<td>$M_{6}^{6} + 8\text{TMA} - \text{OH} + 2\text{TMA} \rightarrow M_{16}^{14} + 16\text{CH}_{4}$</td>
<td>-750.20</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$M_{6}^{6} + 10\text{TMA} - \text{OH} + 2\text{TMA} \rightarrow M_{18}^{16} + 20\text{CH}_{4}$</td>
<td>-922.43</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$M_{6}^{6} + 12\text{TMA} - \text{OH} + 2\text{TMA} \rightarrow M_{20}^{18} + 24\text{CH}_{4}$</td>
<td>-1118.25</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$M_{6}^{6} + 14\text{TMA} - \text{OH} + \text{TMA} \rightarrow M_{22}^{20} + 28\text{CH}_{4}$</td>
<td>-1272.83</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$M_{6}^{6} + 16\text{TMA} - \text{OH} + \text{TMA} \rightarrow M_{24}^{22} + 32\text{CH}_{4}$</td>
<td>-1470.50</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
4.2.4 $M^{8'}_8 - 12 / M^{7}_8 - 12$ and $M^{8'}_8 - 12 / M^{7}_8 - 13$ Reaction Channels.  
A Tri-directional Growth

4.2.4.1 $M^{8'}_8 - 12 / M^{7}_8 - 12$ Reaction Channel

The structures developed considering the growth after the cage as in $M^{8'}_8 - 12$ and the $M^{7}_8 - 12$ termination motif, when at each step the monomeric growth is followed by a termination with $TMA$, obey the following general formula:

$\text{CH}_n\text{AlOCH}_n^+$, where $n = 3k$, with $k = 1, 2, 3, etc.$ and $n \geq 3$

In this development the system becomes quite large with increasing $n$; for $n = 6$ the system already contains 160 atoms. Since the limit of ab initio calculations to some hundred atoms even if high-performance computers are available [60], only the models developed for $n = 3$ and $n = 6$ have been considered for electronic structure calculations under the first principles theory. $n = 3$, $(\text{CH}_3)_{18}\text{Al}_{12}\text{O}_9$, presents three bridging methyl groups, and it has been
called $M_{12}^{9} - 1$ to be differentiate from another geometry with the same chemical composition that will be discussed in the next section.

\[ n = 6, \ (CH_3)_{30}Al_{18}O_{12}, \text{ contains six bridging methyl groups, three groups of two in adjacent positions} \]
The bridging methyl groups present in $M_{12}^{9} - 1$ are of type II, while in $M_{18}^{12}$ beside type II a new type is present, type III, which is again an asymmetrical bridge connecting the same kind of aluminum sites as type II but in a four membered ring.

![Figure 4.2.4 Type III bridging methyl, asymmetrical, connecting AlCO$_2$ and AlC$_2$O sites in a four-membered ring](image)

**Figure 4.2.4** Type III bridging methyl, asymmetrical, connecting AlCO$_2$ and AlC$_2$O sites in a four-membered ring

### 4.2.4.2 $M_{8}^{8'} - 12 / M_{8}^{7} - 13$ Reaction Channel

The structures developed considering the growth after the cage as in $M_{8}^{8'} - 12$ and the $M_{8}^{7} - 13$ termination motif, a tri-directional growth when no bridging methyl groups are formed, obey the following general formula:

$-[-Al(CH_3) - O-]_n - 3Al(CH_3)_3$, where $n = 3k$, with $k = 1, 2, 3, etc.$ and $n > 6$.

Due to the lack of bridging methyl groups, the models emerged from this reaction channel are not considered of interest for the MAO function of dimethylating the metallocene, and only the first and second generations have been considered for electronic structure calculations. However, under the assumption of MAO role as Lewis acid in the metallocene catalytic systems, as a result of the presence of three-coordinate Al sites, these structures could still be
considered MAO catalytically active components since components with coordinatively unsaturated non-octet three-coordinate Al centers are strong Lewis acids.

\[ n = 9, \quad (CH_3)_{18}Al_{12}O_9 \]  
This geometry has already been proposed [7] but in a different context: to explain the MAO composition \((CH_3/Al = 1.5)\); here it emerges from the mechanism.

![Scheme 4.2.24](image)

\[ n = 12, \quad (CH_3)_{21}Al_{15}O_{12} \]

![Scheme 4.2.25](image)
The molecular weights and chemical composition for the proposed structures in $M_8^{8'}-12/M_8^7-12$ and $M_8^{8'}-12/M_8^7-13$ reaction channels, as presented in Table 4.2.5, are in the range of reported values for MAO.

**Table 4.2.5** Summary of the structural data for the models developed in $M_8^{8'}-12/M_8^7-12$ and $M_8^{8'}-12/M_8^7-13$ reaction channels, and their comparison with MAO

<table>
<thead>
<tr>
<th>MF</th>
<th>MW [g/mol]</th>
<th>CH$_3$:Al:O</th>
<th>%CH$_3$br</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\text{CH}<em>3)</em>{18}\text{Al}_{12}\text{O}_9$</td>
<td>738</td>
<td>1.5:1:0.75</td>
<td>17</td>
</tr>
<tr>
<td>$(\text{CH}<em>3)</em>{21}\text{Al}<em>{15}\text{O}</em>{12}$</td>
<td>912</td>
<td>1.4:1:0.8</td>
<td>0</td>
</tr>
<tr>
<td>$(\text{CH}<em>3)</em>{24}\text{Al}<em>{18}\text{O}</em>{15}$</td>
<td>1086</td>
<td>1.33:1:0.83</td>
<td>0</td>
</tr>
<tr>
<td>$(\text{CH}<em>3)</em>{27}\text{Al}<em>{21}\text{O}</em>{18}$</td>
<td>1260</td>
<td>1.29:1:0.86</td>
<td>0</td>
</tr>
<tr>
<td>$(\text{CH}<em>3)</em>{30}\text{Al}<em>{18}\text{O}</em>{12}$</td>
<td>1128</td>
<td>1.6:1:0.67</td>
<td>0</td>
</tr>
<tr>
<td>$(\text{CH}<em>3)</em>{42}\text{Al}<em>{24}\text{O}</em>{15}$</td>
<td>1518</td>
<td>1.75:1:0.63</td>
<td>22</td>
</tr>
<tr>
<td>$-[(\text{CH}<em>3)</em>{1.3-1.5}\text{AlO}_{0.7-0.8}]_n$</td>
<td>700-1200</td>
<td>1.3-1.5:1:0.7-0.8</td>
<td>15-20</td>
</tr>
</tbody>
</table>

Thermodynamically, contrary to the expectations, the “tilted” $M_{12}^{9} - 1$ isomer is slightly more stable that the $M_{12}^{9} - 2$ isomer (in Table 4.2.6 a difference of 3.74 kcal/mol in their $\Delta G$ formation from the hexameric cage).

In conclusion, the species generated through $M_8^{8'}-12/M_8^7-12$ reaction channel are very good candidates to support the experimental evidence
regarding bridging methyl in MAO structure, and, as will be shown later, to explain its role in the metalloocene activation.

**Table 4.2.6** $M_8^8 - 12 / M_8^7 - 12$ and $M_8^8 - 12 / M_8^7 - 12$ reaction channels. Thermodynamic data, in kcal/mol, for the formation of the proposed structures from the hexameric cage.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta E$</th>
<th>$\Delta E^0$</th>
<th>$\Delta H$</th>
<th>$\Delta G$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_6^6 + 3TMA - OH_2 + 3TMA \rightarrow M_{12}^9 - 1 + 6CH_4$</td>
<td>-307.03</td>
<td>-299.74</td>
<td>-301.07</td>
<td>-268.82</td>
</tr>
<tr>
<td>$M_6^6 + 3TMA - OH_2 + 3TMA \rightarrow M_{12}^9 - 2 + 6CH_4$</td>
<td>-300.36</td>
<td>-295.23</td>
<td>-298.15</td>
<td>-265.08</td>
</tr>
<tr>
<td>$M_6^6 + 6TMA - OH_2 + 3TMA \rightarrow M_{15}^{12} + 12CH_4$</td>
<td>-567.71</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$M_6^6 + 9TMA - OH_2 + 3TMA \rightarrow M_{18}^{15} + 16CH_4$</td>
<td>-750.20</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$M_6^6 + 6TMA - OH_2 + 6TMA \rightarrow M_{18}^{12} + 12CH_4$</td>
<td>-552.67</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4.2.5 $M_7^T - 2 / M_7^T - 3$ Reaction Channel

4.2.5.1 The Growth Motifs

So far, reaction paths in MAO formation from structure $M_7^T - 1$ have been considered. As discussed in the beginning of this section, the insertion of the monomer at the hexameric cage in the axial approach favors $M_7^T - 3$ formation (please see Table 4.2.1).
The insertion of a second monomer is a bifurcation point, and $M_8^{s'} - 31$ and $M_8^{s'} - 32$ isomers are formed. Once again, contrary to what common sense would suggest, structure $M_8^{s'} - 32$ is more stable (24.7 kcal/mol) than the $M_8^{s'} - 31$ isomer.

The reaction of $M_8^{s'} - 32$ with another monomer generates $M_9^s$ structure. A similar nonameric cage has been isolated in the case of t-butylaluminimoxanes [6].
Table 4.2.7: \( M_7^- - 2/M_7^- - 3 \) reaction channel. Thermodynamic data, in kcal/mol, for its growth and termination patterns calculated under B3LYP/6-31g** chemistry model.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( \Delta E^0 )</th>
<th>( \Delta H )</th>
<th>( \Delta G )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( M_6^6 + TMA - OH_2 \rightarrow M_7^7 + CH_4 )</td>
<td>1</td>
<td>-68.44</td>
<td>-68.76</td>
</tr>
<tr>
<td>( M_7^7 - 3 + TMA - OH_2 \rightarrow M_9^9 - 3 + CH_4 )</td>
<td>1</td>
<td>-48.42</td>
<td>-48.37</td>
</tr>
<tr>
<td>( M_8^8 - 32 + TMA - OH_2 \rightarrow M_9^9 + 4CH_4 )</td>
<td></td>
<td></td>
<td>-155.25</td>
</tr>
<tr>
<td>( M_7^7 - 3 + M_2^{2+} \rightarrow M_9^9 + 3CH_4 )</td>
<td></td>
<td></td>
<td>-121.98</td>
</tr>
<tr>
<td>( M_7^7 - 2 + TMA \rightarrow M_7^7 - 21 + CH_4 )</td>
<td></td>
<td></td>
<td>-65.32</td>
</tr>
<tr>
<td>( M_7^7 - 2 + TMA \rightarrow M_7^7 - 22 + CH_4 )</td>
<td></td>
<td></td>
<td>-46.89</td>
</tr>
<tr>
<td>( M_7^7 - 3 + TMA \rightarrow M_7^7 - 31 + CH_4 )</td>
<td></td>
<td></td>
<td>-40.98</td>
</tr>
<tr>
<td>( M_7^7 - 3 + TMA \rightarrow M_7^7 - 32 + CH_4 )</td>
<td></td>
<td></td>
<td>-37.70</td>
</tr>
</tbody>
</table>
Through the proposed mechanism, $M_g^2$ structure can also be formed by reaction of $M_g^7 - 3$ with the dimer, or by reaction of the hexameric cage with the trimer.

**4.2.5.2 The Termination Motifs**

Searching for reaction pathways from $M_g^7 - 2$ and $M_g^7 - 3$ structures several termination patterns were identified.

**Scheme 4.2.30** $M_g^7 - 21$

**Scheme 4.2.31** $M_g^7 - 22$
$M_{8}^{7} - 21$ and $M_{8}^{7} - 22$ were identified as the termination models from $M_{7}^{7} - 2$ structure, while $M_{8}^{7} - 31$, $M_{8}^{7} - 32$ and $M_{10}^{9}$ from $M_{7}^{7} - 3$ structure. As mentioned above, $M_{7}^{7} - 3$ formation is thermodynamically favored over $M_{7}^{7} - 2$ formation, so that the energetic associated with the termination patterns will be discussed separately for each series. Again, the search for termination motifs involving bridging methyl groups was the focus.

The series from $M_{7}^{7} - 2$ requires the breaking of a square-hexagonal $Al - O$ bond at the cage. Even though $M_{8}^{7} - 21$ is a more stable structure than $M_{8}^{7} - 22$ and its formation from $M_{7}^{7} - 2$ is thermodynamically favored (please see the energetics of their formation in Table 4.2.7), from structural point of view the latter is a more interesting species. It has an unique five-coordinate aluminum site (Al10), and two bridging methyl groups. The complete molecule emerged from $M_{7}^{7} - 2 / M_{8}^{7} - 22$ growth and $M_{10}^{9} - 2$ termination pattern will be considered for further structural calculations.

![Scheme 4.2.32 $M_{8}^{7} - 31$](image1)

![Scheme 4.2.33 $M_{8}^{7} - 32$](image2)
4.2.5.3 $M_7^7 - 2 / M_7^7 - 3$ Proposed Structures

Based of the above discussion, the proposed models from this reaction channel are:

- $M_{10}^8 - 2$, a rod-like structure featuring two five-coordinate Al sites and four bridging methyl groups, two of type I and other two of new type (type IV), connecting AlO$_3$ and AlC$_2$O sites;
• $M^0_{12} - 3$ cage structure, which has already been proposed as a suitable model for MAO in solutions. It was considered to reflect well the experimentally determined stoichiometry, molecular weight, bridges fraction, inertness towards $TMA$, and reactivity towards donors [7]. In present work, this structure emerges from the mechanism, and along with other structures is a suitable model for MAO, for the reasons described above.

Scheme 4.2.36 $M^0_{12} - 3$
Table 4.2.8  \( M_{10}^{+} - 2 / M_{12}^{+} - 3 \) reaction channel. Structural data for the proposed models and their comparison with MAO

<table>
<thead>
<tr>
<th>Structure</th>
<th>MF</th>
<th>MW [g/mol]</th>
<th>CH(_3):Al:O</th>
<th>%CH(_3) br</th>
</tr>
</thead>
<tbody>
<tr>
<td>( M_{10}^{8} - 2 )</td>
<td>(CH(<em>3))(</em>{14})Al(<em>{10})O(</em>{8})</td>
<td>608</td>
<td>1.4:1:0.8</td>
<td>28</td>
</tr>
<tr>
<td>( M_{12}^{9} - 3 )</td>
<td>(CH(<em>3))(</em>{18})Al(<em>{12})O(</em>{9})</td>
<td>738</td>
<td>1.5:1:0.75</td>
<td>17</td>
</tr>
<tr>
<td>MAO</td>
<td>-[(CH(<em>3))(</em>{1.3-1.5})AlO(<em>{0.7-0.8})](</em>{-n}), ( n=12-20 )</td>
<td>700-1200</td>
<td>1.3-1.5:1:0.7-0.8</td>
<td>15-20</td>
</tr>
</tbody>
</table>

In Table 4.2.8, the structures proposed from \( M_{10}^{+} - 2 / M_{12}^{+} - 3 \) reaction channel have the MAO chemical composition. Regarding the content of bridging methyl groups \( M_{12}^{9} - 3 \) has the MAO bridge fraction, and a fraction with 8% higher than the average experimental value, in the case of \( M_{10}^{8} - 2 \), is not unexpected considering the method used on its determination and the fact that bridging methyl motif is not a characteristic of all the proposed possible MAO components. The molecular weight of the two proposed structures in this reaction channel are slightly at the limit of the most reported average molecular weight for MAO, but as mentioned in the introduction chapter, the overall reported molecular weights for MAO vary between 400 and 3000 g/mol [8,11].

4.2.6 Bridging Methyl Motif and the MAO Co-catalytic Activity

Bridging methyl groups have been identified for ethylaluminoxane based on \(^1\)H NMR [61], and, by analogy, their presence in MAO have been suggested. Often in this work isolated and spectroscopically characterized t-butylaluminoxane species were used as reference. However, no aluminoxane structure displaying the three-center two-electron methyl bridge has been
crystallographically characterized. Due to structural differences between methyl and bulky butyl substituents, the former has the ability to act as a bridging ligand, and it was suggested as possible that some structural types present in MAO will not be found in t-butylaluminoxane series [6].

In situ FTIR studies showed that bridging methyl groups are present and constitute a fundamental feature of MAO, being essential for the activation of metallocene catalysts [7]. As it will be shown in the next section, IR assignments for the symmetrical deformation of bridging methyl groups from DFT calculations on the models proposed are in agreement with experiment.

It is generally accepted that the active species in the metallocene catalyst is a coordinatively unsaturated transition metal cation and that the role of MAO is thus to methylate the metallocene, activate the methylated complex and stabilize the resulting active cationic complex [1].

Complexation

\[ Cp_2MCl_2 + MAO \Leftrightarrow Cp_2MCl_2 \cdot MAO \]

Mono-methylation

\[ Cp_2MCl_2 \cdot MAO \Leftrightarrow Cp_2M(CH_3)Cl + MAO - Cl \]

Activation of the catalyst by di-methylation

\[ Cp_2M(CH_3)Cl \cdot MAO \Leftrightarrow [Cp_2M(CH_3)]^+ + [MAO - Cl]^- \]

Cp stands for cyclopentadienyl; M represents the metal in the metallocene and it can be Zr, Ti or Hf, and \([Cp_2MCH_3]^+\) are considered the catalytically active species. It has been shown that only one of the chlorines of the metallocene is
easily methylated [13], even TMA can do this, but the bridging methyl groups in MAO are necessary for the activation of the catalyst [62].

4.2.7 Suitable Models for MAO Catalytically Active Components

By considering just the molecular weight and the chemical composition of MAO, all of the structures proposed in the above discussed reaction channels are good candidates for the MAO structure. The large majority of the previously proposed models which are \((AlOCH_3)_n\) cages [2] in which the ratio \(CH_3/Al = 1\), while in MAO it has been always reported as being higher than 1, failed to explain its composition.

Taking into account the preceding analysis regarding the necessity of bridging methyl groups in MAO structure for the activation of metallocene catalysts, the following structures are considered suitable structural models for the catalytically active components of the MAO multi-component material:

- the type I series from the \(M_8^{11}/11/11 \) reaction channel, including \(M_{10}^{5}, M_{14}^{12}\) and so on, and the first two species of the type II series from same reaction path, \(M_{12}^{10}\) and \(M_{16}^{14}\);

- \(M_{12}^{12} - 1\) and \(M_{18}^{12}\) from \(M_8^{12}/12/12\) reaction channel, with the mention that the latter is a special case since it contains three groups of two adjacent methyl bridges each and the activation of the metallocene is done by di-methylation;

- \(M_{10}^{5} - 2\) and \(M_{12}^{9} - 3\) from \(M_7^{7} - 2/M_7^{7} - 3\) reaction path.

In the next section, to validate the proposed MAO structures, their calculated IR and NMR data are compared with the experimental data.
4.3 IR and NMR Calculated Spectra for the Proposed Structures. Comparison with Experimental Data for MAO

4.3.1 IR Spectra Analysis

In this section calculated IR assignments for $C-H$ symmetrical deformation bands in the proposed structures are compared with MAO vibrational spectra in toluene [12,63].

Figure 4.3.1 The IR spectrum of MAO in toluene. a) mid-IR region (wavenumbers on logarithmic scale); b) C-H stretching bands; c) far-IR region. The toluene spectrum has been removed.*

*Reprinted from Vibrational Spectroscopy, Volume 24, Eilertsen et al., In Situ FTIR Spectroscopy during addition of trimethylaluminium (TMA) to methylaluminoxane (MAO) shows no formation of MAO-TMA compounds, pages 257-264, Copyright 2000, with permission from Elsevier.
In Figures 4.3.1 the bands responsible for the \( C-H \) symmetrical deformations are positioned at 1260-1190 cm\(^{-1}\). Two clearly determined bands were reported; one attributed to bridging methyl groups (1257 cm\(^{-1}\)), and the other one to the terminal methyl groups (1220-1200 cm\(^{-1}\)).

![Figure 4.3.2](image)

**Figure 4.3.2** Part of the spectra of TMA-depleted MAO in toluene after repeated additions of TMA as a toluene solution. The toluene spectrum has been subtracted. The band attributed to symmetric deformation of terminal methyl in MAO is reported at 1200-1220 cm\(^{-1}\) and the band corresponding to symmetric deformation of bridging methyl groups in MAO is reported at 1257 cm\(^{-1}\). The peaks at 1197 cm\(^{-1}\) and 1250 cm\(^{-1}\) correspond to terminal and bridging methyl groups, respectively, in TMA. Please refer to the copyright permission on the previous page.

The IR MAO spectra in Figure 4.3.2 not only give details of the IR region of interest, but also show no evidence of a chemical reaction between TMA and TMA-depleted MAO in toluene solution at room temperature. The spectra of the mixture is a superposition of the spectra of the two components, with the mention that experiments at 80\(^{\circ}\)C give the same results [12].
It is known that DFT methods tend to overestimate the frequency calculations. However, their overestimation is generally found to be uniform so that scaling factors can be used to give good agreement with the experimentally obtained vibrations. In a study of vibrational frequency prediction using density functional theory for a total of 1066 molecules, a deviation in the range of 34-48 cm\(^{-1}\) is considered a good agreement with experiment [40]. As described in the computational details section, in this work, the vibrational frequencies were calculated for tight optimized geometries at a level of theory and basis sets which are considered to give accurate predictions, B3LYP and 6-31g**, respectively, and used scaled.

![Figure 4.3.3](image)

**Figure 4.3.3** Calculated IR spectrum for \(M_{10}^{3}((\text{CH}_3)_{14}\text{Al}_{10}\text{O}_8)\).

Details in the 1100-1400 cm\(^{-1}\) region corresponding to symmetrical \(C–H\) deformations in bridging (1286 cm\(^{-1}\)) and terminal methyl (1215-1225 cm\(^{-1}\)) groups.
Before discussing the calculated IR spectra must be mentioned that Molden [64], with the Gaussian line-shape option, was the visualization package used to display the Gaussian03 [35] calculated IR vibrational modes.

In $M_{10}^8$ structure, (CH₃)$_{14}$Al$_{10}$O$_8$, the frequencies associated with the terminal methyl groups symmetrical deformation modes are in very good agreement with experiment. The bridging methyl groups (type I, symmetrical) are overestimated by 29 cm⁻¹, still in a good agreement with experiment.

In $M_{12}^{10}$ structure, (CH₃)$_{16}$Al$_{12}$O$_{10}$, the frequencies associated with the terminal methyl groups symmetrical deformation modes are in very good agreement with the experiment. The frequency of vibrational mode associated with bridging methyl groups (type II, asymmetrical) symmetrical stretch is overestimated by 12 cm⁻¹, which is considered a good agreement with experiment.

![Figure 4.3.4 Calculated IR spectrum for $M_{12}^{10}$ ((CH₃)$_{16}$Al$_{12}$O$_{10}$).](image)

Details in the 1100-1400 cm⁻¹ region corresponding to symmetrical $C-H$ deformations in bridging (1269 cm⁻¹) and terminal methyl (1215-1225 cm⁻¹) groups.
In $M_{14}^{12}$ structure, $(\text{CH}_3)_{18}\text{Al}_{14}\text{O}_{12}$, the frequencies associated with the terminal methyl groups symmetrical deformation modes are in very good agreement with experiment. The frequency of vibrational mode associated with bridging methyl groups (type II) symmetrical stretch is overestimated by 29 cm$^{-1}$, which again, is still in good agreement with experiment.

**Figure 4.3.5** Calculated IR spectrum for $M_{14}^{12}((\text{CH}_3)_{22}\text{Al}_{18}\text{O}_{12})$. Details in the 1100-1400 cm$^{-1}$ region corresponding to symmetrical $C-H$ deformations in bridging (1283 cm$^{-1}$) and terminal (1216-1233 cm$^{-1}$) methyl groups.
In $M_{12}^9{\text{−1}}$ structure, $(\text{CH}_3)_{18}\text{Al}_{12}\text{O}_9$, the frequencies associated with the terminal methyl groups symmetrical deformation modes are in good agreement with the experiment (overestimated by 11 cm$^{-1}$). The frequency of vibrational mode associated with bridging methyl groups (type II) symmetrical stretch is also in very good agreement with experiment.

**Figure 4.3.6** Calculated IR spectrum for $M_{12}^9{\text{−1}}((\text{CH}_3)_{18}\text{Al}_{12}\text{O}_9)$. Details in the 1100-1400 cm$^{-1}$ region corresponding to symmetrical $C–H$ deformations in bridging (1248 cm$^{-1}$) and terminal methyl (1211-1231 cm$^{-1}$) groups.
In $M_{12}^9 - 2$, $(\text{CH}_3)_{18}\text{Al}_{12}\text{O}_9$, no bridging methyl groups are present and the frequencies associated with the terminal methyl groups symmetrical deformation modes are in good agreement with experiment.

**Figure 4.3.7** Calculated IR spectrum for $M_{12}^9 - 2 ((\text{CH}_3)_{18}\text{Al}_{12}\text{O}_9)$. No bridging methyl groups. The vibrational mode associated with symmetrical deformation of terminal methyl groups is located at 1207-1232 cm$^{-1}$. 
In $M_{10}^5 - 2$, $(CH_3)_{14}Al_{10}O_8$, the frequencies associated with the terminal methyl groups symmetrical deformation modes are in very good agreement with experiment. In the case of bridging methyl groups (type I and type IV), the vibrational mode associated with their symmetrical stretch is overestimated by 11-19 cm$^{-1}$, which is also in good accordance with experiment.

![Calculated IR spectrum for $M_{10}^5 - 2$ ($(CH_3)_{14}Al_{10}O_8$). The vibrational mode associated with symmetrical deformation of terminal methyl groups is located at 1216 – 1222 cm$^{-1}$, and the band corresponding to symmetrical stretch of bridging methyl groups is located at 1268 – 1276 cm$^{-1}$.](image)

**Figure 4.3.8** Calculated IR spectrum for $M_{10}^5 - 2$ ($(CH_3)_{14}Al_{10}O_8$). The vibrational mode associated with symmetrical deformation of terminal methyl groups is located at 1216 – 1222 cm$^{-1}$, and the band corresponding to symmetrical stretch of bridging methyl groups is located at 1268 – 1276 cm$^{-1}$.
In $M_{12}^9 - 3$ structure, $(\text{CH}_3)_{18}\text{Al}_{12}\text{O}_9$, the frequencies associated with the terminal methyl groups symmetrical deformation modes are overestimated by 15 cm$^{-1}$, while in the case of bridging methyl groups (type I), the vibrational mode associated with their symmetrical deformation is overestimated by 32 cm$^{-1}$.

**Figure 4.3.9** Calculated IR spectrum for $M_{12}^9 - 3((\text{CH}_3)_{18}\text{Al}_{12}\text{O}_9)$. The vibrational mode associated with symmetrical deformation of terminal methyl groups is located at 1213 – 1235 cm$^{-1}$, and the band corresponding to symmetrical stretch of bridging methyl groups is located at 1289 cm$^{-1}$. 
Table 4.3.1 Calculated IR C – H symmetrical deformations band positions in the proposed structures and comparison with MAO

<table>
<thead>
<tr>
<th>Structure</th>
<th>symmetrical stretch band/cm(^{-1})</th>
<th>terminal CH(_3)</th>
<th>µ CH(_3)/type</th>
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</thead>
<tbody>
<tr>
<td>(TMA_2)</td>
<td>calc. 1216.00</td>
<td>1249.49</td>
<td></td>
</tr>
<tr>
<td></td>
<td>exp. [63] 1197</td>
<td>1250</td>
<td></td>
</tr>
<tr>
<td>(M_{10}^8)</td>
<td>1215-1225</td>
<td>1286/I</td>
<td></td>
</tr>
<tr>
<td>(M_{12}^{10})</td>
<td>1215-1225</td>
<td>1269/II</td>
<td></td>
</tr>
<tr>
<td>(M_{14}^{12})</td>
<td>1216-1233</td>
<td>1283/I</td>
<td></td>
</tr>
<tr>
<td>(M_{12}^9 - 1)</td>
<td>1212-1231</td>
<td>1248/II, III</td>
<td></td>
</tr>
<tr>
<td>(M_{12}^9 - 2)</td>
<td>1207-1232</td>
<td>Not present</td>
<td></td>
</tr>
<tr>
<td>(M_{10}^8 - 2)</td>
<td>1216-1222</td>
<td>1268-1276/IV, I</td>
<td></td>
</tr>
<tr>
<td>(M_{12}^9 - 3)</td>
<td>1213-1235</td>
<td>1289/I</td>
<td></td>
</tr>
<tr>
<td><strong>MAO</strong></td>
<td><strong>1200-1220</strong></td>
<td><strong>1257</strong></td>
<td></td>
</tr>
</tbody>
</table>

In Table 4.3.1 calculated IR vibrational modes associated with symmetrical deformation of terminal and bridging methyl groups are in very good agreement with the experimental values, validating the IR analysis for the proposed MAO structures. The predicted frequencies associated with the symmetrical stretch vibrational mode from the type I bridging methyl groups are located at 1283±5 cm\(^{-1}\). The IR calculations show that type II and III bridging methyl groups are undistinguishable, and their corresponding symmetrical stretch vibrational mode is located at 1258±10 cm\(^{-1}\), in very good agreement with experiment, suggesting that the theses types or type of methyl bridges may be
dominant in MAO structure. The predicted frequency associated with the symmetrical stretch vibrational mode from the type IV bridging methyl groups is also in very good agreement with experiment.

Regarding the IR fingerprint of the terminal methyl groups in the proposed structures, the predicted band associated with their symmetrical deformation vibrational modes is located at 1207-1235 cm\(^{-1}\), in a very good accordance with experiment.

From the IR vibrational analysis of MAO can be concluded that the predicted IR vibrational modes for the proposed MAO structural models, via B3LYP functional with 6-31g** polarized spilt-valence basis sets, are in good agreement with experimental IR analysis of MAO, making the proposed structures suitable models for the MAO structure.

4.3.2 \(^{27}\text{Al} \) NMR MAO Analysis

MAO NMR spectroscopic fingerprint, using either \(^{27}\text{Al} \) NMR, \(^{13}\text{C} \) NMR, \(^{1}\text{H} \) NMR or \(^{17}\text{O} \) NMR to characterize final products or \textit{in situ}, is almost featureless. Different NMR methods and techniques have been used to investigate MAO structure, and 19.6T MAS NMR, Frequency-Stepped NMR, Field-Swept NMR \cite{47} and 2D NMR (DOSY) \cite{9} are just a few of them. The literature has a large volume of data, but very often the results are contradictory.

Given the multi-component material nature of MAO a perfect match of its spectra by a single structure is not expected. In this section calculated \(^{27}\text{Al} \) and \(^{1}\text{H} \) NMR spectra for the proposed MAO structures are compared with experiment.

\(^{27}\text{Al} \) NMR spectroscopic measurements of MAO show predominantly four-coordinate Al centers, but also three and five coordinate Al sites were considered
The most commonly, chemical shifts of Al sites in MAO are reported in the range of 110±10 and 149-153 ppm [6,65]. Also, resonances at 60 ppm attributed to a five-coordinate aluminum [4], and at 200 ppm attributed to three-coordinate Al sites [6], have been reported.

From previous studies, due to high quadrupolar moments all Al sites in MAO have high quadrupolar constants requiring high magnetic field in solid state NMR analysis (please refer to Figure 4.3.9).

![Figure 4.3.9](image.png)

**Figure 4.3.9** The maximum Cq values accessible by MAS NMR spectroscopy at a given combination of magnetic field and MAS spin rate.*

*Reprinted from [47] with permission from American Chemical Society, as documented in Letters of Permission.

Before discussing the calculated results must be mentioned that:

- a four-coordinate aluminum center in a $R_2\text{AlO}_2$ coordination environment, the case of t-butylaluminoxanes, for a species similar to
\( M_4^+ \) in this work was reported of having a broad resonance at 142 ppm [6];

- resonance for four-coordinate aluminum center in a \( RAlO_3 \) coordination environment, the case of t-butylaluminoxanes for the hexameric cage similar to \( M_6^+ \) in this work, was reported at 112 ppm [6];
- a three-coordinate aluminum center in the \( ^{27}\text{Al} \) NMR t-butylaluminoxane species spectrum was observed at 200 ppm after heating (800°C) [6];

Table 4.3.2 \( M_8^{8+} - 11/ M_8^+ - 11 \) reaction channel. Calculated \( ^{27}\text{Al} \) NMR parameters under GIAO method at HF/6-31g** level from B3LYP/6-31g** geometries

<table>
<thead>
<tr>
<th>( M_8^{10}_{10} )</th>
<th>( ^{10}\text{Cq} )</th>
<th>( \delta )</th>
<th>( ^{12}\text{Cq} )</th>
<th>( \delta )</th>
<th>( ^{14}\text{Cq} )</th>
<th>( \delta )</th>
<th>( ^{16}\text{Cq} )</th>
<th>( \delta )</th>
<th>( ^{18}\text{Cq} )</th>
<th>( \delta )</th>
<th>( ^{20}\text{Cq} )</th>
<th>( \delta )</th>
<th>( ^{22}\text{Cq} )</th>
<th>( \delta )</th>
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<tr>
<td>( \eta )</td>
<td>( \text{Cq} )</td>
<td>( \delta )</td>
<td>( \eta )</td>
<td>( \text{Cq} )</td>
<td>( \delta )</td>
<td>( \eta )</td>
<td>( \text{Cq} )</td>
<td>( \delta )</td>
<td>( \eta )</td>
<td>( \text{Cq} )</td>
<td>( \delta )</td>
<td>( \eta )</td>
<td>( \text{Cq} )</td>
<td>( \delta )</td>
</tr>
<tr>
<td>0.65</td>
<td>-18.70</td>
<td>120.10</td>
<td>0.33</td>
<td>-16.10</td>
<td>106.90</td>
<td>0.88</td>
<td>19.80</td>
<td>143.70</td>
<td>0.26</td>
<td>-21.22</td>
<td>124.80</td>
<td>0.63</td>
<td>-17.70</td>
<td>120.20</td>
</tr>
<tr>
<td>0.66</td>
<td>-19.10</td>
<td>117.30</td>
<td>0.38</td>
<td>-15.70</td>
<td>109.40</td>
<td>0.90</td>
<td>20.10</td>
<td>143.80</td>
<td>0.27</td>
<td>-20.60</td>
<td>127.30</td>
<td>0.64</td>
<td>-19.85</td>
<td>119.10</td>
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<td>0.68</td>
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<td>0.35</td>
<td>-15.93</td>
<td>109.80</td>
<td>0.91</td>
<td>20.40</td>
<td>144.50</td>
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<td>127.30</td>
<td>0.65</td>
<td>-20.14</td>
<td>120.20</td>
</tr>
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<td>0.70</td>
<td>-19.40</td>
<td>117.40</td>
<td>0.35</td>
<td>-16.11</td>
<td>110.10</td>
<td>0.91</td>
<td>20.10</td>
<td>144.50</td>
<td>0.29</td>
<td>-20.59</td>
<td>127.60</td>
<td>0.65</td>
<td>-20.54</td>
<td>120.00</td>
</tr>
<tr>
<td>0.46</td>
<td>-19.54</td>
<td>118.24</td>
<td>0.24</td>
<td>-15.83</td>
<td>109.58</td>
<td>0.87</td>
<td>26.89</td>
<td>164.95</td>
<td>0.92</td>
<td>-13.45</td>
<td>127.56</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.39</td>
<td>-16.38</td>
<td>117.98</td>
<td>0.35</td>
<td>-16.27</td>
<td>110.18</td>
<td>0.99</td>
<td>26.37</td>
<td>162.39</td>
<td>0.87</td>
<td>-13.89</td>
<td>125.54</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>0.46</td>
<td>-19.28</td>
<td>116.52</td>
<td>0.35</td>
<td>-15.93</td>
<td>109.03</td>
<td>0.88</td>
<td>20.03</td>
<td>143.22</td>
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<td>35.73</td>
<td>194.96</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>0.46</td>
<td>-19.29</td>
<td>116.48</td>
<td>0.36</td>
<td>-15.23</td>
<td>109.38</td>
<td>0.88</td>
<td>20.06</td>
<td>143.23</td>
<td>0.74</td>
<td>35.63</td>
<td>193.60</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
is in accordance with reported chemical shifts for other three-coordinate aluminum compounds with a $R_2AlO$ coordination environment ($\delta = 180 - 200 \text{ ppm}$) [66].

$^{27}$Al chemical shifts are reported relative to trimethylaluminum ($\delta = 153 \text{ ppm}$) [4,6]. Analyzing the calculated $^{27}$Al NMR parameters from $M_8^{8'} - 11 / M_8^{7} - 11$ reaction channel (Table 4.3.2) first must be noticed that based on the chemical shifts, the method gives a good description of the coordination environments that may be found in MAO; the predicted three-coordinate Al sites in $R_2AlO$ coordination environment, four-coordinate Al sites in $R_2AlO_2$ coordination environment, and four-coordinate Al sites in $RALO_2$ coordination environment are in good or excellent agreement with experiment.

For the above considered MAO reaction channel, based on the chemical shift, Al sites in several distinct coordination environments can be identified:

- $\delta = 107 - 127 \text{ ppm}$ corresponding to four-coordinate Al sites in $AlCO_3$ (4 and 6 ring), and $AlCO_2\mu CH_3$ (4 and 6 ring) coordination environments which corresponds to the reported resonance at $\delta = 110 \pm 10 \text{ ppm}$ in MAO spectrum [4];
- $\delta = 195 \text{ ppm}$ corresponding to three-coordinate Al sites in $R_2AlO$ coordination environment which is in agreement with the reported chemical shift for the three-coordinate aluminum center in the $^{27}$Al NMR t-butylaluminoxane species spectrum at 200 ppm [6];
• $\delta = 143 \, ppm$ corresponding to four-coordinate Al sites in $R_2AlO_2$ coordination environment which is in very good agreement with the reported four-coordinate aluminum center at 142 ppm [6] in the case of t-butylaluminoxanes;

• $\delta = 163 \, ppm$ corresponding to four-coordinate Al sites in $AlC_2O\mu CH_3$ coordination environment, which if present couldn’t yet be detected by solid-state $^{27}$Al NMR, and t-butylaluminoxane species with bridging methyl groups had not been crystallographically characterized even though there are claims of synthesizing such species [61,67].

Notice also that for all Al sites in the considered MAO reaction channel the quadupolar coupling constant is higher than 13 MHz, with a maximum around 37 MHz corresponding to the three-coordinate Al site. To detect all the predicted Al sites, according to Figure 4.3.9, magnetic fields higher than the highest used so far (40 T) are required.

The calculated NMR parameters for the structures emerged from $M_8^8 - 12 / M_6^7 - 12$ and $M_8^{8'} - 13 / M_6^7 - 13$ reaction channels are presented in Table 4.3.3. Compared with the above discussed reaction path no new Al sites are added but through the new structures the chemical shift for four-coordinate Al sites in $R_2AlO_2$ coordination environment expands beyond 150 ppm, which is in agreement with the observed resonance at 149-153 ppm in MAO spectra.

$M_7^7 - 2 / M_7^7 - 3$ reaction channel brings a new feature in MAO spectrum, which is a five-coordinate Al site ($AlO_4\mu CH_3$) at 69 ppm and with a high value for
Table 4.3.3 $M_9^{12} / M_9^{12}$ and $M_9^{15} / M_9^{15}$ reaction channels. Calculated $^{27}$Al NMR parameters under GIAO method at HF/6-31g** level for a B3LYP/6-31g** optimized geometry.

<table>
<thead>
<tr>
<th></th>
<th>$\text{AlCO}_3$</th>
<th>$\text{AlCO}_2\mu\text{CH}_3$</th>
<th>$\text{AlC}_2\text{O}_2$</th>
<th>$\text{AlC}_2\text{O}_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\eta$</td>
<td>Cq</td>
<td>$\delta$</td>
<td>$\eta$</td>
</tr>
<tr>
<td>$M_9^{12} - 1$</td>
<td>0.23</td>
<td>-15.93</td>
<td>113.76</td>
<td>0.80</td>
</tr>
<tr>
<td>$M_9^{12} - 2$</td>
<td>0.31</td>
<td>-14.7</td>
<td>110.23</td>
<td>0.92</td>
</tr>
<tr>
<td>$M_9^{15}$</td>
<td>0.39</td>
<td>-17.65</td>
<td>114.73</td>
<td>0.93</td>
</tr>
<tr>
<td>$M_9^{18}$</td>
<td>0.57</td>
<td>-17.64</td>
<td>116.77</td>
<td>0.98</td>
</tr>
</tbody>
</table>

The asymmetry parameter (see Table 4.3.4). In literature there are claims of five-coordinate aluminum in $^{27}$Al NMR MAO spectrum identified by a broad peak at 60ppm [4].

The calculations suggest a resonance at 154±11ppm in MAO spectrum for which AlC$_2$O$\mu$CH$_3$ and AlC$_2$O$_2$ sites are responsible. Interestingly enough, there are claims in the literature of synthesized aluminoxane species that contain bridging methyl groups with Al sites in AlC$_2$O$\mu$CH$_3$ coordination environment, and whose signal was reported at 153 ppm [67]. These species are tetramethyldialuminoxane, [(CH$_3$)$_4$ Al$_2$O$_3$], which was synthesized by reaction of
The TMA and tetraethylboroxane, Et₂B₂O, the so-called organoboron water, at -78°C [67] and tetraethylaluminoxane ([C₅H₅]₂Al₂O) [61].

Table 4.3.4  

<table>
<thead>
<tr>
<th>Site</th>
<th>(M_{10}^{8} = 2)</th>
<th>(M_{12}^{9} = 3)</th>
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</thead>
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<tr>
<td></td>
<td>(\eta)</td>
<td>Cq</td>
</tr>
<tr>
<td>AlCO₃</td>
<td>0.47</td>
<td>-17.65</td>
</tr>
<tr>
<td>AlCO₂µCH₃/4 ring</td>
<td>0.14</td>
<td>-20.91</td>
</tr>
<tr>
<td>AlCO₂µCH₃/6 ring</td>
<td>0.77</td>
<td>-17.18</td>
</tr>
<tr>
<td>AlO₄µCH₃</td>
<td>0.96</td>
<td>9.67</td>
</tr>
<tr>
<td>AlC₂O(µCH₃)</td>
<td>0.67</td>
<td>29.11</td>
</tr>
</tbody>
</table>

4.3.3  \(^1\)H NMR MAO Analysis

In TMA₂, there is a rapid exchange equilibrium between methyl bridges and terminal methyl groups producing an average signal at -0.36 ppm in its \(^1\)H NMR spectrum [10].

At room temperature, the \(^1\)H NMR spectrum of MAO in toluene is composed of a broad featureless peak. When cooling the sample to -80°C the TMA₂ signal is resolved (terminal methyl at -0.495 ppm and bridging methyl at 0.012 ppm), and two new peaks at 0.2 and -0.34 ppm attributed to MAO are revealed [11].
In Table 4.3.5 calculated chemical shifts for bridging methyl groups through a five-coordinate carbon and terminal methyl groups in $TMA_2$ are in very good agreement with the experimental values, validating the calculations for the possible sites in $^1$H NMR MAO spectrum.

**Table 4.3.5** Proposed MAO models. Calculated $^1$H NMR chemical shifts under HF/6-31g** chemistry model and GIAO method for B3LYP/6-31g** optimized geometries

<table>
<thead>
<tr>
<th>Species</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>type</td>
<td>$\delta$</td>
</tr>
<tr>
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</tr>
<tr>
<td></td>
<td>exp.</td>
<td>-0.01</td>
</tr>
<tr>
<td>$M_{10}^8$</td>
<td>I</td>
<td>0.34</td>
</tr>
<tr>
<td>$M_{14}^{12}$</td>
<td>I</td>
<td>0.27</td>
</tr>
<tr>
<td>$M_{12}^{10}$</td>
<td>II</td>
<td>-0.49</td>
</tr>
<tr>
<td>$M_{12}^9-1$</td>
<td>III</td>
<td>-0.37</td>
</tr>
<tr>
<td>$M_{12}^9-3$</td>
<td>II</td>
<td>-0.35</td>
</tr>
<tr>
<td>$M_{18}^{12}$</td>
<td>II</td>
<td>-0.23</td>
</tr>
<tr>
<td></td>
<td>III</td>
<td>-0.28</td>
</tr>
<tr>
<td>$M_{10}^8-2$</td>
<td>I</td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td>IV</td>
<td>-0.45</td>
</tr>
</tbody>
</table>

4.3.4 Conclusions

The calculations identify several possible sites in $^{27}$Al NMR MAO spectrum:

- at $\delta = 117 \pm 10$ ppm, $C_q = 16.5 \pm 5$ MHz and $\eta = 0.46 \pm 0.2$ attributed to four-coordinate Al in $AlCO_3$ (4 and 6 ring), and $AlCO_2\mu CH_3$ (4 and 6
ring) coordination environments which corresponds to the reported resonance at $\delta = 110 \pm 10$ ppm in MAO spectrum [4];

- at $\delta = 154 \pm 11$ ppm, $C_q \approx 20 MHz$ and $\eta \approx 0.9$ attributed to four-coordinate Al in $AlC_2O_2$ and $AlC_2O\mu CH_3$ coordination environments which corresponds to the reported resonance at $\delta = 149 - 153$ ppm in MAO spectrum [6,65];

- at $\delta = 200 \pm 5$ ppm, $C_q = 36 \pm 1.5 MHz$ and $\eta = 0.6 \pm 0.1$ attributed to three-coordinate Al in $AlC_2O$ coordination environment which is in agreement with the reported three-coordinate Al site in $^{27}Al$ NMR spectrum of t-butylaluminum species at 200 ppm [6], as well as in other three-coordinate aluminum compounds with a $R_2AlO$ coordination environment ($\delta = 180 - 200$ ppm) [66];

- at $\delta = 69$ ppm attributed to a five-coordinate Al site in $AlO_4\mu CH_3$ coordination environment corresponding to the reported five-coordinate aluminum site in $^{27}Al$ NMR MAO spectrum at 60 ppm [4].

According to Figure 4.3.9, in 40 Tesla NMR spectrum of MAO all the above described four-coordinate Al sites along with the five-coordinate Al site should be cleanly observed, and the detection of three-coordinate Al sites by solid state NMR requires higher magnetic fields.

From $^1H$ NMR calculations for the proposed MAO structures all terminal methyl groups have chemical shift around $-0.66 \pm 0.03$ ppm, suggesting that in [11] the resonance around $-0.5$ ppm is given not only by the terminal groups in $TMA_2$, but also by the terminal methyl groups in MAO. This finding is in
agreement with other spectroscopic studies in which the $^1$H NMR spectrum of TMA free MAO still has a peak around -0.4 ppm which was normally attributed to TMA [55]. In all the cases the bridging methyl patterns involve a five-coordinate carbon. Type II and type III, connecting $\text{AlCO}_2$ and $\text{AlC}_2\text{O}$ sites in four and six, membered rings, respectively, are undistinguishable reducing the number of distinct types of bridging methyl groups to three. Type I has the chemical shift at 0.27±0.06 ppm, it is the case of type I series of the rod-like structures, and it can be attributed to the peak at 0.2 ppm in [11]. Type II and III have the chemical shift at -0.30±0.07 ppm, and which can be attributed to the peak at -0.34 ppm in [11]. Type IV, in fact the third distinctive bridging methyl type, the bridge in a five-coordinate Al site, with a chemical shift at -0.45 ppm is undistinguishable from the terminal methyl groups signal at -0.5 ppm.
CHAPTER 5

SUMMARY

- Based on quantum molecular dynamics simulations and reaction path calculations, corroborated with experimental structural evidence for aluminoxanes, MAO formation is a step polymerization through a bi-functional monomer, $TMA-OH_2$.

- All isolated aluminoxane species can be explained though the proposed mechanism.

- The fact that in large scale experiments, the dimeric hydroxide similar to $M_2^{2-}$ has been isolated after main components like $[(^{13}Bu)Al(\mu_3-O)]_6$, $[(^{13}Bu)Al(\mu_3-O)]_9$, and $[(^{13}Bu)Al(\mu_3-O)]_{12}$ [5], along with the consideration that for the most step polymerizations there is less than 1% of the original monomer remaining at the reaction point where the average polymer chain contains ~ 10 monomer units, are held as strong arguments supporting the proposed MAO formation mechanism.
After the cage several reaction channels have been identified: a bi-directional growth generating rod-like structures as in $M^7_{8} - 11$, a three-directional growth as in $M^7_{8} - 13$, a special case of the latter when each growing step is followed by the termination and methyl bridges are formed as in $M^7_{8} - 12$, and several different structures from $M^7_{7} - 2$ and $M^7_{7} - 3$.

By considering just the molecular weight and the chemical composition of MAO, which the large majority of the previously proposed models - $(AlOCH_3)_n$ cages in which the ratio $CH_3/Al = 1$ when in MAO it has been always reported as being higher than 1 - failed to explain [2], all of the structures proposed in the above discussed reaction channels are good candidates for the MAO structure.

Taking into account the necessity of bridging methyl groups in MAO structure for the activation of metallocene catalysts, several structures were considered suitable structural models for the catalytically active components of the MAO multi-component material.

The comparison of the calculated IR and NMR parameters of the proposed MAO structures with experiment validates them as suitable models for the MAO structure.
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APPENDIX

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On October 6, 1970, Lacramioara Negureanu was born in Bacau County, Romania, not far from the place in which world famous musician George Enescu used to spend his summer vacations, and the Arch of the Carpatian Mountains. She became interested in math, chemistry and physics while attending the General School No. 27 in Bacau, along with playing volleyball with a team that years later have won national and international contests. In 1989 graduated from “Gheorghe Vrancianu” National High School, a top mathematics and physics learning institution in Romania. While in high school, besides the physical sciences, she was interested in poetry, and classics of literature and philosophy. In June 1995, she graduated with honors from “Alexandru Ioan Cuza” Iasi University, majoring in chemistry and focusing on physical and theoretical chemistry. While in college, between labs and seminars in chemistry, physics and math, she attended lectures in history of music and seminars of classical theatre. One year later she earned a Master Degree in physical chemistry from the same university. Since August 2001, she has been attending the graduate
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