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SCIENTIFIC PAPER

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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 [C_5H_5]$_2ZrCl_2$ being the parent system (Fig. 1). The cyclopentadienyl can be replaced by indenyl and other ligands.
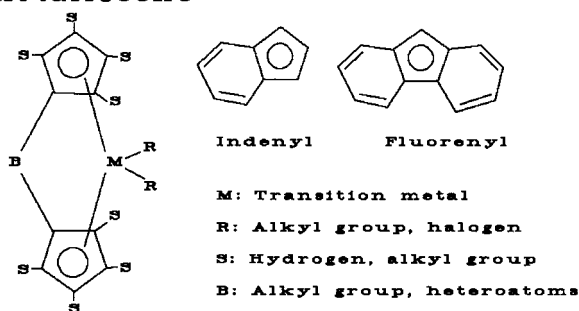
Metallocene

Figure 1. Composition and structure of metallocene complexes

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).
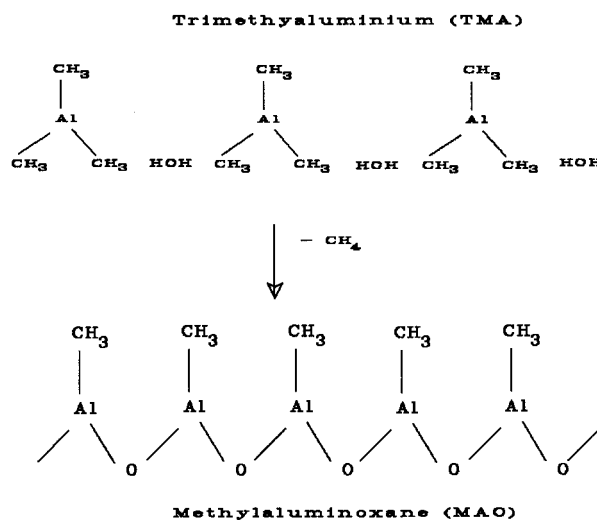

Figure 2. Reaction of trimethylaluminium with water producing methylaluminoxane

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 attenping to elucidate the structure of MAO [7]. There are different equilibria between the oligomers $(CH_3)_2Al[-O-AlCH_3]_n-O-Al(CH_3)_2$ 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 oxoaluminium centers as microphase Al_xO_y–core [1, 4, 5]. The idea is that MAO is consists mostly of trimeric MAO chains, which can form six–member rings whemby intramolecular saturation is obtained [8]. Intermolecular 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 **half–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 enchalthering a chloride ion or a metallocene in a host–guest complex have been suggested [8]. The plausible structure of isobutylmethylalumoxanes [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].
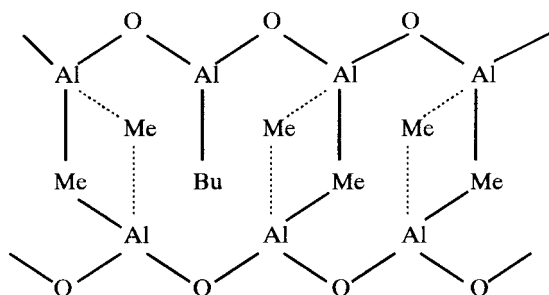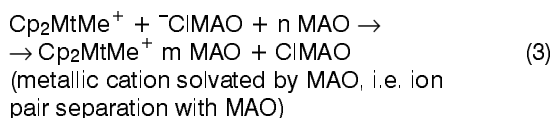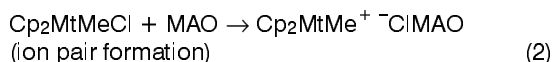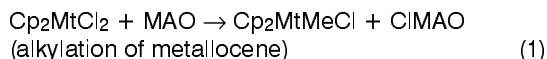

Figure 3. A plausible structure of isobutylmethylalumoxanes [13]

CURRENT EXPLANATION OF POLYMERIZATION ON METALLOCENE COMPLEXES

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

$$Cp_2MtCl_2 + MAO \rightarrow Cp_2MtMeCl + ClMAO$$
(alkylation of metallocene)   (1)

$$Cp_2MtMeCl + MAO \rightarrow Cp_2MtMe^+ \ ^-ClMAO$$
(ion pair formation)   (2)

$$Cp_2MtMe^+ + \ ^-ClMAO + n\,MAO \rightarrow$$
$$\rightarrow Cp_2MtMe^+ \ m\,MAO + ClMAO$$ (3)
(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 to beexpected 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
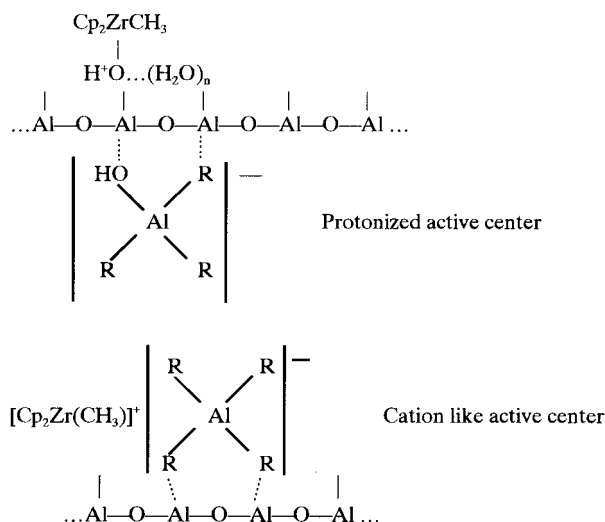

Figure 4. Electron deficit complexes of metallocenes and MAO [15]

value [3]. However, it is still uncertain what part of the MAO structure participates in the activation of metallocene catalysts.

For the catalysts systems /Zr/ + MAO (/Zr/=Cp₂ZrCl₂, Cp₂ZrMeCl, Cp₂ZrMe₂ etc.) the existence of electron deficit 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)
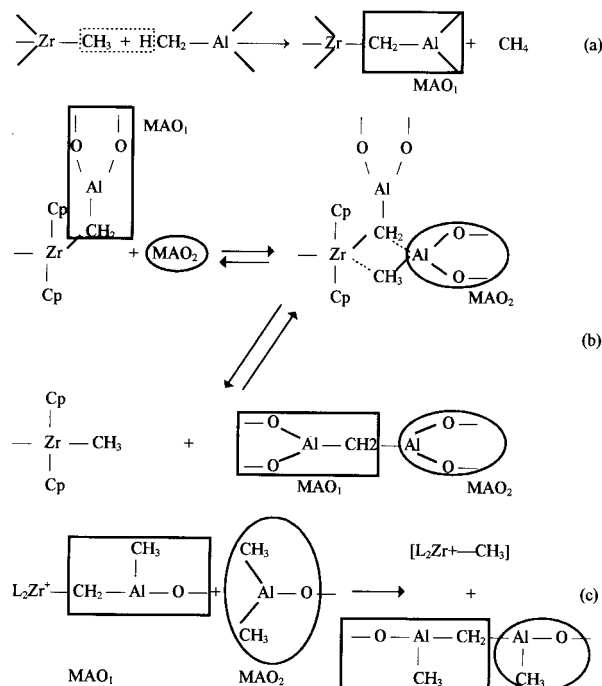

Figure 5. Methane production and catalyst deactivation (a) and reactivation by ligand exchange (b, c) [9,10]

producing Al–CH$_2$–Al crosslinks between the MAO oligomers. When the metallocene is supposted the on silica, condensation reaction between the metallocene and MAO is not observed.

The exact mechanism of the polymerization reaction is unknown. It is believed that monomer molecules (CH$_2$=CHR) are inserted between the metal atom (Zr) and the alkyl ligand [8], i.e. growing polymer chain (Fig. 6).
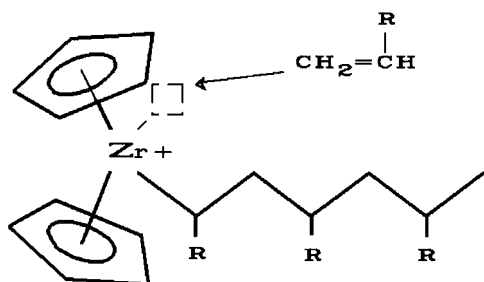

Figure 6. Insertation of a monomer molecule

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 insertation.

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 insertation as the rate–determining step [25, 26]. Hence, in 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).
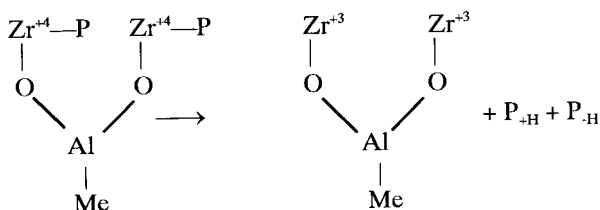

Figure 7. Reduction of catalytically active complexes

The decay of the polymerization rate for both TiCl$_3$ supported on MgCl$_2$ and Cp$_2$ZrCl$_2$/MAO catalysts was shown to be due to reaction between two adjacent transition metal propagation species. In the metallocene/MAO systems, this decay should be less at higher ratio of MAO to metallocene concentrations [18,19]. MAO has been shown to be oligomers of /–O–Al(CH$_3$)–/$_m$. If there is two or more Zr complexed to

a single MAO molecule, i.e. Al/Zr<m 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 whid Zr whose activity is under consideration be designated as MAO$_1$ and those in association–dissociation equilibria with MAO$_1$ as MAO$_2$. Then if any MAO$_2$ with complexed Zr can deactivate the Zr on MAO$_1$, the polymerization activity A should be proportional to Al^2. The empirical fact that A ∝ Al$^{1.75}$ tends to support this analysis [18].
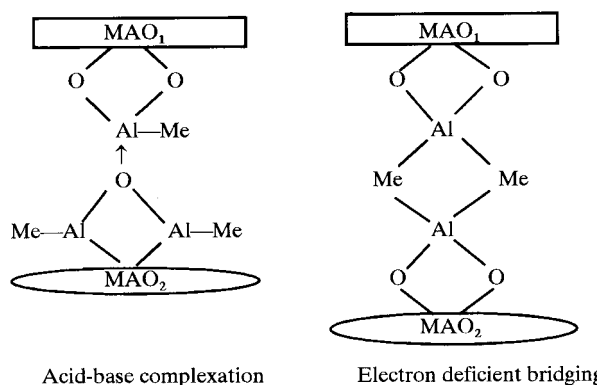
Figure 8. Bridges between two MAO oligomers [18]

There is a dynamic equilibria between temporarily unactivated (C), activated by MAO (C*), inactive (dormant, I1) and deactivated zircocene dimers (I2) (Fig. 9) [1].
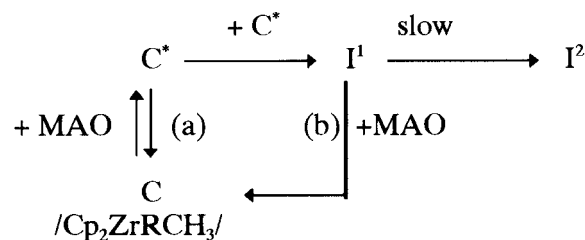
Figure 9. Development stages of metallocenes [1]

The reactive center C* is produced by MAO. Intermadiate I^1, which is inactive but can be reactivated by MAO, (b). Two Zr center are connected by a C$_2$H$_4$ bridge. Product I^2 is produced by combining two I^1 intermediates. I^2 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 (–dCat/dt = k$_d$R$_{pol}$). With a Ti–based Ziegler–Natta catalyst, similar experimental results have been found. The rate of

monomer insertation itself is the critical step, producing deactivated sites in a statistical way. A certain percentage of the monomer insertations (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, wheread 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 Mt^{+4} to Mt^{+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 danates the electrons (oxidation). This oxidation is of the same importance as the reduction of Mt^{+4}.

2. How can the distance between the two Mt^{+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 metallocene 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 metallocene and Ziegler–Natta catalysts [37].

The effects of the nature of metallocene 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 metallocene 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 metallocene catalysts.** There are many parameters involved which determine the kinetics of the polymerization. Tiny changes in the metallocene 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 $TiCl_3$+aluminiumalkyl compounds [39, 40] can be used in the case of polymerization by metallocene/MAO systems. The main oversight of the current explanation amses from the fact that only metallocene 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 metallocene complexes: two MAO linear chains are coupled (Fig. 5a) or branched and crosslinked (Fig. 5b), possibly with methyl–free oxoaluminium centers as microphase Al_xO_y–core [1,4,5]. If can be proposed that after removal of methane molecules from MAO, the structure of the residual MAO is similar to the structure of Al_2O_3, 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).
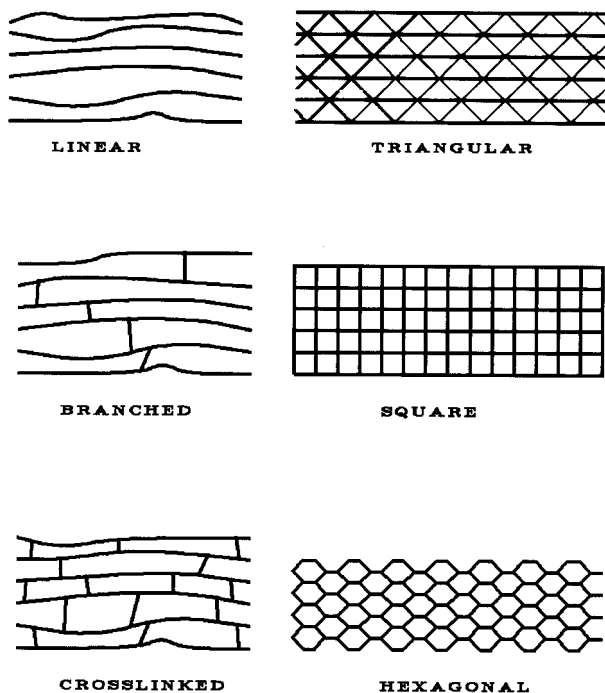
Figure 10. Simplified models of MAO and the support lattice

The active centers are metallocene 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. (TiCl₃ catalysts activated with AlEt₃/methyl–p–cresol contains 38% of Ti^{+2}, 24% of Ti^{+3} and 38% of Ti^{+4} [21]. A conductiometric study performed on the rac–Et(Ind)₂ZrCl₂/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 eyplains 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 abosrption of more and more monomer molecules are
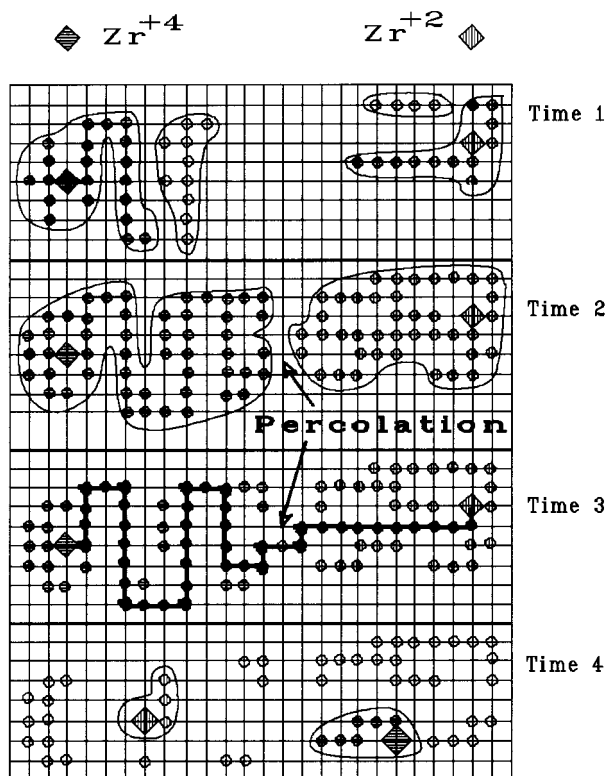

Figure 11. The percolation process cycle

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 freed for the absorption of additional monomer molecules and the attachment of new metallocene 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 insertation mechanism is rejected**. Almost half a century has passed since the insertion mechanism was proposed – half a century of wandering, astray, mitroducing rescue operations for the insertation 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 insertation 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 et ther: 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 mereasing 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
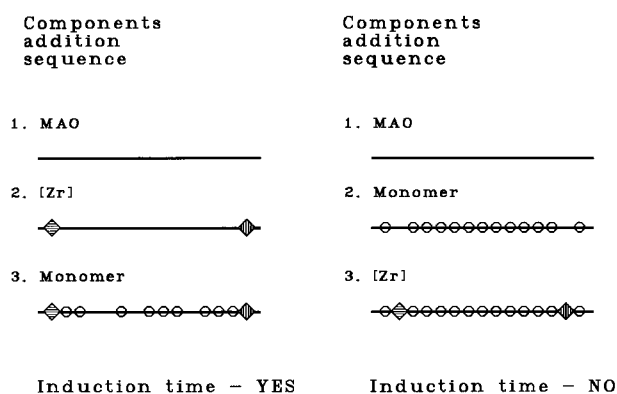
Components addition sequence

1. MAO
_____

2. [Zr]
◆━━━━━━◆

3. Monomer
◆○○━○━○○○━○○○◆

Components addition sequence

1. MAO
_____

2. Monomer
○━○○○○○○○○○○━○

3. [Zr]
○◆○○○○○○○○○○◆○○

Induction time – YES   Induction time – NO

Figure 12. Explanation for the appearance of an induction period

Table 1. Report of computer simulation

Date: April/27/2000
Lattice type: Hexagonal
Surface size: 10240000
Supp–Mon–Cat Mon. saturation time: 1.2
Zr approach rate: 2000
MAO/Zr: 3200

MONOMER
CLUSTERS

| Time (rel. units)	Polymer yield (Moles monom.)	Rpol (mol nom/ Zr/time)	Xn	Xw	u=Xw/Xn	Number of polymer chains	Number of Zr^{4+}	Number of Zr^{2+}	Empty sites [%]	Positive [%]	Negative [%]	Neutral [%]
0.1	306424	704	514	1330	2.58	596	1005	1005	30.1	21.2	13.8	34.8
0.2	467836	351	418	1040	2.48	1118	483	483	28.7	23.2	20.1	27.9
0.3	569996	291	429	984	2.30	1329	272	272	27.0	23.3	25.5	24.2
0.4	661912	305	458	1020	2.23	1446	155	155	25.2	25.0	32.3	17.4
0.5	763576	312	502	1140	2.28	1521	80	80	23.7	12.3	43.6	20.3
0.6	835425	170	538	1310	2.44	1553	48	48	22.2	0.01	56.2	21.4
0.7	858736	4	548	1340	2.45	1568	33	33	20.6	0.01	75.5	3.7
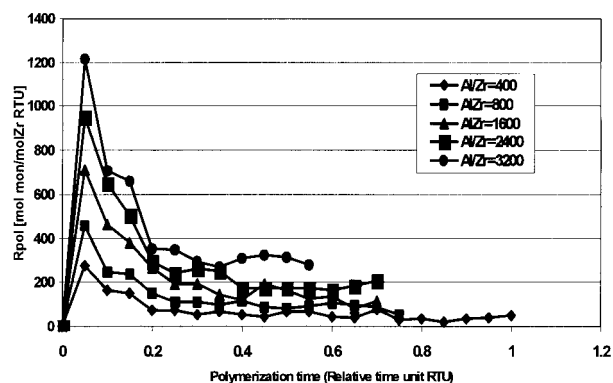
Figure 13. Effect of the Al/Zr ratio on the polymerization rate (Computer simulation of laboratory experiments [7, Fig. 11])

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 metallocene complexes can successfully explain the experimental facts and the controversies amsing in the current explanation:

1. Deactivation of the catalyst is the equalization of the various ionic species of metallocenes. Metallocene equalization and monomer polymerization are not two separate processes but unified in one 'symbiotic' process: absorbed monomer molecules make 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 metallocenes and metallocenes 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: metallocene equalization (absorption, alkylation, 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/metallocene 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. Metallocenes behave not as catalysts but as initiators. MAO behaves as a catalyst. The growth of the polymer chain is not by monomer insertation 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

metallocenes. 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 metallocene 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.

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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 predpostavci da se molekuli monomera umeću između atoma prelaznog metala i rastućeg polimernog lanca. Međutim, postoje mnoge protivurečnosti ovog tumačenja i eksperimentalnih činjenica. U radu se predlaže novo tumačenje koje se zasniva na perkolacionim procesima: apsorpcija molekula monomera na MAO (kao nosaču), premošćavanje rastojanja između dva jona prelaznih metala, njihova dezaktivacija uz istovremeno obrazovanje polimernog lanca. Ovo novo tumačenje je potvrđeno simulacijom navedenih perkolacionih procesa pomoću računara i poređenjem sa rezultatima stvarnih eksperimenata.

Ključne reči: metaloceni ● polimerizacija ● perkolacioni procesi ● teorija ●
Key words: Metallocenes ● Polymerization ● Percolation 8l processes ● Theory ●