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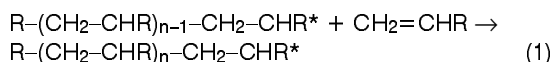
REVIEW PAPER

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## POLYMERIZATION OF ORGANIZED MONOMERS

*The current explanations of olefin and vinyl monomer polymerization propose that monomer molecules are successively added one by one to the growing polymer chain. This may be true if the monomer molecules exist as individual species in a polymerizing system, e.g. in dilute solutions of monomer. There are cases, however, in which monomer molecules are organized: bulk liquid monomer, solid monomer, a monomer monolayer adsorbed on a support, etc. Various supra-molecular species and particles of monomer exist in such cases. In the 1960-ties, Semenov, Kargin and Kabanov proposed a theory of organized monomer polymerization. In the last 25 years, our research group has further developed and applied that theory to various polymerizing systems: the radical polymerization of compressed ethene gas, the radical polymerization of liquid methyl methacrylate, olefin polymerization by transition metals and by Al-based catalysts. An outline of the main achievements are presented in this article.*

All classical explanations of polymerization [1] propose that the polymer chain propagates by the successive addition of monomer molecules *one by one* to the growing chain (1). The same process can be presented as (2) where  $P_n^*$  represents a cation, anion or radical of the growing polymer chain and  $M$  represents the individual monomer molecule.



Kargin and Kabanov [2] emphasized that there are some cases (solid, liquid and adsorbed monomer systems), however, in which monomer molecules are organized and exist as clusters of  $m$  molecules ( $mM$ ). They developed a theory of organized monomer polymerization (TOMP). According to the TOMP, each cluster behaves as a single physical and chemical entity and the whole cluster  $mM$  is enchaind at once in a single propagation step (3). The fundamental difference between (2) and (3) is that the propagation is random at the molecular level in the first case (2), while it is determined at the molecular level but random on the supra-molecular level in the second case (3). In the first case (2), in each propagating step one by one repeating unit of polymer chain is formed, while in the second case (3) one by one chain segment is formed. Hence, in the second case (3) both the polymerization kinetics and polymer structure ( $M_n$ , MWD, stereoregularity, regioregularity, etc.) depend on the organization and arrangement of monomer molecules in those clusters.



We have applied this concept of the TOMP to explain:

- the radical polymerizations of compressed ethene gas;
- the radical polymerizations of liquid methyl methacrylate (MMA);
- the polymerization of olefins by transition metal complexes and
- the polymerization by Al-based catalysts

### ORGANIZATION AND FREE RADICAL POLYMERIZATION OF COMPRESSED ETHENE GAS

It is well known that ethene can polymerize by free radical mechanism at very high pressures (from several hundred to several thousand bars). Classical free radical polymerization reactions (1, 2) have been applied to explain this process. The main open question was: Why was it necessary to have such high pressure and what was its role?

We have explained [3] that the role of pressure was to enable the formation of various supra-molecular species (Fig. 1). The basic rule is that by the increase of pressure, i.e. by the decrease of free volume, such species are formed that need less space for movement (rotation). There are several phases in compressed ethene: ideal gas (at low pressures); the  $\alpha$  phase (consisting of a mixture of single molecules and rotating molecular pairs); the  $\beta$  phase (rotating molecular pairs and rotating bimolecules) and the  $\gamma$  phase (rotating bimolecules, oligomolecules and oligomolecular bundles). The transition from the  $\alpha$  to the  $\beta$  phase occurs at the critical isochore ( $V/V_c = 1$ ), and from the  $\beta$  to the  $\gamma$  phase at the critical isentrope conditions. The thermodynamics, physico-chemical and spectroscopic evidence on ethene self-organization and phase changes by compression have been presented elsewhere [3,4].

The degree of order can be presented by entropy, i.e. high order means low entropy. It was proved that the degree of order, presented by the entropy of compressed ethene, had a crucial effect on the polymerization mechanism and kinetics, as well as on polyethene structure and properties. Ethene

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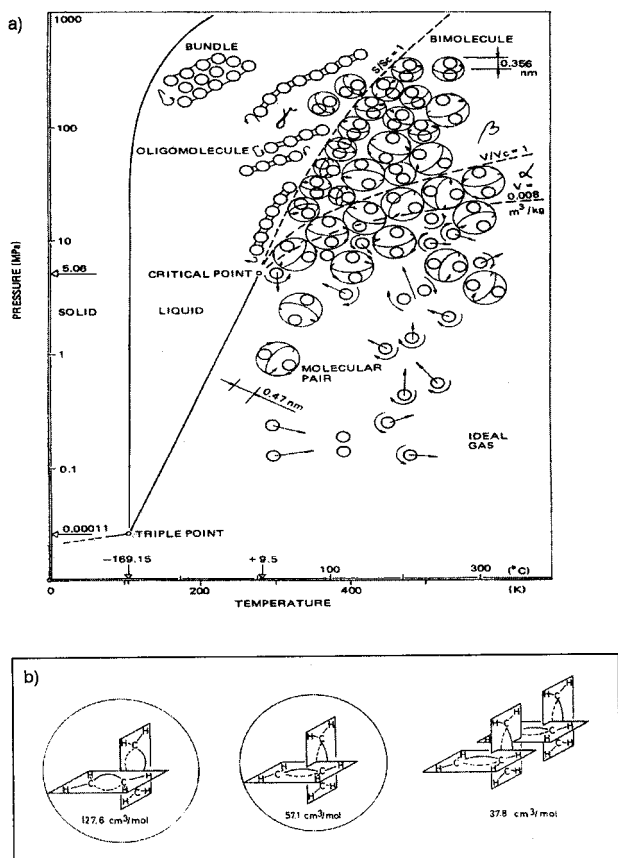


Figure 1. Phase state (a) and supramolecular species (b) of compressed ethene gas (molecular pair, bimolecule and oligomolecule, respectively) [3]

polymerization is possible only under low entropy conditions, i.e. in the  $\beta$  and in  $\gamma$  phase in which bimolecules and oligomolecules exist. As expected by the TOMP, polymerization in the highly organized  $\gamma$  phase occurs after an induction period: the lower the ethene entropy – the higher the induction period [5]. According to the TOMP, polymerization in the less ordered  $\beta$  phase should be without an induction period, as has been confirmed [5]. The maximum polymerization rate should be at the  $\beta$ - $\gamma$  phase transition as has also been confirmed experimentally [5,6].

The degree of order, i.e. ethene entropy, also has a decisive effect on the macromolecular structure of polyethene [6–8]. Despite differences in the polymerization conditions (pressure, temperature, method of initiation) an equal macromolecular structure is obtained if the entropy of ethene is equal. This *isentropic rule* is valid not only for short chain branching (Table 1), but also for different types of short branches (ethyl, butyl, amyl), unsaturated bonds, long chain branches [9], the molecular mass [8], the molecular mass distribution [8] and the density of polyethene [6,8]. Based on the isentropic rule, mathematical models have been derived that relate the structure and properties of polyethene with ethene entropy under the polymerization conditions [6,8,10]. These mathematical models enable the prediction of polyethene structure

Table 1. Synthesis conditions for polyethene with 4–5 branches per 1000 C atoms [8]

Polymerization conditions			Degree of branching (CH <sub>3</sub> /1000 C)
Pressure (MPa)	Temperature (K)	Reduced entropy (S/S <sub>0</sub> )	
5.7	283	0.95	4.0
39	333	0.95	4.6
440	453	0.95	5.0

and properties produced under any polymerization conditions and/or to chose the polymerization conditions in order to produce polyethene with the desired structure and properties.

The great importance of the supramolecular organization of compressed ethene and the corresponding theory of polymerization for the industrial process of low density polyethene production have been presented elsewhere [4, 11, 12].

### SELF-ORGANIZATION AND POLYMERIZATION OF LIQUID MMA

The free radical polymerization of liquid methyl methacrylate (MMA) has been frequently investigated because of the very pronounced autoacceleration phenomenon known as the "gel effect" or "Norris-Trommsdorff effect". At the beginning, the polymerization rate corresponds to first order kinetics as expected according to the classical theory of free radical polymerization (1 and 2). At higher conversion, however, the reaction rate accelerates, and reaches a maximum value, and then drops to zero, before the monomer is depleted. Contrary to the classical theory, the average molecular mass of poly(methyl methacrylate) (PMMA) increases during polymerization. Autoacceleration exists even under isothermal conditions. These unusual phenomena have challenged many researchers to find an adequate explanation, but all of them have failed [13].

Semenov [14], Kargin and Kabanov [2] suggested that these phenomena could be explained by the supramolecular organization of liquid MMA. They suppose that liquid MMA consists of ordered and disordered domains. According to their TOMP, polymerization starts in ordered MMA domains according to classical radical polymerization. Once the disordered monomers are polymerized, the polymerization continues in ordered MMA domains resulting in rate acceleration and in an increase of the molecular mass of PMMA. They did not however give a more detailed insight of the MMA molecule organization.

Later, Sasuga and Takehisa [15,16] confirmed that planar molecules of MMA could be properly aligned producing ordered and disordered domains in liquid MMA (Fig. 2). They did not determine, however, the fraction of MMA in those domains.

In order to determine the fraction of MMA in ordered and disordered domains, we extended the concept of monomer self-organization developed for compressed ethene gas (Fig. 1). This extension will be

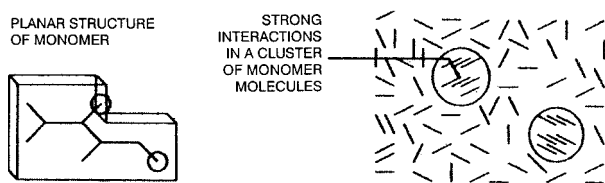


Figure 2. Supramolecular organization of liquid MMA [15,16]

briefly presented here. We determined the volumes of the space necessary for the rotation of supramolecular species of ethene by analyzing how the ethene molecules were packed by compression but occupying all the available free volume. Furthermore, we noticed that these volumes had very characteristic values. The volume for the rotation of an ethene molecular pair, i.e. two rotating ethene molecules at equilibrium distance according to the Lennard–Jones potential, is equal to the specific volume of ethene at the critical point ( $V_c$ ). A rotating ethene bimolecule occupies the volume equal to the constant  $b$  (i.e. co-volume) in the van der Waals equation of state. A rotating ethene oligomolecule occupies a volume equal to the specific volume of the solid phase of ethene at the triple point ( $V_{t,s}$ ). The volume of ethene bundles is equal to the specific volume of ethene at absolute zero temperature ( $V_0$ ). Furthermore, these characteristic volumes of ethene and of its supramolecular particles have also been calculated [4,17] using a very simple mathematical model [18,19] derived by adopting the theory on the behavior of materials under high pressure developed by Savić and Kašanin [20]. Even more, it was confirmed for 143 substances that the same mathematical model can be used to calculate their characteristic volumes from an ideal gas state up to absolute zero temperature [18,19]. Since the same mathematical model can be used to describe these changes, the two following conclusions were drawn:

1. All substances are exposed to the same structural changes from one to another characteristic state.
2. All substances have the same supramolecular structure in the same characteristic state. (It was proved that not only for ethene, but also for 92 other substances the volume of the rotating molecular pair is equal to their critical volume [19]).

So, what is the structure of liquid MMA like? According to Eyring and Marchi [21], a liquid consists of disordered ("gas-like") and ordered ("crystalline-like") domains. Keeping in the mind that the specific volume of liquid MMA has a value between the volume of the van der Waals constant  $b$  and the volume of the solid phase at the triple point  $V_{t,s}$ , we supposed that liquid MMA consisted of rotating bimolecules (disordered domains) and rotating oligomolecules (ordered domains). A very similar conclusion was made by Korolev et al. [22] who proved the existence of physically associated dimers and linear oligomers in more than 1000 organic liquids including MMA. Using the mathematical model described in [19], the volumes of the bimolecule and oligomolecule of MMA were calculated [13] as well as their fractions in disordered

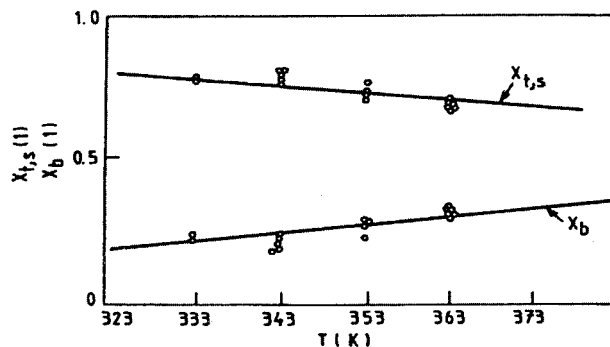


Figure 3. Fractions of ordered ( $X_{t,s}$ ) and disordered ( $X_b$ ) domains of liquid MMA at different temperatures [13]. (Solid lines: predicted by calculation; Points: experimentally determined by polymerization)

(Fig. 3,  $X_b$  line) and ordered domains (Fig. 3, line  $X_{t,s}$ ), respectively.

Then we polymerized MMA, initiated by AIBN, at different temperatures. According to the TOMP, initially the monomer molecules in disordered domains should polymerize followed by the polymerization of monomer in ordered domains. We have proved experimentally [13] that the calculated fractions are equal to the experimentally determined fractions of polymerized monomer in ordered and disordered domains (Fig. 3, points). In addition to that, some other characteristic points on the "monomer conversion – time" curve were theoretically predicted and confirmed experimentally.

### MONOMER SELF-ORGANIZATION AND POLYMERIZATION BY TRANSITION METAL COMPLEXES

Half a century has passed since Karl Ziegler and Giulio Natta discovered that olefins can polymerize in the presence of active centres formed by transition metal (Mt) compounds, as the precursors. In many cases Mt is immobilized on some inorganic support and activated by alkyl aluminium compounds [23]. Almost at the same time it was discovered that Mt oxides can be used as the active centre precursor for olefin polymerization without the alkyl aluminium compound. Some thirty years ago it was discovered that some metallocenes, based on zirconium, titanium and hafnium, in the presence of methylaluminoxane (MAO) can also polymerize olefins.

In all those cases it is believed that the polymer chain propagates by monomer insertion between Mt and the polymer chain bonded to Mt.

Despite very great commercial achievements, there is a lack of an adequate theoretical explanation of Ziegler–Natta (ZN) polymerization. A large number of questions arising from the experimental results remain unanswered:

- The detailed structure of the active centres has never been understood.
- What is the oxidation state of an active centre?
- Are the active centres uniform or non-uniform?

- Does alkylaluminium participate in the active centres?
- How can we correlate the rate equations to the insertion mechanism?
- What is the exact role of the support?
- Why is a full polymerization activity observed only if the support/Mt ratio is extremely high?
- What are the roles of electron donors, hydrogen, MAO and other components?
- There are also many unanswered questions concerning the controversies of the current explanation and polymer structure.

So, it has been concluded that despite intense research activity, no definite, unequivocal polymerization mechanism has yet been defined to describe the behavior of Ziegler-Natta, metallocene and Mt oxide catalysts. In spite of the improvements in catalyst technology, there is still much to be learned about the elementary steps in olefin polymerization.

Boor stated, however, "Each worker has examined some aspect of the problem and has given his view of what is happening. The findings are similar pieces of a puzzle which have to be coupled to form the whole picture; only here, **some critical pieces are still missing**" [23].

According to our opinion, it is evident that the insertion mechanism is wrong. Kargin and Kabanov [2] supposed that the polymerization of olefins that are adsorbed and properly organized on some supports, could also be explained by the TOMP. Hence, we have proposed a different mechanism, i.e. the charge percolation mechanism (CPM) of olefin polymerization by supported transition metal (Mt) complexes [24-26]. It is well known that different oxidation states of Mt are obtained by activation, i.e.  $Mt^{+(n-1)}$ ,  $Mt^{+(n)}$  to  $Mt^{+(n+1)}$ , producing irregular charge distribution over the support surface. The tendency to equalize the oxidation states into  $Mt^{+(n)}$  by a charge transfer from  $Mt^{+(n-1)}$  (donor, D) to  $Mt^{+(n+1)}$  (acceptor, A) cannot be fulfilled since the Mt ions are immobilized and highly separated on the support. But, monomer molecules are gradually adsorbed on the support producing clusters with stacked  $\pi$ -bonds making a  $\pi$ -bond bridge between D and A (Fig. 4). Once a bridge is formed (percolation moment), a charge transfer occurs. D and A equalize their oxidation states simultaneously with the polymerization of monomer. The polymer chain is desorbed from the support making the surface free for the subsequent monomer adsorption. The whole process is repeated by the oxidation-reduction of another AD ensemble.

The active centres of  $Mt^{+4}$  and  $Mt^{+2}$ , i.e. A and D, are transformed to  $Mt^{+3}$  and deactivated. (Experimental evidence is presented in [30].) Hence, monomer polymerization and Mt deactivation are mutually interdependent processes: there is no polymerization without A and D deactivation, and there is no such A and D deactivation without polymerization. Both components (Mt and the monomer) are chemically changed. Both are reactants. Neither one of them is the catalyst.

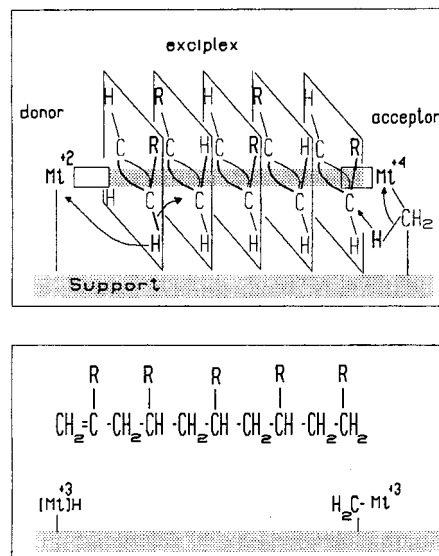


Figure 4. Monomer self-organization and the charge percolation mechanism of Ziegler-Natta polymerization (upper) and polymer detachment (below) [24-26]

The support has a very important role. It offers a high surface area to bring both components together, by immobilization of Mt and by monomer adsorption. Thanks to the support, it is possible that both reactions (the oxido-reduction of Mt and the polymerization of monomer) are merged and performed at the same location, simultaneously, in a common process. Furthermore, once both reactions are completed, the support becomes free for the subsequent immobilization of Mt and monomer adsorption. The support is the catalyst for both processes.

The main processes that determine the polymerization and polymer structure are AD ensemble formation, monomer adsorption and self-assembling. Both processes are time dependent [34].

AD ensemble formation includes the immobilization of Mt precursors onto the support, Mt alkylation, the heterogenization of the Mt oxidation states (mainly by the partial reduction of  $Mt^{+(n+1)}$  to  $Mt^{+(n-1)}$ ), A and D coordination with monomer molecules. The rate of AD ensemble formation and their actual concentration at the support depend on the type and concentration of process participants (Mt precursor, support, alkylating and reducing agents, monomer, electron donor), temperature, pressure, etc.

The monomer adsorption rate depends on the type of support and monomer, their concentrations in the reaction medium, pressure and temperature. It is very important to keep in mind that the coverage of the support by monomer and monomer self-assembly are time dependent processes [34]. Hence, a monomer bridge between A and D is formed gradually (Fig. 5.). After the removal of polymer, additional monomer adsorption will form another monomer bridge between the residual A and D that are more separated.

No polymer is formed until a bridge between some A and D is completed. A critical moment is when the

very last monomer is adsorbed that makes a bridge complete. Such processes are analyzed by the theory of critical phenomena, particularly by the percolation theory [48]. The described processes based on the CPM can be easily simulated by computer. Many aspects of the CPM have been systematically elaborated [24], the results presented at scientific conferences [25–40] and published [41]. Here we present only a few examples of the CPM and TOMP applications in the explanation of polymerization by Mt complexes.

• • D • • • A • • D • • • • • A • • • •

a) Immobilized acceptors (A) and donors (D) separated by empty sites (•) on the support

• m D • • • A m • D • • • • • m A • • • •

b) Monomer (m) adsorption

m m D m • • a p p d • m • m • m A • • m

c) Formed monomer bridge, polymerized monomer (p), deactivated acceptor (a) and donor (d)

m m D m • • • • • m • m • m A • • m

d) Polymer is removed making free adsorption sites for additional monomer adsorption

Figure 5. Phases of an elementary percolation step presented on a segment of a support adsorption row

It can be proposed, on the basis of the CPM, that the very first bridges must be formed between A and D that are situated close to each other on the support surface. Consequently, oligomers with a low degree of polymerization ( $X_n$ ) will be obtained initially, but  $X_n$  should increase with polymerization time [35]. Simultaneously, the number of active centres should decrease. Experimental data [42] confirmed such a prediction of the CPM (Fig. 6). We have simulated the experiments presented in Figure 6. The results of the simulation (Fig. 7) have the same trends as the experimental data. A very good correlation was obtained between the experimental and the predicted values of the polymer molecular mass and molecular mass distribution of the polymer obtained by propene polymerization in the presence of  $\text{TiCl}_4/\text{MgCl}_2$  [35].

The most important issues are the productivity of Mt ( $P_{Mt}$ , i.e. the quantity of polymerized monomer per used quantity of Mt) and the productivity of the support ( $P_s$ , i.e. quantity of polymerized monomer per used quantity of support). Both of them depend on the concentration of Mt at the support. The trends predicted by computer simulation [33,35] and calculation [38] (Fig. 8), based on the theory of active centre ensembles developed by Kobozev [43] and on the CPM, are in agreement with the experimental trends of olefin polymerization in the presence of all types of Ziegler–Natta [30, 33], Mt oxide and metallocene precursors [34]. We have confirmed that statement by

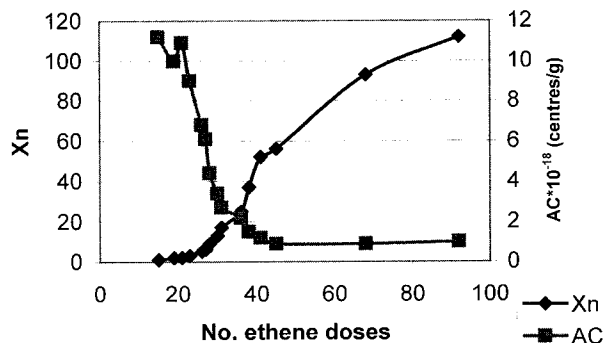


Figure 6. The mean  $X_n$  of ethene oligomers and the concentration of active centres (AC) obtained as a function of the quantity of adsorbed ethene on  $\text{CrO}_x/\text{SiO}_2$  [42]

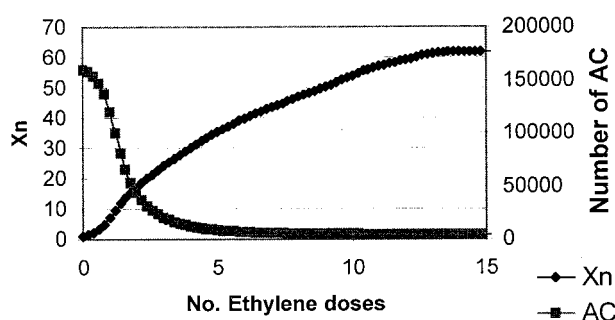


Figure 7. The mean  $X_n$  of ethene oligomers and the concentration of active centres (AC) obtained as a function of the quantity of adsorbed ethene on  $\text{CrO}_x/\text{SiO}_2$ . (Predicted by simulation of the experimental data [42] presented in Fig. 6)

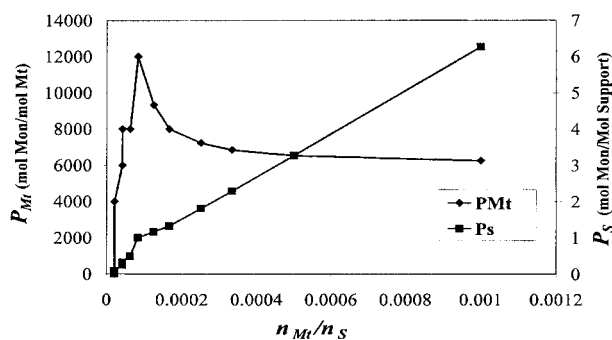


Figure 8. Predicted effect (by calculation) of the surface concentration of active centres  $n_{Mt}/n_s$  on the metal productivity  $P_{Mt}$  and support productivity  $P_s$  [38]

several dozen of experimental examples, but only one is presented here (Fig. 9).

#### OLEFIN SELF-ORGANIZATION AND STEREO-REGULAR POLYMER FORMATION BY Al-BASED CATALYSTS [40]

Recently W. Hirahata et al. [45,46] presented that ethene, propene and 1-hexene can be polymerized in the presence of  $\text{Al}(\text{i-Bu})_3$  and  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  (TBAF) supported on  $\text{SiO}_2$  and other inorganic supports. They proposed that  $\text{Al}(\text{i-Bu})_3$  and TBAF react producing ionic

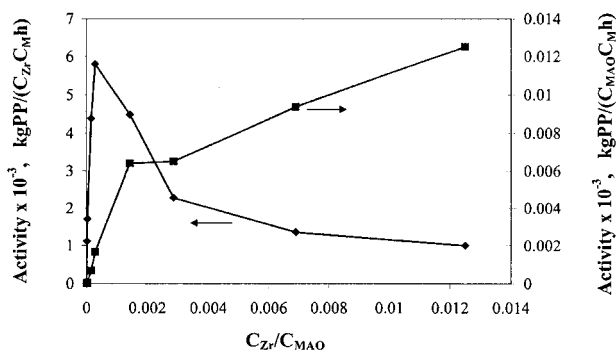
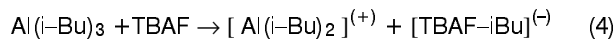


Figure 9. Activity of *rac*-ethene bis (4,5,6,7-tetrahydro-1-indenyl) zirconium dichloride/methylaluminoxane (MAO) in propene polymerization [44]. ( $C_{Zr}$ ,  $C_{MAO}$  and  $C_M$  are the concentrations of zirconocene, MAO and monomer, respectively).

species (4). These ionic species alone have low activity in ethene and propene polymerization. But after the addition of  $\text{SiO}_2$  (or some other inorganic supports) a high polymerization activity can be revealed and high molecular weight polymer can be produced without using a conventional solid catalyst component that includes transition metals and metallocene complexes. Even more surprising is the fact that high isotactic and syndiotactic polypropenes are obtained without transition metal active centers. The mechanism of that polymerization has not been explained. It is evident that the classical insertion mechanism cannot be used in this case.



We explained this polymerization by the TOMP [2] and charge percolation mechanism (CPM) [40]. According to the CPM, monomer clusters are present on the support making a bridge between the Mt donor and Mt acceptor (Fig. 4). In the case of Al-based and B-based catalysts for olefin polymerization, the positively charged Al complex (4) should be treated as an electron acceptor and the negatively charged B complex as an electron donor. So, the same CPM should be applied, but the Mt acceptors and Mt donors should be replaced by the Al-acceptors and B-donors.

It was mentioned that the fundamental difference between disordered (2) and organized (3) monomers is that the propagation is random on the molecular level in the first case (2), while it is determined on the molecular level but random on the supra-molecular level in the second case (3). In the first case (2), a one by one repeating unit is formed, while in the second case (3) a one by one chain segment is formed. Hence, in the second case (3) both the polymerization kinetics and polymer structure ( $M_n$ , MWD, stereoregularity, regioregularity, etc.) depend on the organization and arrangement of the monomer molecules in monomer clusters.

Monomer clusters can be formed by monomer adsorption on some support, or by cooling of the liquid, or by a combination of adsorption and cooling. There are many possible arrangements of organized monomer

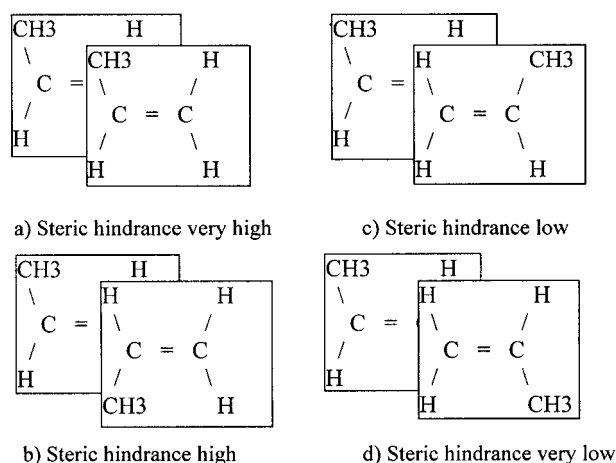


Figure 10. Some possible arrangements of substituents in clustered monomers. (Only a part, i.e. the "repeating unit" of the cluster with two molecules is presented).

systems. Some of them for propene are presented in Fig. 10. Arrangements (a) and (b) are less stable and less probable due to high steric hindrance (repulsive interactions of the  $\text{CH}_3$  groups). There is lower steric hindrance in arrangement (c), but the lowest one is in arrangement (d). Hence, arrangement (d) is the most preferable and it can be achieved in the condensed (liquid) state.

In the case of adsorbed monomer, the orientation of the bulky  $\text{CH}_3$  group toward the support should reduce the adsorbate-support interaction and should occupy a considerable surface area. Hence, arrangement (c) is more preferable than arrangement (d) in the adsorbed monomer monolayer on the solid support, supposing that the support is on the bottom side of the monomer monolayer. There is experimental evidence [47] for such arrangements of adsorbed propene. It is important to emphasize that monomer self-assembling is a time dependent process. Pressure and temperature also have considerable effects. These issues, however, are presented elsewhere [34] and will not be discussed in this article.

The enchainment of monomer arrangement (c) contributes to isotactic PP, i.e. "mm" structures (Fig. 11). Similarly, the enchainment of monomer arrangement (d) contributes to syndiotactic PP, i.e. "rr" structures. The transition form of (c) to (d) arrangements should contribute to "mr" structures. The polymerization of (a) and (b) monomer arrangements contributes to 2,1 erythro and threo enchainments.

Now, we shall present our interpretation of the experimental examples presented in [45,46]. According to the CPM, the following conditions must be fulfilled for successful polymerization:

- the existence of an acceptor (A) and a donor (D);
- the existence of a monomer cluster that connects A and D.

In comparative examples 1 and 3 in ref. [46] there was no borate (no donor), but in comparative example 2 there was no triisobutylaluminium (i.e. no acceptor). The

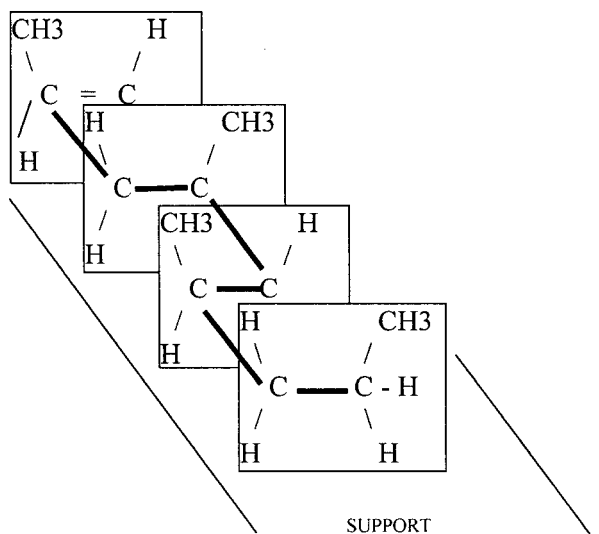


Figure 11. Enchainment of (c) monomer arrangement at the moment of polymer chain formation. (This configuration is not convenient for the PP chain and it is transformed to a spiral configuration during chain detachment from the support).

above-mentioned conditions were not fulfilled and, consequently, no polymer was obtained. The above-mentioned conditions were fulfilled in all other experiments and polymer was obtained.

In example 15 propene was adsorbed on silica. The adsorbed propene should have a molecular arrangement as presented in Figs. 10c and 11. Consequently, mainly isotactic polypropene is predicted by the CPM as was confirmed experimentally, i.e. the content of *mm* diads was 0.93.

There was no support in comparative example 4, but the polymerization was performed in liquid propene. The propene molecules are arranged as presented in Figure 10d and by the randomly alternating segments presented in Figure 10c (and maybe to a lower extent by the segments presented in Figures 10a and 10b). Concerning stereo-regularity, a relatively high content of syndiotactic fractions can be expected, as was confirmed experimentally [46], i.e. *rr* = 0.49.

In the examples 13 and 14 in ref. [46], the polymerizations were performed partially in liquid and partially in adsorbed propene. Hence, the self-assembling of propene was performed by both processes, i.e. by cooling and by adsorption on a support. We supposed that polymerization occurred in both the phases, i.e. in the liquid and in the monolayer of propene adsorbed on the support. Consequently, the total polypropene yield should contain two fractions: one originating from the liquid and a second from the adsorbed phase. We calculated the quantities of both fractions and predicted the structure of the whole polypropene by the CMP and TOMP. These predictions were in quite good agreement with the experimental results [45,46] (Table 2). It may be concluded that the stereoregularity of the polymer chain is the result of the enchainment of properly arranged organized monomers, as proposed by Kargin and Kabanov [2].

Table 2. Prediction of PP structure by the charge percolation mechanism

PP Structure		Example 13	
		Predicted by the CPM	Experimental [46]
Isotactic bonds	<i>mm</i>	0.67	0.63
Atactic bonds	<i>mr</i>	0.16	0.20
Syndiotactic bonds	<i>rr</i>	0.17	0.17
Mol. weight	<i>Mn</i>	44121	54646
MWD	<i>Mw/Mn</i>	12.3	9.9
PP Structure		Example 14	
		Predicted by the CPM	Experimental [46]
Isotactic bonds	<i>mm</i>	0.46	0.57
Atactic bonds	<i>mr</i>	0.25	0.23
Syndiotactic bonds	<i>rr</i>	0.29	0.20
Mol. weight	<i>Mn</i>	66474	95445
MWD	<i>Mw/Mn</i>	14.5	10.1

## CONCLUSION

The theory of organized monomers polymerization, originally proposed by Semenov, Kargin and Kabanov in the 1960-ies, was successfully applied to explain various polymerization processes such as: the radical polymerization of compressed ethene gas, the radical polymerization of liquid methyl methacrylate, olefin polymerization by transition metals and by Al-based catalysts. Monomer self-organization has a decisive effect on the mechanism and kinetics of polymerization, as well as on the structure and properties of the polymers.

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## IZVOD

### POLIMERIZACIJA ORGANIZOVANIH MONOMERA

(Pregledni rad)

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Savremena tumačenja polimerizacije olefina i vinilnih monomera pretpostavljaju da se jedan po jedan molekul monomera dodaje rastućem polimernom lancu. Ovo može biti istina ako molekuli monomera postoje kao pojedinačne čestice u polimerizacionom sistemu, npr. u razblaženim rastvorima monomera. Međutim, postoje slučajevi kod kojih su molekuli monomera organizovani: u masi tečnog monomera, u čvrstom monomeru, u monosloju monomera adsorbovanom na nosaču i dr. U tim slučajevima postoje različite nadmolekulske vrste i čestice. Semenov, Kargin i Kabanov su 1960-tih godina predložili teoriju polimerizacije organizovanih monomera. U prethodnih 25 godina, naša istraživačka grupa je dalje razvila i primenila ovu teoriju na različite polimerizacione sisteme: radikalna polimerizacija komprimovanog gasovitog etena, radikalna polimerizacija tečnog metilmetakrilata, polimerizacija olefina pomoću prelaznih metala i pomoću aluminijumskih katalizatora. U ovom radu su prikazana naša glavna dostignuća u ovoj oblasti.

Ključne reči: Polimerizacija • Organizovani monomeri • Olefini • metilmetakrilat • Prelazni metali • Ziegler-Natta • Metaloceni •

Key words: Polymerization • Organized monomers • Olefins • Methyl methacrylate • Transition metals • Ziegler-Natta • Metalloenes •