PERCOLATION PROCESSES IN POLYMERIZATION ON METALLOCENE COMPLEXES

The current explanation of the polymerization of olefin and vinyl compounds by metallocene complexes and methylaluminoxane (MAO) is based on the proposal that monomer molecules are inserted between a transition metal atom and the growing polymer chain. There are many controversies, however, between the current explanation and the experimental facts. In this paper a new explanation based on the percolation processes is proposed: absorption of monomer molecules on MAO, bridging the distance between the two ions of the transition metal, their deactivation and simultaneous a polymer chain formation. This new explanation is in agreement with the experimental facts and is confirmed by computer simulation of the percolation processes.

Polymerization of olefin and vinyl compounds by metallocene complexes is a revolution in the polymer industry for producing both specialized and commodity polymers [1]. Bis(cyclopentadienyl)groups IV metal complexes have currently been introduced in the industry as a new generation of Ziegler–Natta catalysts for the polymerization of olefins and other monomers that have double bonds. Among the group IV metallocenes of titanium, zirconium and hafnium, the zirconocene compounds deserve the most interest. Hence, the so-called 'metallocene catalysts' are mostly zirconocene derivatives, with zirconocene dichloride \( \text{[C}_2\text{H}_5\text{ZrCl}_2 \text{]} \) being the parent system (Fig. 1). The cyclopentadienyl can be replaced by indenyl and other ligands.

![Figure 1. Composition and structure of metallocene complexes](image1.png)

The development of metallocene catalysis for olefin polymerization is closely tied to the discovery and use of the cocatalyst methylaluminoxane (MAO). MAO is obtained in the reaction of trimethylaluminium (TMA) with water (Fig. 2).

![Figure 2. Reaction of trimethylaluminium with water producing methylaluminoxane](image2.png)

The structure of MAO is complex and not known [1, 3–6] as studies to analyze this system suffer from the dynamic behavior of MAO, which by multiple equilibria such as disproportionation, changes its size and structure with both temperature and solvent [7]. The term "black box" is used to describe the inherent difficulties in attempting to elucidate the structure of MAO [7]. There are different equilibria between the oligomers \( (\text{CH}_3\text{Al})_n \text{Al}-(\text{OCt})\text{Al}-(\text{CH}_3\text{Al})_n \) with \( n=5-20 \) [1,3-6,8]. The molecular weight of the MAO oligomer determined cryoscopically in benzene lies between 1000–1500 g/mole.

It was shown that MAO oligomers can be linear, cyclic or crosslinked with methyl-free oxoalumium centers as microphase \( \text{Al}_n\text{O}_m\text{Al}_n \)–core [1, 4, 5]. The idea is that MAO consists mostly of trimeric MAO chains, which can form six-member rings whereby intramolecular saturation is obtained [8]. Intramolecular saturation of two of these six-member rings is connected with the formation of a dimer. Two of these dimers could form a so-called hail-opened dodecamer.
through the formation of intermolecular coordinative binding [8]. A cage structure resembling a half-open dodecaeder [9,10] or hexamer [5, 6] can be formed. Sinn [11] has reported on a cage model structure of MAO (like a soccer ball [5]) which contains unreacted TMA inside the cage. Cluster structures capable of enclathrating a chloride ion or a metallocene in a host-guest complex have been suggested [8]. The plausible structure of isobutylmethylaluminoxanes [13] is presented in Fig. 3. MAO solutions always contain gels, giving the impression that it is a swellable, rather than a soluble material [4, 12].

![Figure 3. A plausible structure of isobutylmethylaluminoxanes [13](Image)](Image)

**CURRENT EXPLANATION OF POLYMERIZATION ON METALLOECENE COMPLEXES**

The following set of reactions shows a possible scheme [2] of how MAO interact with metallocenes:

1. **Cp₂Mt₂Cl₂ + MAO → Cp₂Mt₂MeCl + Cl·MAO** (alkylation of metallocene)
2. **Cp₂Mt₂MeCl + MAO → Cp₂Mt₂Me⁺⁻Cl·MAO** (ion pair formation)
3. **Cp₂Mt₂Me⁺⁻Cl·MAO + n MAO → Cp₂Mt₂Me⁺ⁿ⁻Cl·n·MAO** (metallic cation solvated by MAO, i.e. ion pair separation with MAO)

(Mt = Metal; Me = methyl group; Cp = cyclopentadienyl group)

It was concluded that the value obtained for 'm' (m=3), the number of MAO molecules coordinated to the metal cation, is rather surprising. A value of three seems quite large because of the large size of the MAO oligomers. However, because MAO is present in large excess, MAO molecules may solvate the cation, thus separating the previously formed ion pairs. This is unexpected that the new species, a metallic cation solvated by MAO, would be much more active than the ion pair and much more stable than the free cation solvated only by the solvent (toluene). The increasing activity with increasing of MAO concentration may be explained by assuming an equilibrium between the previously formed ion pair and MAO, which solvates the species, thus separating the ion pair [2].

When n > 10 (degree of polymerization of MAO), then the polymerization activity reaches its maximum value [3]. However, it is still uncertain what part of the MAO structure participates in the activation of metallocene catalysts.

For the catalyst systems ZrCl₄ + MAO (ZrCl₄=Cp₂ZrCl₂, Cp₂ZrMeCl, Cp₂ZrMe₂ etc.) the existence of electron deficient complexes (Fig. 4) was suggested [15].

In addition to the reactions (1–3), it was found [9,10] that there are some other reactions (Fig. 5) of MAO with metallocene producing more than 50 moles of methane per mole of zirconium in 2 h. This picture is complicated by the self-condensation of MAO (4b).

![Figure 4. Electron deficient complexes of metallocenes and MAO](Image)

![Figure 5. Methane production and catalyst deactivation (a) and reactivation by ligand exchange (b, c) [9,10](Image)
producing Al–CH₂–Al crosslinks between the MAO oligomers. When the metallocone is supported on silica, condensation reaction between the metallocone and MAO is not observed.

The exact mechanism of the polymerization reaction is unknown. It is believed that monomer molecules (CH₂=CHR) are inserted between the metal atom (Zr) and the alkyl ligand [8], i.e. growing polymer chain (Fig. 6).

![Figure 6. Insertion of a monomer molecule](image)

There is no spectroscopic evidence, however, for π-complexation of monomer to Zr and Ti atoms [17]. The results of Chien may provide kinetic evidence for π-complexation of the monomer with catalytic species prior to insertion.

A near linear dependency of the activity on the concentration of ethene is observed [1], i.e. the reaction order for propagation is 1 with respect to the monomer. Reaction orders with respect to the propene concentration of 1.7 [25, 26], 1.3 [1], 1.2–1.4 [27] have been determined. This is significantly higher than expected for the model of monomer-metal π-complex formation followed by insertion as the rate-determining step [25, 26]. Hence, it can be assumed that two propene molecules participate in the rate-determining step [1, 25, 26].

It was noted [18, 19] that the catalytically active complexes are deactivated during the polymerization by reduction of the transition metal (Fig. 7).

![Figure 7. Reduction of catalytically active complexes](image)

The decay of the polymerization rate for both TiCl₃ supported on MgCl₂ and C₆H₅ZrCl₂/MAO catalysts was shown to be due to reaction between two adjacent transition metal propagation species. In the metallocone/MAO systems, this decay should be less at higher ratio of MAO to metallocone concentrations [18,19]. MAO has been shown to be oligomers of O–Al(CH₃)₃/n. If there is two or more Zr complexed to a single MAO molecule, i.e. Al/Zr<cm the catalyst will suffer rapid deactivation. The observation of the study [18] is that the threshold Al/Zr is several hundred times greater than the value of m. It is possible to understand the high requirements for MAO by postulating dynamic association–dissociation equilibria of MAO involving acid-base complexation and/or electron deficient bridges (Fig. 8). Let MAO complexed with Zr whose activity is under consideration be designated as MAO₁ and those in association–dissociation equilibria with MAO₁ as MAO₂. Then if any MAO₂ with complexed Zr can deactivate the Zr on MAO₁, the polymerization activity A should be proportional to A². The empirical fact that A ∝ A¹.²⁵ tends to support this analysis [18].

![Figure 8. Bridges between two MAO oligomers](image)

There is a dynamic equilibria between temporarily unactivated (C), activated (C¹), inactive (dominant, I) and deactivated zirconocene dimers (I₂) (Fig. 9) [1].

![Figure 9. Development stages of metallocones](image)

The reactive center C¹ is produced by MAO. Intermediate I¹, which is inactive but can be reactivated by MAO, (b). Two Zr center are connected by a C₂H₄ bridge. Product I² is produced by combining two I¹ intermediates. I² is inactive and can not be reactivated.

The deactivation processes are second order with respect to catalytically active sites [1, 8, 21–24]. This process is accentuated in the presence of monomer, compared to monomer-free catalytic systems. It was found [15] that the deactivation rate of the catalyst increases with increasing polymerization rate (∆dM/dt = kRₚ₀) with a Ti-based Ziegler–Natta catalyst, similar experimental results have been found. The rate of
monomer insertion itself is the critical step, producing deactivated sites in a statistical way. A certain percentage of the monomer insertions (represented by $k_d$) leads to deactivated sites independent of temperature ($E_d = 4$ kJ/mole, i.e. close to zero). How two occurs is not clear. Deactivation by impurities in the monomer (ethene) can be excluded [15].

The rate of decay (catalysts deactivation) is highly dependent on the Zr-concentration; at low Zr levels there is no observed decrease in the polymerization rate, whereas at high Zr levels there is a substantial loss of activity during the first hour of polymerization. Second order deactivation with respect to active sites fits better than first order deactivation [24].

**EXPERIMENTAL FACTS AND CONTROVERSIES WITH THE CURRENT EXPLANATION**

There are many controversies between the current explanation and the experimental facts. Here only some of them will be considered.

**Reduction and deactivation of the transition metal**

The second order reduction of the transition metal from $M^{+4}$ to $M^{+3}$ is an experimentally confirmed fact (Fig. 7) [15,18,19]. There are some open questions and controversies in this explanation:

1. The origin of the two electrons necessary for this reduction is not presented. It is necessary to determine the component that donates the electrons (oxidation). This oxidation is of the same importance as the reduction of $M^{+4}$.
2. How can the distance between the two $M^{+4}$ be overcome?
3. What is the role of the monomer in the deactivation processes? Why is the deactivation rate proportional to the rate of monomer polymerization?

**Extremely high Al/Zr ratios**

The full co-catalytic functionality of MAO towards zirconocenes is unknown. It has been found that very high ratios of MAO to metalloocene are required to achieve a good polymerization activity: 1 000: 1 to 10 000:1. Extremely high Al/Zr ratios, 150 000:1 or even 500 000:1, were employed for the highest activities reported in the literature.

**Induction period**

The reaction is performed in a solvent. Toluene is the most popular one. After all components had been added to the solvent, it was sometimes found that the reaction did not commence immediately, but only after some induction period [17, 21, 24, 28-34]. There are many cases, however without the appearance of an induction period [30, 35, 36]. After this initial period, a build-up of the reaction rate was noticed in most experiments. The reaction rate reaches a maximum value and then diminishes, in some cases slowly, but in other cases rapidly.

**The polymerization mechanism is not known**

Despite intensive research, no definite, unequivocal polymerization mechanism has yet been proposed which describes the behavior of metalloocene and Ziegler-Natta catalysts [37].

The effects of the nature of metalloocene complexes of group IV metals on their performance in catalytic ethylene and propylene polymerization have been investigated [38]. The author's group synthesized over 650 metalloocene and half-sandwich catalyst precursors to test their catalytic potential and to study the influences of various catalysts parameters on the properties of the resulting polymers. After a lot of work, they concluded: "What did we learn? We have to confess that we still do not understand all details in order to be able to predict the exact properties of the designed metalloocene catalysts. There are many parameters involved which determine the kinetics of the polymerization. Tiny changes in the metalloocene complex can have a drastic effect on the activity of the catalyst and on the properties of the polymers. Even molecular modeling cannot answer all the questions: it can only confirm trends."

**NEW EXPLANATION BASED ON THE PERCOLATION THEORY**

Many fragments from published data were presented in the previous sections. Now, it is necessary to gather all the fragments to make a common mosaic picture.

It can be proposed that a percolation concept similar to that applied to explain Ziegler-Natta polymerization on TiCl₃-aluminium alkyl compounds [39, 40] can be used in the case of polymerization by metalloocene/MAO systems. The main oversight of the current explanation arises from the fact that only metalloocene complexes are considered as important for polymerization. The role of MAO (in homogenous systems) and the role of the surface (catalysts and/or support – in heterogeneous systems) are almost completely neglected although the experiments have confirmed the ultimate importance of them. Anyway, it is only mentioned in the current explanation that MAO and/or the surface should be considered as a field for the performance of the polymerization process.)

MAO is a polymer that has a linear, cyclic, branched or crosslinked structure (Figures 3, 4, 5 and 8). The structure of MAO is changed in the presence of metalloocene complexes: two MAO linear chains are coupled (Fig. 5a) or branched and crosslinked (Fig. 5b), possibly with methyl-free oxoaluminium centers as microphase Al₆O₆-core [1,4,5]. It can be proposed that after removal of methane molecules from MAO, the structure of the residual MAO is similar to the structure of Al₂O₃, i.e. planar was a honeycomb-like lattice (with or without defects). For further analysis, the a simplified models of MAO and the support lattice, presented in Fig. 10, were used (other types of arrangements can be proposed and analyzed, too).
The active centers are metalloene complexes attached to the lattice (Fig. 11, time 1). The characteristic of transition metals is that they can exist in different ionic states (titanium, zirconium and hafnium can be +2, +3 and +4; chromium +2, +3, +4, +5, +6) and can be easily transformed from one ionic state to another. (TiCl₄ catalysts activated with AEt₃/methyl-p-cresol contains 38% of Ti⁴⁺, 24% of Ti⁺³ and 38% of Ti⁺⁺ [21]. A conductometric study performed on the rac-\text{Et}_{(Ind)}ZrCl₂/MAO system for different MAO/Zr ratios is also in agreement with the formation of ionic species having different natures and degrees of ionization. This explains the formation of various types of active zirconium species. The catalytic activity may be correlated to the nature and to the relative concentration of the active ionic species present in the medium. Interestingly, when the polymerization has reached completion after several hours, the active zirconocenium species have reverted to their initial non-complexed form [41].

There are active centers with metal ions having high (+4) and having a low degree of ionization (+2). There is a tendency to equalize the degree of ionization by the transfer of one electron. (Perhaps, there is also a tendency for the reduction of two transition metal atoms presented in Fig. 7). However, this cannot be realized since the metal ions are fixed and separated by segments of MAO. The monomer clusters are formed around the metal atoms by absorption of monomer molecules that have movable electrons in the π bonds. The size of the clusters are initially small and the active centers are still separated (Fig. 11, time 1). With the absorption of more and more monomer molecules are absorbed with time, the sizes of the cluster increase. At one moment two cluster face each other (percolation threshold) and the absorbed monomer molecules form a bridge between unequal active centers (Fig. 11, time 2). The monomer molecules polymerize simultaneously by the transfer of an electron for the equalization of the active centers (Fig. 11, time 3). After that, along the percolation path there are no more monomer molecules with π electrons that enable them to be attached to the MAO lattice, hence the just created polymer chain, without π electrons, detaches from the MAO lattice. Simultaneously, the two active centers become inactive (Fig. 11, time 4). (Interestingly, when the polymerization has reached completion after several hours, the active zirconocenium species have reverted to their initial non-complexed form [41]).

The lattice becomes fixed for the absorption of additional monomer molecules and the attachment of new metalloene complexes. The whole process cycle is repeated on the MAO lattice but with the participation of other active centers and monomer molecules.

So, the general draft of the mosaic picture is completed. All fragments (statement, empirical facts and controversies) mentioned in the current explanation are included in this mosaic, except the most fundamental one: the insertion mechanism is rejected. Almost half a century has passed since the insertion mechanism was proposed – half a century of wandering, astray, introducing rescue operations for the insertion mechanism, but without success. (For an excellent
survey see [37]). Even Odyssey did not experience such an odyssey. It is time to say "Stop for the insertion concept", to back out of the maze and cut-de-sacs and to try to find some another way. Our percolation concept is a promising one.

The polymer yield, polymerization rate, polymer molecular mass and its distribution, as well as the structure and stereoregularity of the polymer chains depend on the type of MAO or support lattice, the concentration of active centers (i.e. the MAO/metallocene ratio), the initial polymerization conditions and the evolution of the system with time.

**COMPUTER SIMULATION AND EXPERIMENTAL EVIDENCE**

The percolation concept that we have developed can easily be computer simulated using the Monte-Carlo simulation procedure. We wrote such a computer program [42,43] that enables simulation over a wide range of operating conditions and which includes the MAO/metallocene ratio, total metallocene concentration, pressure and temperature effects, the solubility of the polymer, chain transfer agents, type of MAO or support lattice (linear branched, crosslinked, triangular, square and hexagonal) etc. The polymer yield, polymerization rate, number and weight average degree of polymerization, molecular mass distribution and the degree of transition metal deactivation are reported during the simulation (Table 1).

We have computer simulated the results of laboratory experiments published in literature. Very good correlation between the laboratory and simulated experiments was achieved.

According to the percolation concept, after the metallocene complexes react with MAO producing active centers attached to MAO, the absorption of monomer should take some time to cover the MAO lattice and to make the very first percolation path between two active centers (Fig 12., left side). So, according to the percolation concept and computer simulation, an induction period should appear if the components are added to the solvent in the following sequence: 1. MAO, 2. metallocene and 3. monomer. (This sequence of component addition was used in the experiments [17, 21, 24, 28-34] all of which had an induction period.) The induction period should be very short or not appear if the MAO lattice is saturated with absorbed monomer before the metallocene complex is added (Fig 12., right side), i.e. if the sequence of component addition is ether: 1. MAO, 2. monomer and 3. metallocenes or 1. monomer, 2. MAO and 3. metallocene. (This sequence of component addition was used in the experiments [30, 35, 36] that proceeded without an induction period.)

According to the percolation concept, both polymer yield and polymerization rate should increase with increasing of MAO/metallocene ratio. High MAO/metallocene ratios means a long distance between the active centers, long percolation path, i.e. a great number of monomer molecules are polymerized in each

<table>
<thead>
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<th>Components addition sequence</th>
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<td>1. MAO</td>
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<td>2. Monomer</td>
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<tr>
<td>3. Monomer</td>
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Induction time - YES Induction time - NO

*Figure 12: Explanation for the appearance of an induction period*

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**Table 1. Report of computer simulation**

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percolation step. The results of the simulation of the laboratory experiments published by Charpentier et al. (Fig. 11 in [7]) very good correlation between the simulated experiments and the laboratory experiments was obtained.

CONCLUSION

A new percolation concept of polymerizations by metalloocene complexes can successfully explain the experimental facts and the controversies aiming in the current explanation:

1. Deactivation of the catalyst is the equalization of the various ionic species of metalloenes. Metalloocene equalization and monomer polymerization are not two separate processes but unified in one 'symbiotic' process: absorbed monomer molecules take a bridge for electron transfer between the separated active centers and monomers polymerize with the help of that electron transfer between the active centers. (Monomers do a favor to metalloenes and metalloenes simultaneously do a return favor to monomers.)

2. The role of MAO is to enable and to unify the performance of both processes in one percolation process: metalloocene equalization (absorption, alkylolation, separation, electron transfer) and monomer polymerization (absorption, cluster formation and growth, polymer formation and detachment). The greater the distance between the active centers attached on the MAO lattice, the greater the polymer yield and polymerization rate. Hence, a very high MAO/metalloocene ratio is preferred.

3. Induction period appearance can be successfully explained by this percolation concept. It is confirmed by laboratory experiments, as well by computer simulated experiments.

4. Metalloenes behave not as catalysts but as initiators. MAO behaves as a catalyst. The growth of the polymer chain is not by monomer insertion but by percolation through the monomer clusters between a pair of active centers. Hence, the classical chemical kinetics can not be used to explain polymerizations by metalloenes. Kinetics based on critical phenomena (percolation processes) is more promising.

The percolation concept can be used to explain the effect of polymerization conditions on the molecular mass and its distribution, as well as on the stereoregularity of the polymer chains. This will be explained in some subsequent article.

It has been noted by many authors that polymerization by metalloocene complexes is analogous to the enzyme-substrate complex reaction [9, 10, 17, 44–46]. The percolation concept presented here is also very similar to enzymatic reactions [16]. This will also be explained in a subsequent article.

REFERENCES

IZVOD

PERKOLACIONI PROCESI PRI POLIMERIZACIJI NA METALOCENSKIM KOMPLEKSIMA

(Naučni rad)

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Postojeće tumačenje polimerizacije u prisustvu metalocenskih kompleksa i metilaluminoksana (MAO) se zasniva na predstavci da se molekuli monomer umeću uže prometnih lanaca i stvaraju polimer. Međutim, postoje mnoge nejasnosti u ovom tumačenju i eksperimentalnim činjenicama. U radu se prelaze novi tumačenje koje se zasniva na perkolacioni teoriji: napravljene su izmjene između dva jona prometnih lanaca, njihova deaktivacija uz istovremeno obrazovanje polimernog lanca. Ovo novi tumačenje je potvrđeno simulacijom navedenih perkolacionih procesa pomoću računara i poredenjem sa rezultatima stvarnih eksperimenta.

Ključne reči: metaloceni • polimerizacija • perkolacioni proces • teorija •
Key words: Metallocenes • Polymerization • Percolation • Theory •