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The Structure of the Active Centres and Stereoregulation in the Ionic-Coordination Polymerisation of α-Alkenes and 1,3-Dienes on Ziegler-Natta Catalysts

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The development of theories of the mechanism of the stereospecific polymerisation of α-alkenes and dienes on Ziegler-Natta catalysts has been examined. Theories of the formation and structure of the active centres, the role of the heterogeneous component of the catalyst, the mechanism of chain initiation and growth, and the mechanism of stereoregulation in the polymerisation of alkenes and dienes have been discussed.
The bibliography contains 115 references.

CONTENTS

I. Introduction 17
II. Nature of the active centres and mechanism of polymerisation 17
III. Mechanism of stereoregulation 28
IV. Summary 36

I. INTRODUCTION

An important contribution to the development of the chemical kinetics of processes including polymerisation and polymer degradation was made by Academician N.M.Emanuel'. In his work, particular attention was paid to the study of radical reactions, and also reactions involving complexes and various ionic coordination compounds†.

Ziegler–Natta catalysts involving the salts of metal groups IV–VIII and organic compounds of groups I–III of Mendeleev's periodic system of the elements have been used for more than 30 years for the industrial production of stereoregular polymers of a number of α-alkenes and dienes. There is still lack of agreement, however, on the mechanism of polymerisation and stereoregulation in the presence of these catalysts. The present review examines existing theories in this field.

The following abbreviations are used: M represents a metal from groups I–III, M′ a transition metal, $\bar{P}$ the degree of polymerisation, OMC an organometallic compound, OAC an organoaluminium compound, MA a macromolecule, AC an active centre, PAC an active centre at the physical adsorption stage, CAC a chemical adsorption centre (a potential polymerisation AC), and MO a molecular orbital.

† N.M.Emanuel, G.E.Zaikov, and Z.K.Maizus, "Oxidation of Organic Compounds: Medium Effects in Radical Reactions", Pergamon Press, Oxford, 1984, 645 pp.

II. NATURE OF THE ACTIVE CENTRES AND MECHANISM OF POLYMERISATION

1. Empirical Schemes

One of the first mechanisms, namely the stepwise anionic reaction mechanism, was proposed for the process in 1955 by Ziegler and co-workers.[1] The scheme is based on the following reactions: 1) the stepwise addition of the OAC to the alkene, and 2) the displacement of the Al atom from the alkene chain with the participation of $TiCl_4$ (al = 1/3 Al), which controls the ratio of reactions (1) and (2) in scheme 1:

Scheme 1

$$R(CH_2\text{—}CH_2)_n\text{al} + C_2H_4 \rightarrow R(CH_2\text{—}CH_2)_{n+1}\text{al} \qquad (1)$$

$$R(CH_2\text{—}CH_2)_{n+1}\text{al} \xrightarrow[TiCl_4]{C_2H_4} R(CH_2\text{—}CH_2)_n\text{—}CH{=}CH_2 + RAl \qquad (2)$$

This mechanism was very quickly rejected. In particular, according to Ref.1, more easily ionised OMC (Na or K pentyls) should form more active catalytic systems than R_3Al. This does not agree with the experimental data, however. Moreover, according to the Ziegler mechanism, the individual OMC should also bring about the polymerisation of α-alkenes to macromolecular polymeric products, but this does not take place. There are many other examples where the Ziegler theory does not agree with the experimental data, in particular the reliably established fact that the transition metal–carbon bond plays an active role in chain growth.

In the period 1955–1960, a large number of papers were published, which not only discussed the anionic mechanism[2-4] but also successively put forward the ionic-coordination,[5-18] free-radical,[19-21] cationic,[22,23] and radical-ion[24-26] mechanisms for the process.

The free-radical mechanism, based on the reactions:

$$R_3Al + TiCl_4 \rightarrow RTiCl_3 + R_2AlCl$$
$$RTiCl_3 \rightarrow R^{\cdot} + TiCl_3$$

was also quickly rejected, since it did not explain many fundamental experimental data, in particular the following: a) radical chain transfer agents do not influence $\overline{P}$ for the polymers, b) familiar inhibitors of free-radical reactions have a positive influence on the process (the reaction rate, $\overline{P}$, and the stereospecificity of the process increase), c) change in the nature of the components of the Ziegler–Natta catalyst generally leads to a change in the reactivity of the monomers in copolymerisation, d) the time of existence of the growing MA is much greater than that in free-radical polymerisation, e) the formation of "live" polymer chains is possible,[27–30] etc.

The cationic mechanism was also rejected, even if only because the order of activity of the monomers in complex formation with Ziegler–Natta catalysts (butadiene > isoprene > styrene > isobutylene > α-methylstyrene) differs markedly from the order of the activities of these monomers in their reaction with Lewis acids.

The ion–radical mechanism:

$$A^{\cdot} + C_2H_4 \rightarrow A{-}CH_2{-}\dot{C}H_2 \rightleftarrows A^{+-}CH_2{-}CH_2^{\cdot}$$
$$A^{\cdot} = \text{radical}$$

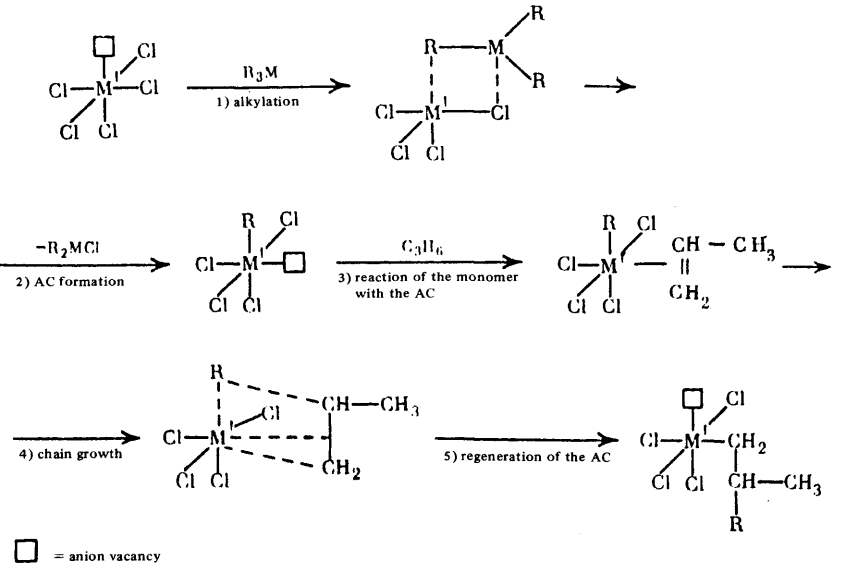
also does not agree with many of the above experimental data. This mechanism does not explain the chain termination associated with the removal of the MA from the catalyst surface, or the presence in the MA of organic groups previously present in the OMC.

Beginning in the nineteen-sixties, various versions of the ionic-coordination mechanism of polymerisation on Ziegler–Natta catalysts, which takes account of the important role of the reaction of the OMC with the M′ salts in the production of the AC, were accepted, and for more than 20 years now, two theoretical schemes have coexisted and been widely discussed, based on: a) the single-metal model of the AC,[4,16,17,31–49] etc., and b) by two-metal model of the AC,[2,5,7–11,13–15,18,50–61] etc.

a) Single-metal Model of the Active Centre

Without going into details of all the proposed schemes, it can be stated that the single-metal model of the AC includes the alkylation of M′ without a change in its oxidation state. Chain initiation and growth in the polymerisation take place by the insertion of the alkene at the M′–C bond. The specific feature of the mechanism of polymerisation on Ziegler–Natta catalysts is that all the stages controlling the process, that is the initiation, growth, and all forms of limitation of the chains, involve highly active alkyl radicals, forming weak covalent bonds with M′.

The essential features of the process are most fully reflected by the Cossee–Arlman scheme.[17,33,34] According to this scheme, the active beginning of the polymerisation is due entirely to M′ and its ligands. On the edges of the $M'X_n$ crystals, AC are formed, having one anion vacancy in the octahedral coordination sphere of M′. The coordination of the monomer to the AC leads to the rupture of the C=C bond and the insertion of the monomer at the M′–C bond. The migration of the gorwing chain restores the complex to its original state, so that the addition of the next monomeric unit becomes possible:



The fact that the OMC of the most electropositive metals are suitable for obtaining active catalytic systems is due to their high alkylating power.

During growth, the chain oscillates between two positions on the $(M')^{n+}$ ion, increasing by one unit each time. In the Cossee–Arlman scheme as modified by Rodriguez and Van Looy,[59] the migration of the growing MA is not regarded as essential.

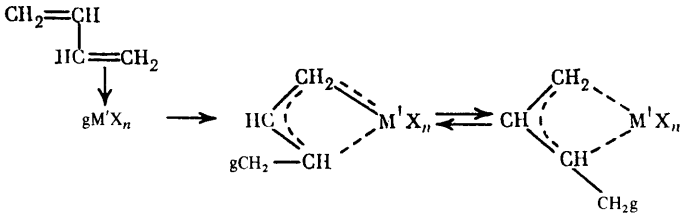
Later papers, for example Refs.36–40, while retaining the main ideas of Cossee given above, examined individual aspects of the problem in more detail. In particular, it was suggested[39] that the catalytic process is not a purely surface phenomenon, and that all the M' atoms take part in the reaction. The use of $(TiCl_3.AlCl_3)$–R_2AlCl leads to the production of the characteristic crystal structure of $Ti_8Cl_{24}.Al_2Cl_6$, which contains cavities whose dimensions allow R_3Al and the monomer to diffuse to M'. R_3Al alkylates $TiCl_3$, after which the process develops according to the Cossee–Arlman scheme.[33]

In Ref.40, a general mechanism was proposed for both the polymerisation of the monomers and the metathesis processes (see Ref.62).

Dolgoplosk and co-workers[36–38] suggest that in the polymerisation of dienes the initiation involves a π-allyl complex in the *anti*-conformation. The diene takes part in the process almost always as a bidentate ligand:

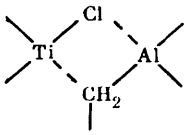
If however the AC has only one anion vacancy, the diene can coordinate only through one C=C bond in the trans conformation:

Scheme 3

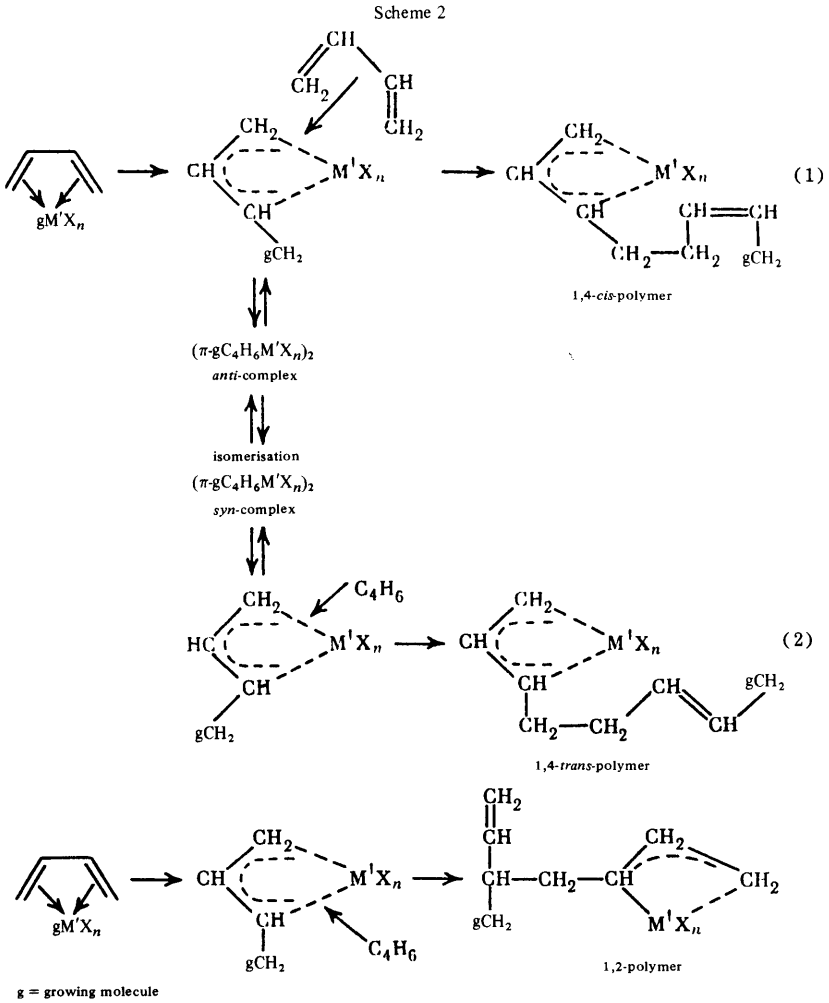


b) The Two-metal Model of the Active Centre

The polymerisation mechanism for the two-metal model of the AC assumes the existence of complexes formed by the M' salt and the OMC, of the type



Scheme 2



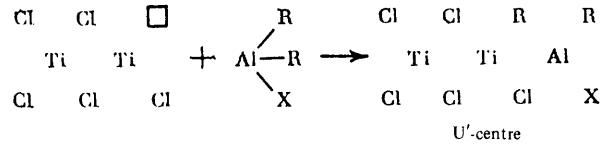
The polymerisation involves the formation of a complex by the catalyst with the monomer. Since the electropositive nature of the atom M′ increases with decrease in its oxidation number, only compounds of M′ with low oxidation numbers can show catalytic activity. The $(M')^{n+}$ cation initiates the process, and the negatively charged ionic complex of the

OMC (R_3^-, $-\overset{|}{\underset{|}{Al^+}}$) brings about the growth of the MA.

According to Refs.7, 11, 19, 52, etc., chain growth takes place in the surface layer of the crystal lattice of a mixed salt of M′, in particular $TiCl_3.R_2AlCl$. The role of $TiCl_3$ reduces to the activation and stabilisation of the OAC, and the negatively charged $R^{\delta-}$ group initiates the "unwinding" of the MA from the Ti atom, which forms a complex with the monomer molecules.

According to Refs.11 and 18, the reaction of the heterogeneous ($M'X_n$) and homogeneous (R_mM) components gives impurity crystals containing surface electronic defects of the "colour centre" type. One route for their formation involves the chemisorption of the OMC on the ionic lattice of the M′ salt (R_3Al on $TiCl_3$), primarily in the positions of existing crystal defects.

Real crystals of M′ halides (the heterogeneous component of the Ziegler–Natta catalysts) always have an excess of negative charge. The chloride ions are removed more easily from the edges of the crystalline plate than from its centre.[33] As a result, in real crystals the Cl vacancies are situated at the edges of the crystals and in the positions of the dislocations, where polymerisation takes place preferentially.[64,65] Thus the crystal lattice of $TiCl_3$ is completed by the cationic fragment R_2Al^+, which is formed from R_3Al in the field of the surface Cl^- anions. An impurity crystal is formed. Since crystals of this type are essentially ionic systems, for which it is advantageous to remain electrically neutral, this requires the "formation", conjugated with the above process, of a vacancy in the region of which R^- is localised. In the process, on the one hand, the anion defect is "saturated", and on the other hand the unstable $R^{\delta-}$ is stabilised. The crystal lattice defect produced—a potential polymerisation AC—is called a U′-centre:[11,18]

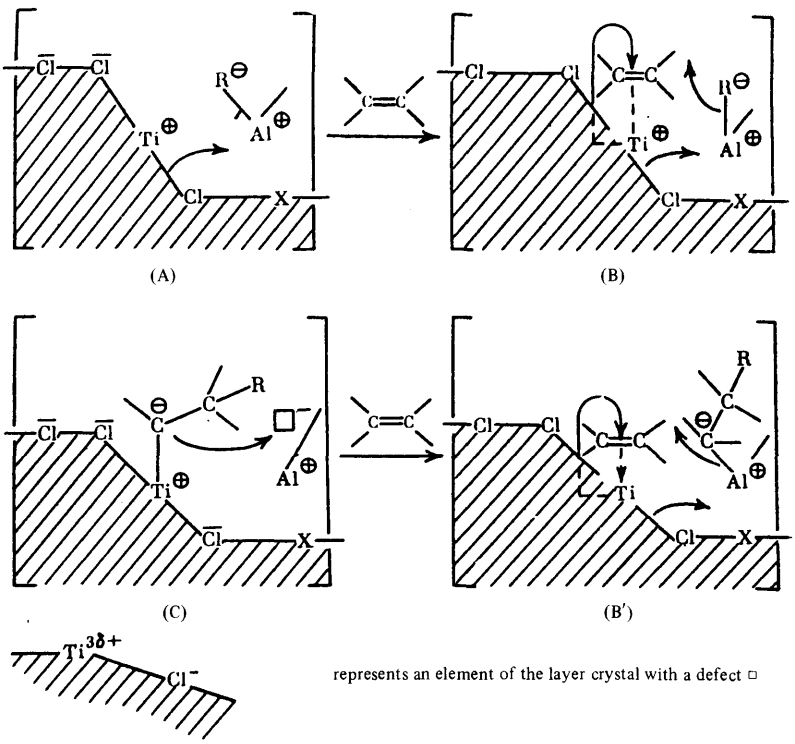


U′-centre

The polymerisation always involves the formation of a ternary complex $\rangle C{=}C\langle .M'X_n.R_nMX_{3-n}$ ($n = 3-1$), so that the heterogeneous component should be capable of forming a complex not only with the OMC but also with the monomer. In the case of ionic solids, the adsorption capacity is related to the defect nature of their structure and depends on temperature, the concentration of foreign impurities in the form of other structural defects which can take part in electronic processes, etc.

The monomer, chemisorbed on the potential AC, reacts with M′, which contains partly filled *d* orbitals (for example Ti), to form a molecular complex similar in character to the familiar π-complexes of alkenes with Pt, Cu, and Ag.[18]

The reaction of $M'Cl_n$ with the monomer takes place by a donor–acceptor mechanism, and that with the OMC by an acceptor–donor mechanism to give an impurity ionic crystal. As a result, $R^{\delta-}$ of the OAC acquires an increased negative charge. Electron transfer becomes possible through the closed system:[18]

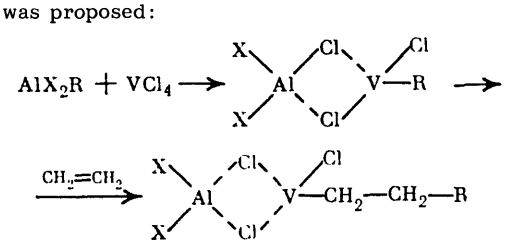


The scheme assumes simultaneous electrophilic and nucleophilic attack on the monomer molecule by the components of the catalytic complex, so that the heterogeneous catalytic polymerisation of alkenes and dienes under the influence of Ziegler–Natta catalysts can be regarded as "push–pull" reactions, involving the successive introduction of the monomer, its coordination, attack by Ti^{3+} and R–Al$<$, and insertion at the Ti–C bond to give the MA, that is the operating principle of an automatic conveyer is established. As a result of cooperative synchronous electron transfer processes (the "concerted" mechanism), a σ-bond is formed between a carbon atom of the $R^{\delta-}$ group and a neighbouring carbon atom of the monomer. The group R, belonging initially to the OAC, becomes the terminal group in the MA formed; this leads to the reappearance of an active group $R^{\delta-}$, larger by one monomer unit, and localised on the anion vacancy, and the AC is regenerated.

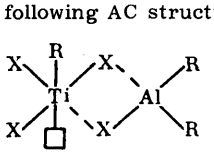
In this scheme, the nature of the interaction of the catalytic system and the monomer, and also the stability of the ternary complexes formed, should naturally be influenced by all the parameters characterising the heterogeneous component, and also its structural-chemical features, in particular the crystallographic radius, the magnitude of the charge, the ionisation potential of $(M')^{n+1}$, the crystal lattice structure, etc., and this is confirmed by a large amount of experimental data. An important role is also played by the atomic radius of M, the polarity of the M–C bond in the OMC, the chemical nature and structure of the monomer, the electron affinity of the monomer, polar and steric factors, etc.

These ideas are consistent with practically all the experimental data, including the effect of the modification of Ziegler–Natta catalysts by ethers, amines, sulphides,[27,28] aromatic compounds,[66,67] oxygen, and peroxides,[30] and are fairly universal. (By ignoring various features, it is possible to arrive at the schemes mentioned above, proposed in Refs.1, 6, 9, 10, 14, 15, 17, 57, 58, etc.).

In the polymerisation mechanism schemes described above, based on the two-metal model of the AC, it is assumed that both the atoms M′ and M are in the first coordination sphere of the AC. In some papers[60,61,68–70] it is postulated that M′ is in the second coordination sphere of the AC# and influences the polymerisation only through the electronic structure of the complex formed. For example, in Ref.70 the following scheme was proposed:



A similar viewpoint is held by the authors of Refs.60 and 61, who proposed the following AC structure:



They do not however take account of the fact that in heterogeneous systems, AC of this type probably cannot be formed.

#Particularly in the case of homogeneous Ziegler–Natta catalysts.

Thus the first, almost twenty-year, period of the study of various aspects of the chemistry and technology of polymerisation on Ziegler–Natta catalysts is characterised by the appearance of a large number of different empirical schemes, but often without detailed consideration of the problem and observation of the fundamental requirement that the theoretical postulates correspond to all the available experimental data. It is therefore possible to exclude from consideration the purely ionic, radical–ion, and free-radical polymerisation mechanisms. The examination of ionic–coordination polymerisation on Ziegler–Natta catalysts is now based essentially on one of the two concepts of single-metal or two-metal catalysis, differing in the structure of the AC and the mechanism of the process.

Up to the present, the Cossee–Arlman scheme (Refs.41 to 49, etc.) with a single-metal model of the AC has been most popular. At the same time, its fundamental unsatisfactory features are well known. This scheme: a) does not make specific the role of the OMC in the regulation of the activity and stereospecificity of Ziegler–Natta catalysts; b) does not explain why in many cases the OAC influences the activity and stereospecificity of the catalysts, and why organozinc compounds, which are good alkylating agents, give less active and less stereospecific active centres; c) does not explain why electron-donor ligands (amines, arenes) improve considerably the activity and stereospecificity of Ziegler–Natta catalytic systems; d) does not explain why only a small proportion of the alkylated M′ starts polymer chains, etc. Another weak feature of the scheme is the oscillating migration of the growing MA chain during polymerisation.

An attempt has been made[59] to eliminate these unsatisfactory features of the Cossee–Arlman scheme while retaining its basic postulates; its was suggested that the AC is a four-coordinate alkylated M′ atom with two anion vacancies, one of which is subsequently occupied by the OAC. This treatment, however, leads essentially to the fundamentally different two-metal AC structure.

Thus early empirical schemes, based entirely on a logical analysis of experimental data and general theoretical postulates, have not produced a satisfactory simple theory of the mechanism of catalysis in polymerisation on Ziegler–Natta catalysts. In a short period of time (less than 10 years) quantum-chemical studies have provided a deeper understanding of the problem.

2. Present-day Trends

The principal unsatisfactory features of early empirical theories of the mechanism of polymerisation on Ziegler–Natta catalysts are a restricted approach to the solution of the problem, the hypothetical nature of the choice of the AC model, the neglect of the characteristic features of the structure of the heterogeneous component, etc. This explains the development of a large number of theories and the lack of unambiguous solutions, and it should be borne in mind that it is impossible to determine the mechanism of polymerisation on Ziegler–Natta catalysts using only existing experimental methods.

Although the single-metal AC model appears simpler, it is being used and developed intensively. There are however no grounds for neglecting the two-metal AC model, which provides a much more convincing interpretation of the mechanism of polymerisation on Ziegler–Natta catalysts in sufficiently good agreement with practically all experimental data, many of which cannot be explained by other hypotheses, including the Cossee–Arlman single-metal catalysis scheme.[17,33,34]

The following reliable and generally accepted experimental facts must always be borne in mind: a) the AC are formed only by the reaction of both components of the catalytic system; b) all stages of the catalysis involve the M′ atom and the surrounding ligands, and the M compounds; c) the polymer chain grows in "hairlike" fashion, and one of the substituents R of the OMC molecule is situated at the end of the MA being formed; d) the rate of the process and the structure of the polymer are determined by the nature of not only M′ but also the OMC, that is by the structure of the AC, which in turn depends on the nature of the ligands in the coordination sphere (monomer, counter-ion, co-catalyst, modifying additives, solvent, and any other added reagent with electron-donor or electron-acceptor properties); e) the oxidation state of M′ (Ti, V, Cr) in the AC is generally 3+; f) the growing MA are arranged in spirals and are concentrated chiefly on the side faces and dislocations at the points where the M′ ions appear on the crystal surface; g) polymerisation on Ziegler–Natta catalysts is characterised by relatively low activation energy values (E_{act}).

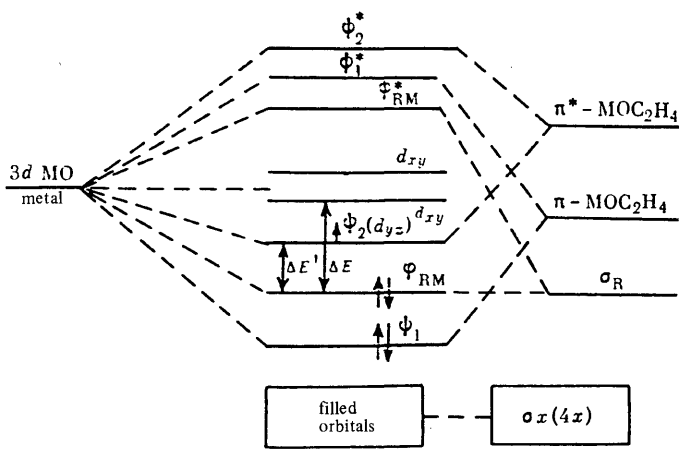
At the same time, many problems of specific polymerisation under the influence of Ziegler–Natta catalysts cannot be solved experimentally by existing methods. This applies particularly to the structure of the AC, the separate stages of chain initiation, growth, and termination, etc. A number of fundamental problems can be solved by combining experiment with modern methods of calculation and process modelling using the techniques of quantum chemistry, numerical experiment (monte Carlo, molecular dynamics), etc.[17,68,69,71–108]

a) Modelling the Process of Polymerisation on Ziegler–Natta Catalysts

The determination of the mechanism of ionic–coordination polymerisation on Ziegler–Natta catalysts is directly related to the determination of the structure of the AC.

A characteristic feature of the first studies[71–75] was the investigation of various particular problems regarding AC, selected according to the subjective opinions of the research workers. The mechanism of polymerisation on both single-metal[17,76–85] and two-metal[68,69,75,86–96] AC was examined.

Single-metal model of the active centre. The first paper applying quantum mechanics to polymerisation on Ziegler–Natta catalysts was published by Cossee.[17] It examined a simplified molecular diagram of an octahedral alkylated complex $M'Cl_4R$ and ethylene:



In the formation of the complex of the alkene with $RTiCl_4$, ΔE in the diagram corresponds to the energy which must be acquired by the electron taking part in the antibonding of the Ti–C bond. A high value of ΔE facilitates the preservation of the Ti–C bond in the absence of the alkene. When the alkene is bound in the complex, the interaction of the *d* orbitals of M′ and the π^* antibonding orbitals of the monomer produces a new energy level $\psi_2(d_{yz})$, which lies below the energy level of the 3*d* orbital of the original M′, and the excitation of the electron of the M′–C bond (ϕ_{RM}) can take place much more easily. The Ti–C bond therefore readily undergoes homolysis. If $\Delta E'$ is smaller than the difference in the critical energies,[97] the R group is "ejected" as a radical, which in a coordinated process subsequently adds on to the nearest carbon atom of the alkane. At the same time, a C atom of the alkene adds on to M′. When the reaction is repeated, the R group returns to its original position. According to Cossee's model,[17] only some M′ ensure the necessary conditions for the process. According to the MO diagram, for the M′ compound to show catalytic activity it is not essential to have an electron in each of the orbitals d_{yz}, d_{xz}, and d_{zy}. The $\psi_2(d_{yz})$ orbital, however, must not contain two electrons simultaneously. This means that only $(M')^{n+}$ ions having 0–3 unpaired *d* electrons are suitable as catalysts. The specific action of the M′ ion is possible only when the 3*d* level of M′ lies between the bonding and antibonding energy levels of the alkenes. Later analogous MO studies[77] of the complexes CH_3TiCl_3, CH_3TiCl_4, CH_3TiCl_4. $.CH_2{=}CH_2$ by the Wolfsberg–Helmholz–Ballhausen method added nothing new to these ideas.

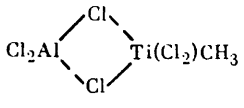
In Ref.76, the Hückel extended iteration method was used to study the migration of the CH_3 group to a coordinated ethylene molecule on the signle-metal AC $Ti(Cl/2)_4CH_3$ and to confirm the data of Ref.17; thus the *d* level of M′ lies between the π and π^* levels of ethylene, the bonds between R and the Ti atoms are localised, and the corresponding levels lie only 16000 cm^{-1} below the non-bonding d_{xz} and d_{yz} orbitals of M′. The chief difference between the Ti–C bond and the Ti–Cl bond lies in the much lower electronegativity of the two interacting atoms (the overlap integrals are the same in both cases). The results of the calculation indicated that the low kinetic stability of the Ti–C bond is due to the small energy difference between the MO bonding M′ to C and the unoccupied *d* orbitals.

Subsequent studies cast doubt on Cossee's conclusion that the driving force of the reaction is the decrease in the strength of the Ti–C bond resulting from the manifestation of π-acceptor properties by the alkene on coordination to M′.[41,42] The process of polymerisation on the Ziegler catalytic systems $[CH_3TiCl_4.C_2H_4]^n$ (the charge n = 0, −1, −2) and $Ti(CH_3)Cl_3.C_2H_4$ was studied on the basis of Cossee's scheme using CNDO and SCF X_α-SW methods.[78–80] The assumption that there is extensive overlap of the $3d_{yz}$ orbital of Ti and the π^* orbital of ethylene, which is the basis of many postulates of Cossee's theory, and hence of the driving force of the polymerisation reaction, was not confirmed. Moreover, according to Ref.78, Cossee's polymerisation mechanism can apply only in particular cases. The results obtained in Refs.78–80 agreed with the results of quantum-chemical studies assuming a two-metal model for the AC.[68,69]

Semi-empirical MO calculations of a hypothetical reaction path assuming that intermediate compounds of the metallocyclopentane type are formed in the polymerisation of alkenes were carried out in Ref.79. It should be noted, however, that the polymerisation scheme proposed in Ref.79 is not consistent with the experimental data.

The concept of the single-metal catalysis of polymerisation on Ziegler–Natta catalysts was developed systematically in a recent series of papers.[81–85] In these studies, the CNDO/2 and MINDO/3 methods were used to study the complexes $[RTiCl_4]^{2-}.C_2H_4$ (Cossee's AC model) and $Al(CH_3)_3.C_2H_4$, $AlH_3.C_2H_4$, and $(CH_3)_2AlH.C_2H_4$. The latter were chosen to investigate the general regular features of the catalytic transformations of α-alkenes. The studies gave the following results: a) a two-stage reaction path involving the formation of a π-complex by the alkene with the Ti ion is energetically favourable; b) the insertion stage requires only a small E_{act} and is accompanied by the formation of a stable *cis*-configuration of the alkyl and the growing MA; after the insertion of the monomer, *cis–trans* isomerisation is possible; c) the limiting stage is the coordination of the alkene with rearrangement on the AC of the growing end of the MA under the influence of the coordinated monomer; d) a stable AC structure is formed by a Ti ion with four octahedrally arranged Cl^- ions and one R group. The activation energy of the stages involving the coordination and insertion of the monomer with the participation of the AC is made up of the energy of rupture of the π-bond of the alkene and the energy required to change the coordination state of the AC. An analysis of experimental data on the polymerisation of alkenes on the individual compounds $M'R_n$ or $M'X_m.R_{n-m}$ (R = methyl, benzyl, neopentyl, tetramethylallyl, or allyl; X = halogen or cyclopentadienyl) also established[85] that the presence of a M'-C σ-bond in the individual compounds is not a sufficient condition for their catalytic activity in the polymerisation of alkenes. Particular importance is assigned to the coordination state of $M'X_mR_{n-m}$ ($M'R_n$). It is only when octahedral structures are formed in the AC–alkene complexes that sufficiently stable π-complexes can be produced on the AC. Data from other papers were also confirmed: in single-metal Ziegler catalysis, the $3d-\pi^*$ molecular orbital overlap is extremely slight, and the Ti–C bond is determined almost entirely by the highest bonding orbital of the alkene complex.[81–85]

The two-metal model of the active centre. In one of the first papers,[68] the polymerisation of ethylene under the influence of a homogeneous catalytic system was studied by the CNDO method.

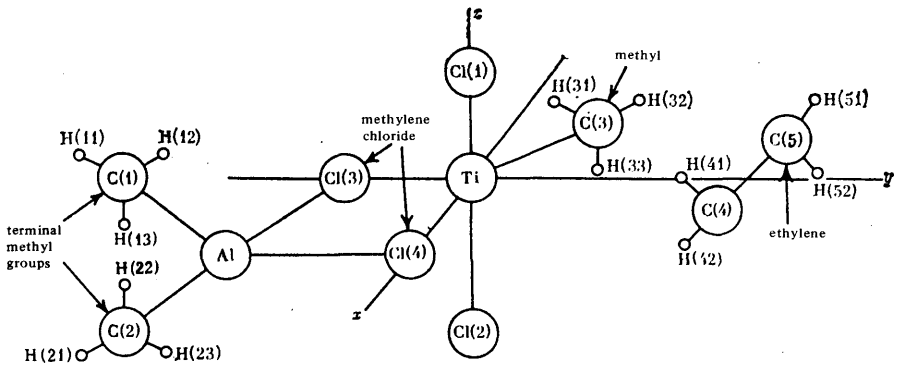


It was found that there is comparatively little perturbation of the electronic structure of ethylene in the complex, and extensive polarisation of the Ti–C bond. The authors cited assume that the R group and the monomer, at all microstages of the growth of the polymer chain, can remain joined to the Ti atoms, and that practically no energy is required for the rupture of the bonds. The driving force of the displacement of the $R^{\delta-}$ group may be the reaction of the slight positive charge in the monomer (in the complex) and the fairly strong negative charge of the terminal C atom of the R group (the growing chain). Comparision of the intermediate π-complex of ethylene and the compound formed by the insertion of the monomer shows that the energy of the complex not containing the alkene is lower. The optimum structure in this case is a trigonal bipyramid without a vacant position. Thus when the alkene is coordinated to the AC, rearrangement of the complex takes place to give a trigonal bipyramid–octahedron, accompanied by the production of a vacant position. The energy required for the rearrangement can be regarded as E_{act} for the chain growth reaction.

The results of the calculations led to some general conclusions:[68] 1) the high activity of Ziegler–Natta catalysts in the polymerisation of alkenes is due to the increased lability of the C–M' bond in the AC compared with typical ionic AC and to the geometry of the complex of the monomer with the AC, favourable for the insertion of the alkene at the C–M' bond, 2) the contribution of the dative interaction of the Ti^{3+}–alkene bond is slight, and there is little $3d-\pi^*$ orbital overlap, 3) the properties of the $Ti-CH_3$ bond are determined almost entirely by the highest bonding orbital of the alkene complex (the contribution of the Ti atom to this bond is practically associated only with the *d* orbitals of M'), and 4) the OAC has no significant influence on the energy levels of the AC, which are of decisive importance for the polymerisation process. The role of the OAC when soluble catalysts are used reduces to the stabilisation of an AC structure with a high coordination number for the $M'(Ti^{3+})$ ion as a result of the formation of bridging bonds between M and M'. It should be noted, however, that the last conclusion is not completely correct, and that the function of the OAC in ionic–coordination catalysis is probably more varied (Refs.11, 71, 75, 86, 87, 93, 95, etc.).

The results of a study[96] of polymerisation in the presence of homogeneous Ziegler–Natta catalysts ($Ti(OCH_3)_4-R_3Al$) practically coincided with the conclusions reached in Ref.68.

A non-empirical SCF LACAO MO method (the restricted Hartree–Fock (RHF) method)[69] was used to carry out a calculation for the reaction $TiCl_4 + (CH_3)_3Al + C_2H_4 \rightarrow TiCl_4.(CH_3)_3Al.C_2H_4$, modelling the polymerisation of alkenes on Ziegler–Natta catalysts.

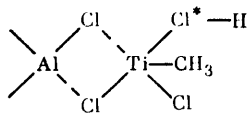


According to the calculation, the polymerisation takes place in three main stages: 1) the coordination of ethylene to $TiCl_4(CH_3)_3Al(AC)$, accompanied by the transfer of the CH_3 group of the AC from the trigonal position originally occupied to an octahedral position, 2) the reaction of ethylene with the CH_3 group of the AC and the rupture of the π-bond of ethylene, and 3) the formation of the MA. Following Refs.11 and 17, a "concerted" mechanism of polymerisation is assumed.

Unfortunately, the authors of Ref.68, 69, and 96 ignored the equally well argued model of the two-metal AC, according to which the cocatalyst (or a fragment of it) is situated on the same side of the M′ atom as the growing chain and the monomer coordinated to the AC. This version is possible in both homogeneous and heterogeneous Ziegler–Natta systems.

The two-metal model of the AC has been used in a series of interesting papers.[71,75,93–95]

The unrestricted Hartree–Fock (UHF) method in the CNDO approximation with allowance for configuration interaction (CI)§ has been used to study the homolysis of the metal–carbon σ-bond in OMC of Ti and Al atoms. A model was proposed, explaining from a single viewpoint the at first sight contradictory data on the relative stability, thermal stability, and reactivity of the M–C bond in different OMC. A fundamental difference between the Ti and Al atoms is the ability of M′ to change its oxidation state with relatively slight deformation of the M′–C bond. The decisive factors in this case are not only the similarity in the energies of the *s*, *p*, and *d* atomic orbitals but also the less diffuse character of the *d* atomic orbitals compared with *s* and *p* orbitals. For the same excitation energy, this rearrangement ensures greater deformations of the M′–C bond and facilitates the formation of a partly bound alkyl ligand, capable of taking part in subsequent concerted processes in the coordination sphere of M′. The magnitude of $\Delta E_{S_0 \to T_j}$ (the energy of the transfer to the lowest triplet excited electronic state) in compounds of the same type formed by a given M′ correlates with the relative elongation of the bond after which the change in the oxidation state of M′ begins. The lower $\Delta E_{S_0 \to T_j}$, the more labile the Ti–C bond, that is $\Delta E_{S_0 \to T_j}$ can be used as an indication of the reactivity of the OMC. The AC most probably have a two-metal structure:



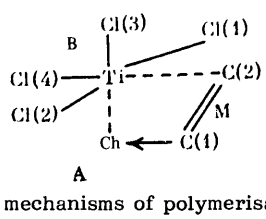
It is assumed that there is no coordination vacancy on the Ti atom. The alkene displaces the saturated fragment $C_\gamma RR^*$ of the growing MA, overcoming the energy barrier to insertion at the Ti–R bond. Preference for the AC with a two-metal structure is also observed for homogeneous Ziegler–Natta systems: $L_2TiRCl.AlCl_3$ (L = Cp, Cl; R = Cl, CH_3, C_2H_5, C_4H_7).[95] The activity of the Ti–C bond in catalysis is due to the ease of formation of a "quasi-octahedral" structure by the Ti atoms in the complex.

§For comparison, the same calculations were repeated by the restricted Hartree–Fock (RHF) method, widely used in quantum-chemical calculations for coordination–ionic polymerisation. It was noted that the observed change in the oxidation state of M′ with deformation of the σ-bond (UHF calculation) cannot be detected by the usual quantum-chemical methods taking no account of the dynamics of the correlation contribution to the energy (RHF method without allowance for CI).

Unfortunately, Refs.71, 75, and 93–95 gave no answer to the question of the geometric structure of the AC and the mechanism of polymerisation on Ziegler–Natta catalysis.

Thus modern methods for studying the ionic–coordination polymerisation of α-alkenes and dienes by quantum-chemical methods have made it possible to extend theories of the characteristic features of the electronic structure of the assumed AC and the catalytic complexes formed with and without the participation of the monomer, and also to refine various details of the mechanism of the polymerisation processes. At the same time, the studies carried out are not free from serious defects. In particular, in most studies the structure of the AC (single-metal or two-metal model), as already noted, is assumed in advance in accordance with the subjective opinions and tastes of the authors. The calculations, particularly those relating to the stage of AC formation, generally did not take account of the characteristic features of the structure of the surface of the heterogeneous component of the catalysts, and the position of the OMC was not studied, and was usually assumed *a priori* (before the calculations). These are essentially incorrect assumptions. It is sufficient to note that the phase state of the catalyst and the position of the OMC influence the steric environment of the AC being formed and their electronic structure, so that stereoregular polymers, for example isotactic polyalkenes, are formed in heterogeneous systems, whereas syndiotactic or atactic polyalkenes are formed in homogeneous systems with similar compositions. It may be stated that the use of quantum chemistry has shown that the two-metal model is highly probable. This is confirmed, in particular, by the results of a study[86] of the polymerisation of ethylene by the CNDO method. Two AC models, the single-metal model of Cossee[17] and the two-metal model (scheme 4 [18]), were compared under identical conditions. The authors examined the stages of coordination and insertion of the monomer (M) (shown by the arrow in scheme 5 below), in the course of which the monomer is displaced from the original coordination position into the position previously occupied by the chain, increasing by two carbon atoms the distance between the growing MA (Ch) and the Ti atom.

Scheme 5



A

Comparison of the mechanisms of polymerisation from the dependence of the energy of the system, the charges on the atoms, and the bond orders on the reaction coordinate indicates unambiguously a preference for the two-metal model of the AC,[11,18] according to which the cocatalyst (R_3Al) is on the same side of the Ti atom as the monomer and the growing MA (position A), compared with the single-metal AC model of Cossee,[17,33] in which R_3Al is on the other side of the Ti atom from the monomer and Ch (position B). According to Ref.86, the growth of the MA most probably takes place with the participation of the $Al–R–Ti^{\delta+}$ group. The organoaluminium compound coordinated to Ti chloride takes direct part in the addition of the monomer to the growing chain by simultaneous nucleophilic (by $R–Al<$) and electrophilic by $Ti^{\delta+}$) attack on the monomer (the "concerted" mechanism), as previously assumed in Refs.11, 18, 69, 76, etc. The OAC plays an active role by stabilising the monomer on coordination to the AC, facilitates its introduction into the growing MA, and decreases E_{act} for the polymerisation process.

3. Recent Progress

A distinguishing feature of papers published in the period 1980–1982 [87–92] was the combination of quantum-chemical calculations (in the CNDO approximation), empirical methods ("atom–atom" potentials), and numerical experiment methods (Monte Carlo). The dynamics of the formation of the AC produced by the reaction of organic compounds of M (Li, Na, Be, Zn, Mg, Al, etc.) with salts of M′ (Ti, V, Cr, etc.) were examined. In the calculations, account was taken of the real structure of the surface of the heterogeneous component of the catalyst. The polymerisation process was studied for a number of α-alkenes (ethylene, propene) and 1,3-dienes (butadiene, isoprene, piperylene, 4-methylpenta-1,3-diene, etc.).

The studies carried out have made it possible to determine much more reliably the characteristic features of the structure of the AC and the effect of stereoregulation in the polymerisation of α-alkenes and dienes in the presence of Ziegler–Natta catalysts.

a) Structure of the Active Centres

The process of AC formation by the reaction of the components of the catalytic system takes place in two stages. [87–91] In the first stage, at large intermolecular distances between the OMC and the crystal of the M′ salt, the reaction between the components of the catalytic system is due to Coulombic and dispersion forces; reversible physical adsorption takes place, accompanied by the orientation of the components of the Ziegler–Natta catalyst relative to one another without change in their structure, and the frequency with which the subsequent non-equilibrium stages of the reaction take place on a particular AC is proportional to the equilibrium population of this centre at the stage of physical adsorption.

The second stage is the chemical adsorption of the OMC on the crystal of the M′ salt. Here the principal role is played by exchange forces, which bring about a redistribution of the charges and a change in the structure of the interacting components. The process of chemical adsorption leads to the formation of the AC.

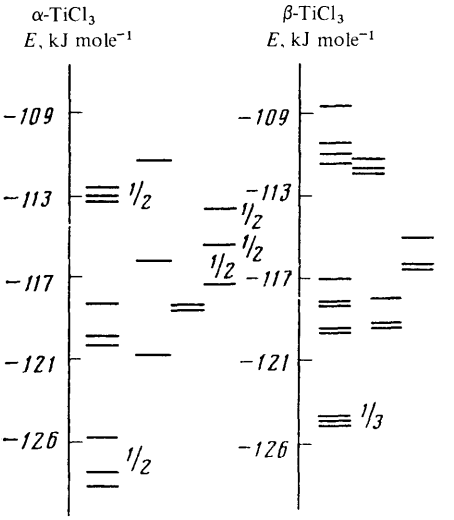


Figure 1. Energy level spectrum of the interaction of the physical adsorption of $(CH_3)_2AlCl$ on the surface of α- and β-$TiCl_3$.

For each system there are several types of physical adsorption centre with different energies (Fig.1) and structures (Figs.2 and 3). Among these it is possible to distinguish

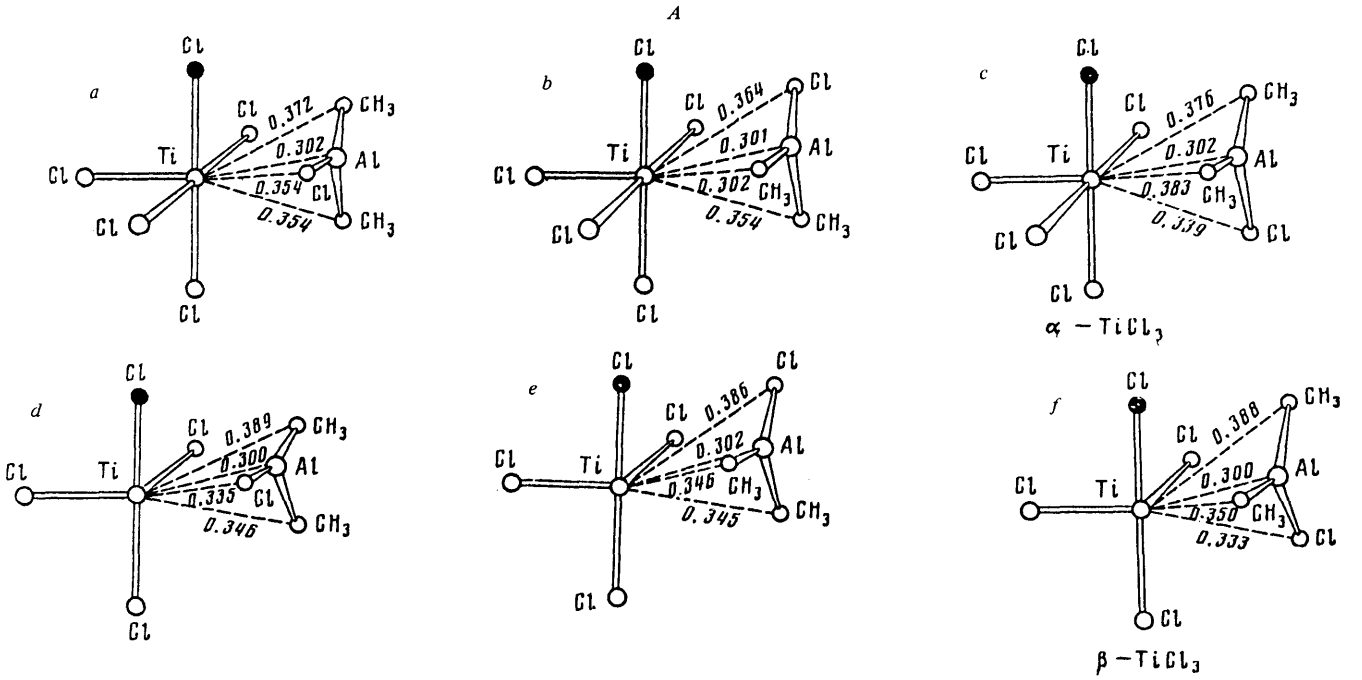


Figure 2. Structure of the physical adsorption centres of organometallic compounds on the surface of α- and β-$TiCl_3$ crystals (configurations corresponding to the energy minimum, distances given in nm): *A*) $Al(CH_3)_2Cl$ (*a–c*—PAC-1, *d–f*—PAC-2); *B*) $Be(CH_3)_2$, $Mg(CH_3)_2$ (*a,b,d,e*—PAC-1, *c,f*—PAC-2); *C*) $NaCH_3$ (*a–c*—PAC-3).

centres of the same type with identical three-dimensional structures: PAC-1 (physical adsorption centres formed mainly on the surface of the crystals of $TiCl_3$ and VCl_3), PAC-2 (β-$TiCl_3$, $CoCl_2$, $NiCl_2$), and PAC-3 ($CrCl_3$, $CoCl_2$, $TiCl_3$) (Figs.2 and 3). Estimation of the equilibrium populations (the relative concentration or proportions of different PAC) showed[87-89,91] that the populations (proportions) of the various specific PAC distinguished above are probably related to the yields of isotactic polyalkenes and *trans*-poly-1,4-dienes (PAC-1), atactic polyalkenes and

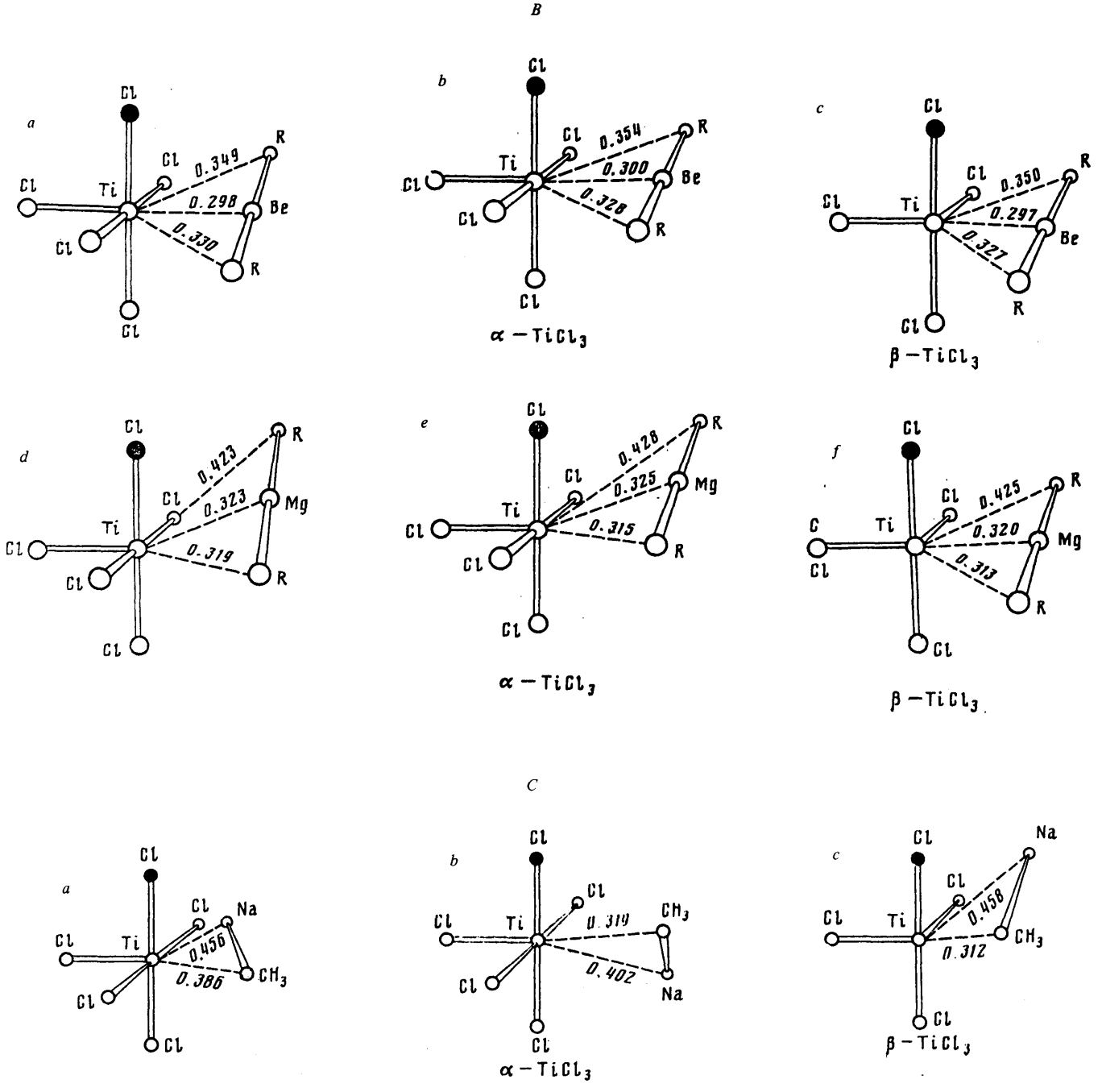


Figure 2 (contd.).

cis-poly-1,4-dienes (PAC-2), and atactic polyalkenes and poly-1,2(3,4)-dienes (PAC-3) respectively (Table 1).

The use of the Monte Carlo method[90] made it possible, in calculations of the populations of the PAC, to take account of not only the depth of the potential wells of the energy surfaces in the sorption of the OMC on the crystal, but also their form. At the stage of the physical adsorption of R_nM on the surface of the $TiCl_3$ crystals, the quantitative composition of the centres which on chemisorption are transformed into stereospecific AC was determined. The OMC molecule is fairly firmly fixed on the surface of the crystal, preserving a definite orientation. An important feature is that in the physical adsorption of different OMC on the crystal surface of $M'Cl_3$, structures of the PAC-1, PAC-2, and PAC-3 type with similar geometries are formed, that is the stereospecificity of the action of the Ziegler–Natta catalysts is probably established.

The transformation of the physical adsorption centres into AC in the chemisorption and insertion of the monomer into the growing chain has been examined in detail for the system $(CH_3)_2AlCl–TiCl_3(VCl_3)$.[91] The energy of the configuration was determined using a modified "two-atom complex" method, in which the bond index was used to take account of the directed character and saturated character of the bonds (calculation by the CNDO/2 method).

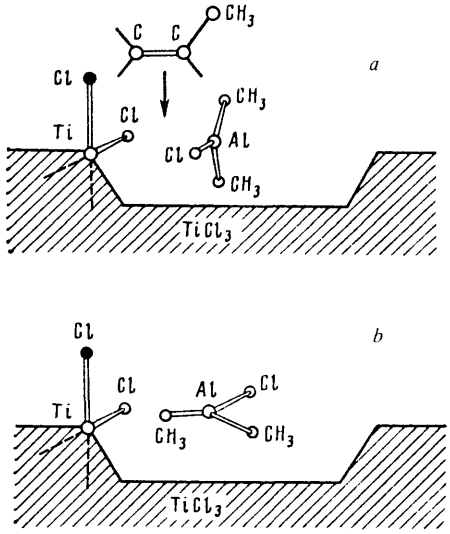


Figure 3. Position of the aluminium alkyl on the surface of the $TiCl_3$ crystal (physical adsorption stage): *a*) PAC-1, *b*) PAC-3

Table 1. Proportions of different AC and the yield of polymeric stereo-isomeric products in Ziegler–Natta catalytic systems.[42,87–91]

Catalytic system	Proportions of the AC, %			Yield of stereo-isomers*, % (experiment)								
	CAC-1 (PAC-1)	CAC-2 (PAC-2)	CAC-3 (PAC-3)	poly-propylene	polystyrene	poly-3-methyl-but-1-ene	1,4-*trans*-PBD	1,4-*cis*-PBD	1,2-PBD	1,4-*trans*-PI**	1,4-*cis*-PI	3,4-PI
α-$TiCl_3$ + AlR_3	80	—	20	75—95	90	80.4	80	12	8	95—100	—	—
γ-$TiCl_3$ + AlR_3	80	—	20	80	—	—	92	8	—	—	—	—
δ-$TiCl_3$ + AlR_3	80	—	20	83	—	—	—	—	—	—	—	—
VCl_3 + AlR_3	80	—	20	73	68	—	99	1	—	100	—	—
$CrCl_2$ + AlR_3	45	—	55	36	—	—	60	—	40	—	—	—
$TiCl_2$ + $AlEt_2$	98	—	2	80—90	—	—	95.4	—	5.5	—	—	—
α-$TiCl_3$ + BeR_2	92	—	8	94—97	—	—	—	—	—	—	—	—
α-$TiCl_3$ + LiR	60	—	40	10—90	—	—	70	3	27	—	—	—
α-$TiCl_3$ + MgR_2	75	—	25	78—85	—	—	88	—	12	—	—	—
α-$TiCl_3$ + ZnR_2	0	0	100	30—40	—	—	27	6	67	—	—	—
β-$TiCl_3$ + AlR_3	60	30	10	40—50	—	—	66	29	5	15	85	—
α-$TiCl_3$ + NaR	0	0	100	0	—	—	27	10	63	—	—	—
$CoCl_2$($NiCl_2$, $FeCl_2$) + AlR_3	20	65	15	20	—	—	10	74	16	—	—	—
β-$TiCl_3$ + $AlRCl_2$	100	—	—	—	—	—	100	—	—	—	—	—

*Isotactic polyalkenes; **PI = polyisoprene.

In the formation of the AC in a system of the type $M'Cl_n \cdot R_mMCl_{3-m}$, the initial stage is the formation of a bridging bond between Ti and Al;[91] the OMC completes the crystal lattice, forming a U' centre similar to that previously described in Refs.11 and 18; the Al atom occupies a position equivalent to the position of Ti; and the alkyl group R occupies a position close to the position of Cl in the layer crystals of $TiCl_3$ (the two-metal AC model). The most important feature of the AC formed (CAC-1, Fig.4*a*) is the formation, with the participation of the R group of the OMC and the M' and M atoms, of a three-dimensional "tent" structure, which plays an important role in the orientation of the monomer in the stereospecific polymerisation process. The AC geometry obtained from the calculations differs little from that proposed in Ref.86 for the two-metal Ti–Al AC model. In the presence of β-$TiCl_3$ and the OMC, in addition to CAC-1, appreciable quantities of other centres, in particular CAC-2 (Fig.4*b*), are also formed on the crystal surface. Their structure in many respects is similar to that of CAC-1, but an important difference is that the Ti atoms react with two R groups (two bridging bonds are formed between the M' and M atoms), so that a different AC coordination sphere is produced, which sterically resembles a "flower" and which is also responsible for the specific orientation of the corresponding monomers in ionic–coordination polymerisation on Ziegler–Natta catalysts.

Thus the combined approach using different methods of study has apparently made it possible: a) to determine clearly the dynamics of formation of the AC while avoiding the main unsatisfactory feature of practically all studies in this field, namely the hypothetical nature of the choice of the AC model; and b) to determine the structure of the polymerisation AC formed on the crystal faces and to show with a much higher probability that the AC of Ziegler–Natta catalysts have a two-metal structure (both components of the catalyst determine the structure of the AC and the mechanism of polymerisation).

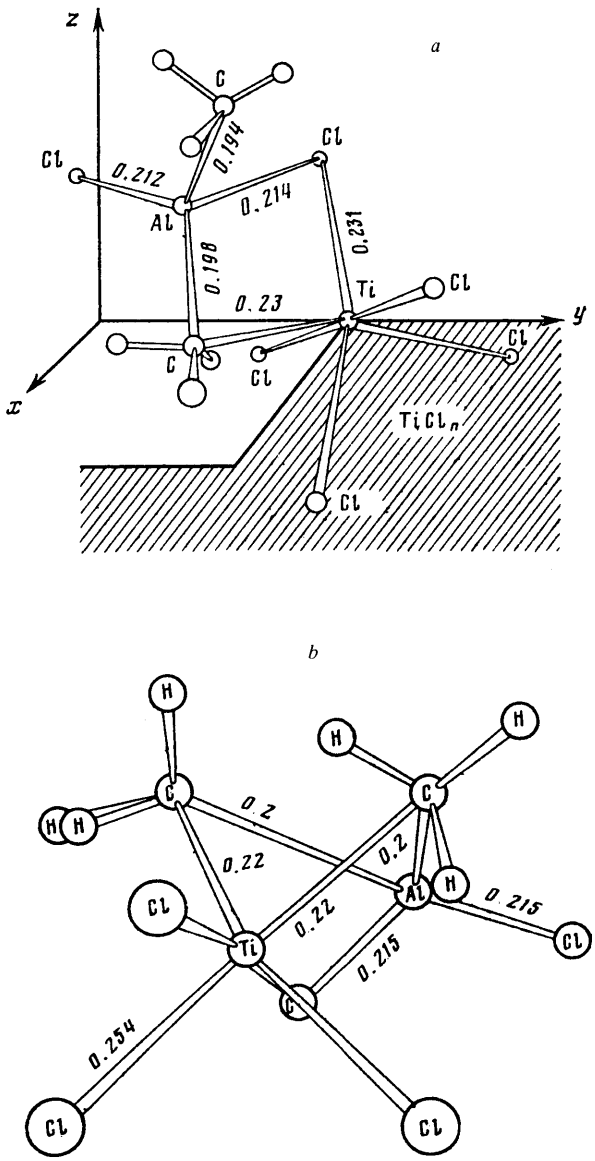


Figure 4. Geometry of the model active centre for the catalytic systems (distances given in nm): *a*) α-$TiCl_3$–$Al(CH_3)_2Cl$ (CAC-1); *b*) β-$TiCl_3$–$Al(CH_3)_2Cl$ (CAC-2).

III. MECHANISM OF STEREOREGULATION

1. Empirical Theories

In the polymerisation of α-alkenes and 1,3-dienes under the influence of Ziegler–Natta catalysts, polymers with different micro-structures are obtained, depending on the nature of the components $M'X_n$ and MR_m selected (Table 1). However, although the nature of the AC and the mechanism of the process in the first 10–20 years after its discovery were the subject of a large number of experimental and theoretical studies, the authors of published papers preferred at best to restrict themselves to general phrases about the mechanism of stereoregulation. The existing opinions were essentially probabilistic. Before 1960, no special consideration was given to the question of stereoregulation in polymerisation on Ziegler–Natta catalysts. Since 1960, increasing attention has been paid to this question, and published papers have been specially devoted to the study (including studies by essentially new methods) and interpretation of the surprising property of Ziegler–Natta catalytic systems, namely their ability to give stereoregular polymers based on α-alkenes and dienes with a high steric purity.

a) Mechanism of the Stereoregulation of α-Alkenes

The single-metal model of the active centre. In one of the first papers[6] it was assumed that the stereospecificity of action of the $TiCl_3$–$(C_2H_5)_3Al$ system is due to electrostatic factors. The monomer, situated between the positively charged and negatively charged ions of the catalytic complex, occupies a rigorously definite spatial position.

Cossee and Arlman[33,34,63] assumed that the octahedral $RTiCl_4$ group is positioned unsymmetrically (does not have a plane of symmetry), and that the positions of the R group and the coordination vacancy in the lattice are non-equivalent, from both the steric viewpoint and the viewpoint of

ionic character. This situation predetermines the configuration of the asymmetric carbon atom, that is it allows only one orientation of the coordinated alkene molecule, and this explains the stereospecificity of the action of Ziegler–Natta catalysis.

There are two possible reaction paths: a) after rearrangement, the R group remains in the new position, the monomer is coordinated in the newly formed vacancy, and the whole process is repeated, leading to the alternate participation of the anion vacancy in the acts of chain growth and to the formation of a syndiotactic polymer; b) the longer R group returns to the original position before the introduction of the next monomer molecule. This leads to the repeated introduction of each successive monomer unit into the chain with the preservation of a stereospecifically identical position. In particular, an isotactic polymer is formed in this way. The preference for the isotactic or syndiotactic configuration is determined by the ratio of the rates of the return of the R group to the original position and the introduction of the monomer into the growing chain.

In Ref.98, the migration of the growing MA is not regarded as essential. It is assumed that the insertion of the monomer at the M–C bond takes place without coordination. This suggestion does not appear convincing, however.

In Refs.99 and 100 it was suggested that the stereospecific control is determined by steric factors, namely the reaction of the alkene with the growing chain and the nearest M′ atom.

According to Regs.49 and 101, there are two types of AC on the surface of $(C_2H_5)_3Al[(C_2H_5)AlCl]–TiCl_3$ systems: a) stable AC on which isotactic polymers are formed; and b) unstable AC, which give atactic polyalkenes. The ratio of the centres determines the micro-structure of the MA formed.

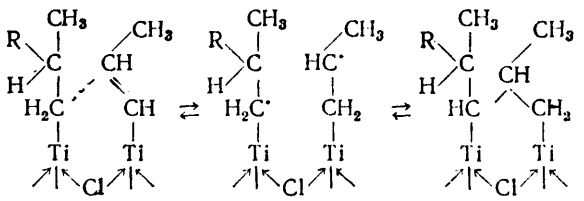
The two-metal model of the active centre. As suggested in Ref.5, the formation of macro-chains with the isotactic configuration of the pseudo-symmetrical carbon atom on a heterogeneous AC is due to the asymmetric character of the assumed two-metal AC. Complex formation by the AC and the alkene takes place with opening of the π-bond of the monomer and the production of *d*- and *l*-configurations, depending on the structure of the AC.

According to Ref.7, the stereospecificity of action of Ziegler–Natta catalysts is determined only by the structure of the monomer, whereas according to Ref.52 it depends only on the quantity of Ti^{2+} ions involved in the polymerisation. Isotactic polyalkenes and poly-1,2-dienes, and also *cis*-poly-1,4-dienes, are formed on isolated Ti^{2+} ions. Syndiotactic polymers and *trans*-poly-1,4-dienes are formed with the simultaneous participation of two Ti^{2+} ions.

In Ref.8 it is stated that the stereospecificity of the MA is determined when the monomer is coordinated, as a result of its orientation by the ions of the catalytic complex fixed on the surface of the heterogeneous catalyst (that is by electrostatic factors). The monomer then enters the anionic complex. The existence of hydrogen bonds between the methyl groups and the most electronegative atoms (chlorine) in the complex prevents the free rotation of the growing MA chain.

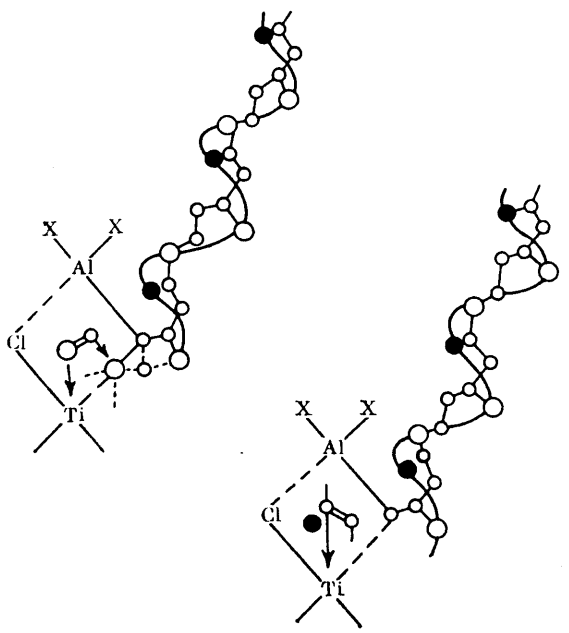
A similar viewpoint was put forward in Refs.10, 13, etc. According to Ref.13, the growing MA moves along breaks in the layers of the $TiCl_2$ and $TiCl_3$ crystals.

In Ref.12 it was assumed that a six-membered complex is formed in the transition state; the OMC serves only to form the initial active M–C bond, which takes no further part in the process:



The presence of hydrogen bonds between successive monomeric units of the growing MA and the AC predetermines the stereospecificity of the growth reaction.

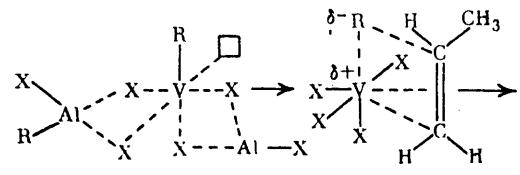
According to Ref.102, the growing MA is a spiral, and the rate of the addition ensuring the symmetry of the spiral is greater than that of any other addition, so that an isotactic polymer is formed from α-alkenes.



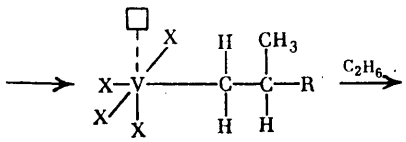
In Ref.59, the stereospecificity of Ziegler–Natta catalysts was attributed to steric factors. In the opinion of the authors cited, the monomer forms a complex with an alkylated octahedral M′(Ti) atom, situated on the lateral faces and defects of an $M'X_n$ crystal with two vacancies, by only the one most probable method, in such a way that the R substituent is directed away from the R groups on the M(Al) atom.

In Ref.103, a scheme for the formation of syndiotactic and atactic polyalkenes was proposed, for the case of the

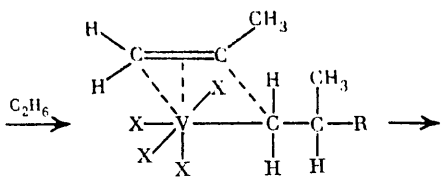
homogeneous VCl_4–$(C_2H_5)_2AlCl$ system:



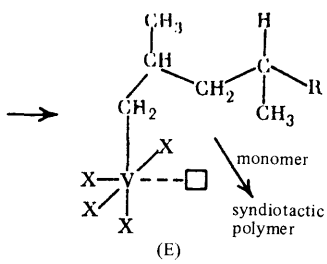
(A) (B)



(C)



(D)



(E)

It is assumed that: a) the coordination of the monomer leading to "head to tail" addition is energetically most favourable; b) the orientation of the CH_3 group in the monomer chain, which leads to syndiotactic addition as a result of methyl–methyl interactions, is more favourable than the orientation leading to isotactic addition; c) rotation about the R–M′ bond is hindered by steric factors; d) when the barrier to rotation is overcome, for example by increasing the temperature or by using M′(V) complexes with small ligands, the preference for any one orientation of the CH_3 group of the entering monomer disappears, so that an atactic polymer is formed.

Thus in all the papers examined above, the stereospecificity of action of Zielger–Natta catalysts is attributed to steric and (or) electrostatic factors, but no clear details of the process are given.

It seems obvious that for the same catalysts, the mechanism of stereoregulation in ionic–coordination polymerisation should be the same for α-alkenes and 1,3-dienes. Stereoregularity in the case of dienes, however, assumes the possibility of not only the isotactic and syndiotactic construction of the MA (1,2- or 3,4-) but also *cis*-, *trans*-, and other forms of isomerism (Table 1). Thus for the polymerisation of dienes, many workers have proposed specific mechanisms relating only to these compounds.

b) Mechanims of the Stereoregulation of Dienes

Single-metal models. Arlman,[34] using Cossee's model, related the formation of 1,4-*trans*- or 1,4-*cis*-structures to unidentate or bidentate coordination of the monomer to the AC, determined by the accessible space around the M′ ion. Unidentate coordination of the monomer leads to the formation of 1,2-, 3,4-, or 1,4-*trans*-units, and bidentate coordination gives 1,4-*cis*-units. A similar view was put forward in Ref. 104. The probability of a given type of coordination is determined by the electronic structure of the M′ atom. 1,4-*cis*-Polydienes are obtained when the energy levels of the bonding orbitals of M′ and the highest occupied MO of the monomer are close together; when the energy levels differ considerably, polymers with the 1,2- or 1,4-*trans*-structures are formed. The electronegativity of the ligands, which influences the position of the energy levels of the MO of the transition metal, is an important factor in stereoregulation. A similar approach to the examination of the mechanism of stereoregulation was used in Refs. 105 and 106.

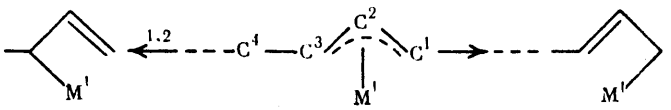
In detailed papers by Dolgoplosk and co-workers,[36–38] the stereoregularity of the MA is related not to the type of coordination of the monomer to the AC but to the configuration of the π-alkenyl unit of the growing MA. At the coordination stage, the diene almost always acts as a bidentate ligand. The introduction of the diene into the chain leads to the formation of a π-allyl complex in the *anti*-conformation. The ratio of the *cis*–*trans* units in the MA is determined by the ratio of the rates of the growth of the chain and the *anti*–*syn*(*cis*-*trans*)-isomerisation of the terminal unit in the AC (scheme 2).

Electron-donor solvating agents, which shield M′, increase the lifetime of the terminal unit in the AC, and hence the proportion of *anti*–*syn*-isomerisation. On an AC having only one anion vacancy, dienes are chemisorbed through one double bond (unidentate) in the transoid conformation and enter the chain with the formation of a *syn*-unit (scheme 3). According to scheme 2, reaction (1) leads to the formation of a *cis*-unit, and reaction (2) (isomerisation) to the formation of a *trans*-unit. If the rate of growth is much greater than the rate of isomerisation, the system correspondingly forms chiefly 1,4-*cis*-polydienes.

NMR studies of π-crotylnickel iodide and π-allylnickel fluoroacetate[43,107] showed that the growing terminal group has the *syn*-π-allyl configuration, irrespective of whether *cis*- or *trans*-polymerisation takes place. Thus the 1,4-*cis*- or 1,4-*trans*-polymerisation of dienes can be explained[107] by the intramolecular coordination (*syn*–*anti*) of the double bond situated next to the π-allyl bond at the end of the MA. In this case the *syn*-form, as in the theory of Dolgoplosk,[36–38] favours *trans*-polymerisation, whereas the *anti*-form favours the *cis*-polymerisation of the dienes. At the same time it should be borne in mind that the coordination of the penultimate double bonds of the growing polybutadiene chain is most probably excluded.[106]

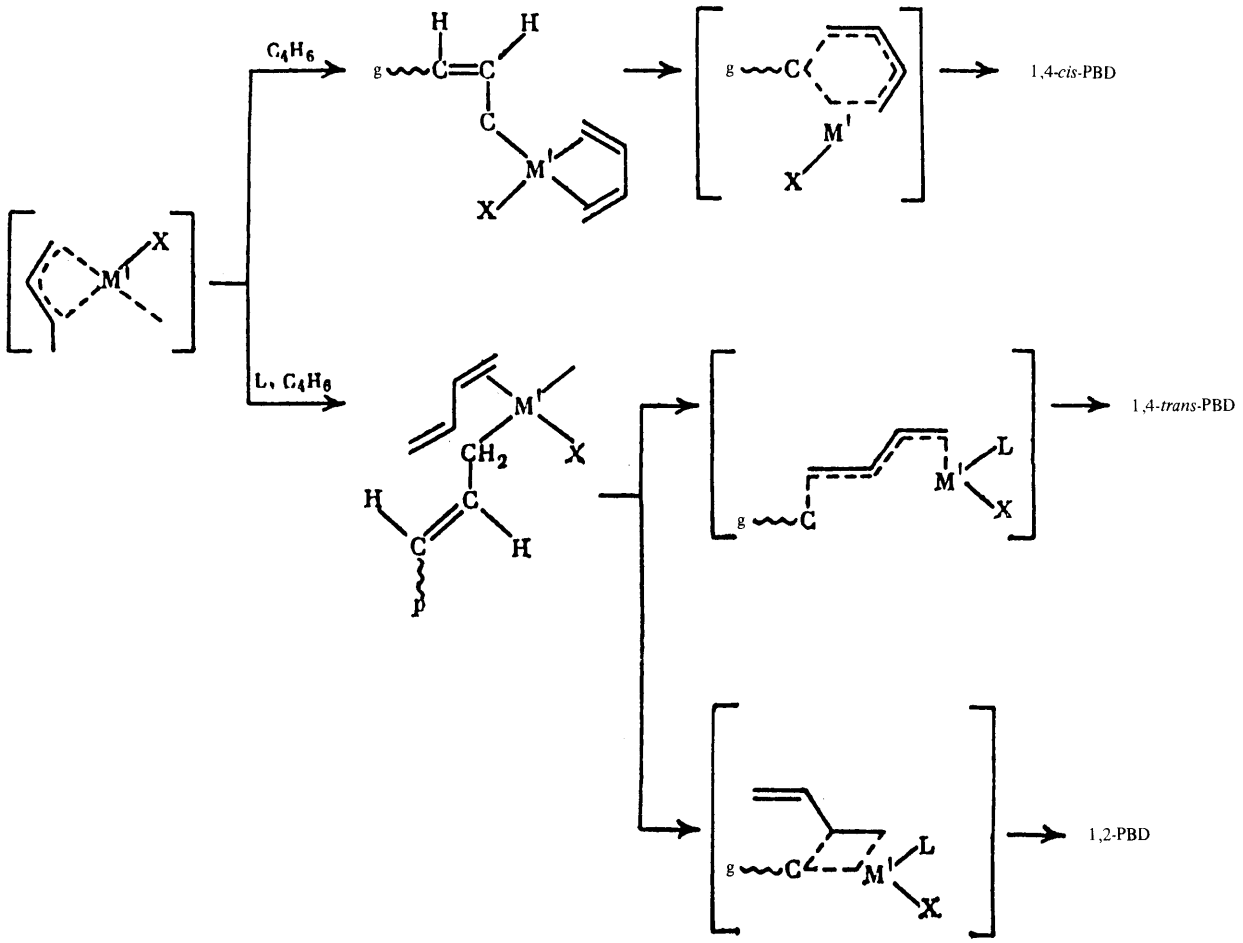
The concept of π-allyl control of stereospecificity is also supported by other authors.[108] In their opinion, in the polymerisation of dienes a π-allyl bond is formed between the M′ atom and the last unit of the growing MA. The π-allyl unit contains two reactive atoms, C(1) and C(3). The reaction of the sorbed monomer with C(1) leads to the production of 1,4-*trans*- or 1,4-*cis*-polymers (depending on whether the structure of the allyl group is *syn* or *anti*),

whereas the reaction with C(3) gives 1,2-structures:

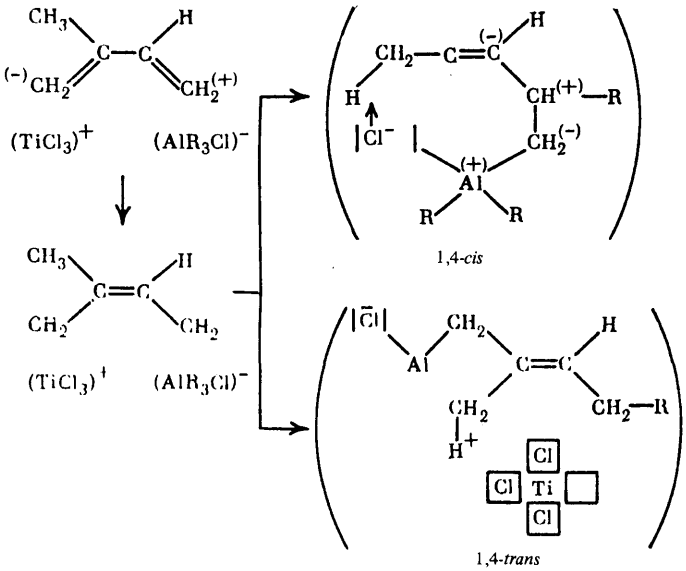


Here, the sorbed monomer reacts with the less extensively substituted and hence more reactive carbon atom. In a later paper by the same authors[109] it is also stated that the formation of 1,4-*trans*-polymers depends on the type of catalyst and may take place either with the coordination of only one C=C double bond to the AC, or with the coordination with the monomer through two double bonds with the formation of an *anti*-butenyl group and subsequent *anti–syn*-isomerisation. According to Ref.109, the formation of isotactic (*erythro*-di-isotactic) and syndiotactic (*threo*-disyndiotactic) polydienes is determined by the reaction of the monomer molecules with the ligand environment or with the butenyl group of the AC.

Various authors have tried to summarise the available experimental results and schemes for the mechanism of the stereospecific polymerisation of dienes. In particular, in Ref.43 the mechanism of formation of stereoregular polybutadienes (PBD) in solution is represented by the scheme:



Two-metal models. According to Ref.8, the polymerisation of dienes takes place on ionic complexes $(TiCl_3)^+(AlR_3Cl)^-$, like the polymerisation of α-alkenes. The chief factor determining *cis*- or *trans*-addition is the geometric configuration of the monomers.



This hypothesis does not explain many familiar experimental facts, in particular why 1,4-*trans*-polydienes are mainly formed in the presence of α-$TiCl_3$, and 1,4-*cis*- and 1,4-*trans*-polydienes on β-$TiCl_3$.[41-49]

In Ref.110 it is considered that the structure of the polymers formed is determined only by the geometric structure of the crystal lattice of the heterogeneous component. This hypothesis, however, applies only to the polymerisation of isoprene on $TiCl_3$, and does not deal with the stereospecificity of action of other catalysts and monomers. It also does not explain the role of the cocatalyst and the influence of various additives on the stereoregulation process.

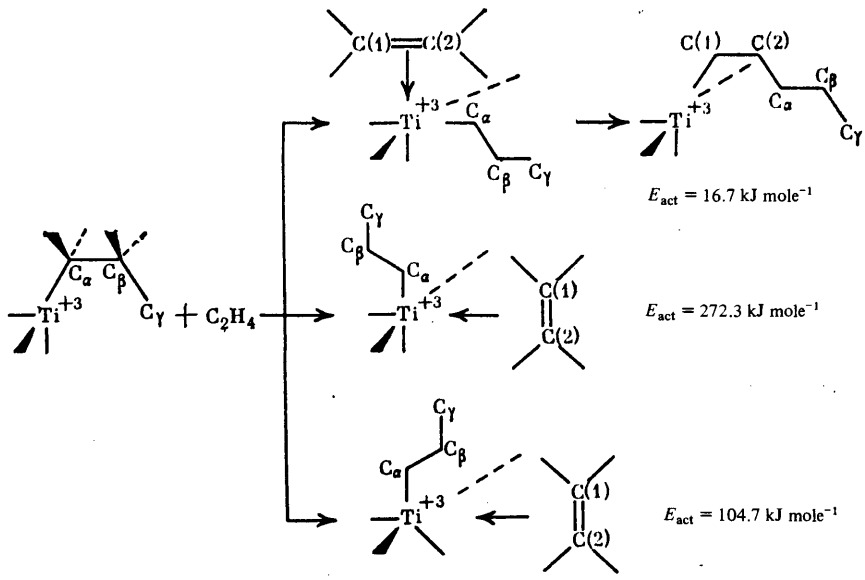
Thus to explain the stereospecific action of Ziegler catalysts for the polymerisation of dienes, research workers have introduced not only electrostatic but also steric factors and various data on the structure of the monomers (polymers).

Two main views regarding the mechanism of stereoregulation in the polymerisation of dienes in the presence of Ziegler–Natta catalysts are widely discussed in the literature: a) the theory of *cis–trans* geometric control, which takes account of the presence of two C=C bonds in the conjugated dienes and hence the possible coordination of the diene through one or two double bonds to the AC (unidentate and bidentate coordination); and b) the theory that the configuration of the polymers is determined by the π-alkenyl polymer–M′ bond (the *anti*-form facilitates the formation of *cis*-units). The schemes put forward, however, do not provide a convincing interpretation of many available experimental data, for example the influence of the nature of M′ on the stereospecificity of action of Ziegler–Natta catalysts, etc.

2. Present-day Trends

a) Mechanism of the Stereoregulation of α-Alkenes

Detailed studies of the mechanism of stereoregulation in polymerisation on Ziegler–Natta catalysts using quantum-chemical methods were begun comparatively recently, and only a few have as yet been published. Two series of studies are noteworthy. In one series[81-85] it was shown that there are three possible paths for the introduction of the monomer into the coordination sphere of M′ in AC with the *cis*-structure of the growing MA.



The smallest E_{act} corresponds to the introduction of the monomer on C_α side, after which *cis–trans*-isomerisation is possible. The energetic non-equivalence of the different paths for the introduction of the monomer into the AC with the *cis*-configuration of the growing MA eliminates the need for the migration of the R group from one octahedral position to another, as in the Cossee mechanism. The active centre with the *cis*-MA leads to the formation of isotactic polymers, and that with the *trans*-MA to the formation of atactic polymers. The probability of the *cis–trans*-isomerisation of the R group of the AC, however, depends on the structure of the surface of the Ziegler–Natta catalyst and the presence of various adsorbed reagents in the immediate environment.

In Refs.111 and 112 the Cossee model was used to estimate the energy of the non-bonding interactions in the coordination of the monomer with the AC on the surface of the crystal for different cases of diastereo-isomerism, and it was concluded that the stereospecificity of Ziegler–Natta catalysts is due to the chirality of the ligand environment of the catalytically active Ti atom. The latter determines the orientation of the first C–C bond of the chain, which influences the subsequent mode of insertion of the monomer. In the case of the alkylation of Ti chlorides by trimethylaluminium, however, the system is not stereospecific with respect to the polymerisation of alkenes. An obvious meritorious feature of these studies is that, as in Refs.87–92, account was taken of the real surface of the heterogeneous component.

b) The Mechanism of the Stereoregulation of 1,3-Dienes

In Ref.113, from an analysis of the MO diagram of the active catalyst–monomer complex, it was suggested that the microstructure of polybutadiene is determined by the mode of coordination of the monomer (bidentate or unidentate), and depends on the electron density at the M′ atom. The probability of coordination of a given type is determined by the difference in the energy levels of the bonding molecular orbitals of M′, which accepts electrons from butadiene, and the highest occupied MO of butadiene. When these levels are close together, 1,4-*cis*-polydienes are obtained; when they differ considerably, polymers with 1,2- or 1,4-*trans*-structures are formed. The electronegativity of the ligands, which influences the position of the energy levels of M′, obviously also influences the stereospecificity of action of Ziegler–Natta catalysts.

Thus the quantum-chemical study of stereoregulation has apparently not made it possible to extend significantly the empirical theories and has only confirmed that the stereospecificity of action of Ziegler–Natta catalytic systems is due to both steric and electrostatic factors.

3. Recent Progress

In Refs.87–92 it has been clearly shown that the stereospecificity of action of Ziegler–Natta catalysts is determined by the three-dimensional structure of the coordination sphere of the AC and by the chemical character of the monomer, and it has been shown that the nature and mechanism of stereoregulation are the same for the polymerisation of α-alkenes and dienes.

a) Polymerisation of α-Alkenes

Stereoregulation in the polymerisation of α-alkenes is determined by the geometric structure of the AC.[87–90] The use of α-$TiCl_3$–R_2AlCl on a titanium trichloride surface leads to the formation of one of the most frequently encountered OMC configuration with an energy $E_1 = -127.61$ kJ mole^{-1} and $F_1 = 38\%$ (F_i is the fraction of the individual configuration with energy E_i in the total balance of the PAC; $i = 1$, 2, 3, etc.), and also configurations with similar structures with $E_2 = -126.78$ kJ mole^{-1}, $F_2 = 27\%$ and $E_3 = -125.1$ kJ mole^{-1}, $F_3 = 14\%$ (*a–c* in Fig.2*A*). The last two configurations differ from the first only in the "interchange" of the Cl atom and the CH_3 group, while the position of the Al atom remains unchanged. The total contribution of these configurations is about 80%.

For β-$TiCl_3$ a large number of different versions of the arrangement of R_2AlCl on the crystal surface has been found, but in this case also it is possible to distinguish three most favourable configurations with energies of −120, −124.68, and −119.9 kJ mole^{-1} (*d–f* in Fig.2*A*). The total contribution of these configurations is much smaller than in the case of α-$TiCl_3$, and amounts to 30%; as in the case of α-$TiCl_3$, these configurations differ only in the interchange of the Cl atom and the CH_3 group while the position of the Al atom remains unchanged. Moreover, it has been found that the geometry of the PAC has much in common for the different forms (α and β) of $TiCl_3$. In both cases there is a good correspondence between the yield of stereoregular polymers of alkenes and the proportions of PAC-1. The only difference between the α- and β-forms of $TiCl_3$, which have hexagonal close-packed Cl atoms, but which differ in the positions of the Ti atoms, is that when α-$TiCl_3$ is used the quantity of PAC-1 formed is approximately 80% of the total (Fig.2*A* and Table 1), and the MA obtained are correspondingly highly isotactic, whereas when β-$TiCl_3$ is used the proportion of these PAC is only 30%.

An important feature is that PAC with similar structures (Fig.2*B*) are also formed in the systems R_2Be–α-$TiCl_3$ ($F = 94\%$), R_2Be–β-$TiCl_3$ ($F = 50\%$), R_2Mg–α-$TiCl_3$ ($F = 75\%$), and R_2Mg–β-$TiCl_3$ ($F = 20\%$),[89,90] etc. Here also there is good agreement between the yield of isotactic polyalkenes and the PAC-1 population (Table 1).

The geometries of PAC of the same type formed on the surface of α-$TiCl_3$ and β-$TiCl_3$ in combination with different OMC are practically identical (Fig.2).

The chief difference between the PAC-1 configurations distinguished and other configurations formed as a result of the sorption of OMC on the crystals is the unique position on the $TiCl_3$ surface of the weakly bound Cl and Ti atoms and the M and Cl atoms and R groups of the OMC molecule, as a result of which, when the monomer molecule approaches, the C=C bond may be attacked simultaneously by both the Ti atom and the RA1< fragment (Fig.3). The "push–pull" mechanism corresponds to the concept of the two-metal catalysis[11,18] of the polymerisation of α-alkenes (schemes 4 and 5). A propene molecule on the crystal surface is probably fixed only in one position in which the CH_3 group of propylene is directed away from the surface, leading to an isotactic sequence in the addition of the monomeric units of the MA in the polymerisation of propene on Ziegler–Natta catalysts.

A similar process is characteristic of the specific PAC of the same type formed by the combination of various OMC with the α- or β-forms of $TiCl_3$, VCl_3, etc., and is not observed on other PAC (for example those formed by the reaction of $TiCl_3$ with RNa or R_2Zn), whose structures differ from that of the centres given in Fig.3*a*. An example is the

configuration with $E = -119.66$ kJ mole^{-1} ($S = 3\%$) on the surface of α-$TiCl_3$ (Fig.3*b*). In this case the OAC molecule is coplanar with the crystal surface, and a specific arrangement of the atoms, as in PAC-1, is not observed. A propene molecule may be fixed on an AC of this type in several positions, leading to non-stereoregular polymerisation.

Additional confirmation that the PAC-1 are responsible for the production of isotactic polyalkenes is provided by the fact that with increase in temperature from 300 K to 330 K, according to calculations for R_2AlCl–$TiCl_3$ systems, the proportion of stereoregular AC of the same type decreases by an average of 5% (the value at 330 K is 75% and 25% for α- and β-$TiCl_3$ respectively[87]). This agrees with experimental data on the yield of isotactic polypropylene in the polymerisation of the monomer.[114] In accordance with experiment[41,42] and calculations,[87,88] on going from the solid surface to the catalyst solution, the appearance of the corresponding energy spectrum in the reaction of $M'Cl_n$ with the OMC becomes impossible, and the formation of stereoregular polymers of α-alkenes is excluded.

The calculation for systems containing NaR [89] showed three configurations: one on α-$TiCl_3$ with an energy of -135.14 kJ mole^{-1}, and two on β-$TiCl_3$, with energies of -117.83 kJ mole^{-1} (Ti atom with one vacancy) and -114.65 kJ mole^{-1} (Ti atoms with two vacancies) (Fig.2*C*). This system does not contain centres whose structure might be similar to PAC-1 when the α- and β-forms of $TiCl_3$ are used (Figs.2*A* and 2*B*), as in the previous systems. The arrangement of NaR on the surface of the $TiCl_3$ crystal is similar to the arrangement of the OAC in a non-stereospecific centre, in which one of the R groups is closer to the Ti atom than the Al atom. Polymerisation in the $TiCl_3$–RNa system takes place as on the non-stereospecific (for α-alkenes) centres PAC-3 in $TiCl_3$–OMC systems (Fig.3*b*). The difference between these catalytic systems is revealed by the fact that in the presence of NaR all the centres are non-stereospecific for the polymerisation of α-alkenes, whereas in the other systems involving OMC, non-stereospecific AC make up only a fraction of the total number. Thus for each system there are several types of PAC, and stereospecific PAC are encountered in catalysts containing both α-$TiCl_3(VCl_3)$ and β-$TiCl_3$. The calculated proportions of stereospecific centres in the above series of systems correlates with the experimental yields of isotactic polypropylene and other polyalkenes (Table 1).

The stereospecificity of the AC depends both on the nature of the OMC and on the nature of the arrangement of the OMC on the surface of the $M'X_n$ crystal. In catalysts containing compounds of metals of the first group, there are practically no stereospecific PAC either in brown β-$TiCl_3$ or in the violet α- and γ-forms of $TiCl_3$. In heterogeneous catalysts based on $TiCl_3$ and OMC of the metals of the second and third groups, stereospecific AC are mainly formed, and their concentration is appreciably greater in the systems with the α-, γ-, and δ-forms of the $TiCl_3$ crystal, correlating with the yield of isotactic polyalkenes.

b) Polymerisation of Dienes

The formation of specific polymerisation centres of the same type, determining the stereo-isomerism of the macromolecules, when MOC are adsorbed on an $M'Cl_n$ surface is a general phenomenon for processes involving both polyalkenes and polydienes.

A strict correlation is observed between the yield of 1,4-*trans*- and 1,4-*cis*-polydienes in the polymerisation of dienes in the presence of different forms of $TiCl_3$ and OMC and the proportions of PAC-1 (CAC-1) and PAC-2 (CAC-2) respectively (Table 1)¶. An interesting feature is that calculations carried out for catalysts based on α-(γ-)$TiCl_3$–OMC and $CrCl_3$–OMC revealed differences in the nature of the change in the proportions of 1,4-*trans*- and 1,2-polydienes with change in the temperature of preparation of the catalyst. The results of the calculations were confirmed experimentally (Table 2). On the CAC-1 ("tent") in the polymerisation of dienes, the formation of 1,4-*trans*-units is energetically favourable, and in the process of chain growth there is no hindrance to the physical adsorption of the subsequent monomer molecules (Fig.5).[92] The unidentate coordination and the energetically favourable character of the formation of 1,4-*trans*-polydienes, brought about by the presence of the CAC-1 ("tent"), are responsible for a number of characteristic features of the polymerisation of dienes in the AlR_3–α-$TiCl_3$ system: the formation of up to 80–90% 1,4-*trans*-polydienes and a correspondingly small proportion of 1,2- and 3,4-structures, and a decrease in the rate of polymerisation of substituted dienes (isoprene, pentadiene, etc.) compared with butadiene, because of the definite steric hindrance to the approach of the molecule to the CAC-1 on the side of the substituent. This effect may also explain the anomalous behaviour of 1,4-diphenylbutadiene and 4-methylpenta-1,3-diene in their polymerisation in the presence of Ziegler–Natta catalysts.[92] 1,4-Diphenylbutadiene is not polymerised for steric reasons, as can be clearly seen from Stuart–Briegleb models. For the same reasons, 4-methylpenta-1,3-diene forms practically only 1,2-poly-4-methylpentadiene.

Table 2. Dependence of the yield of stereo-isomers of polybutadiene on the temperature of the preparation of the catalytic complex in systems involving $CrCl_3$ and $TiCl_3$.

Catalytic system	T^*_{prep}, °C	Proportion of AC, % (calculated)		Yield of polybutadiene, %	
		PAC-1	PAC-3	1,2-	1,4-*trans*
$CrCl_2 + AlR_3$	40	45.9	54.1	36.3	63.7
	50	46.3	53.7	39.4	60.6
	60	47.1	52.9	27.8	72.2
	70	47.6	52.4	25.6	74.4
	80	48.1	51.9	24.7	75.3
γ-$TiCl_3$+AlR_3	40	80	20	10	90
	50	79.5	20.5	7	92
	60	79	21	11	87
	70	78.5	21.5	12	86
	80	77	23	13	85

*T_{prep} is the temperature of preparation of the catalytic complex.

Note. Al/Cr = 2, [$CrCl_3$ = 0.01 M, [M] = 2.5 M; Al/Ti = 2, [$TiCl_3$] = 0.04 M, [M] = 1 M; polymerisation temperature 50 °C.

On CAC-2, which have an essentially different steric structure ("flower") and which are formed, for example, when β-$TiCl_3$ is used in combination with R_3Al or R_2AlCl, bidentate coordination of the monomers with the formation

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¶ The chemical adsorption centres (CAC) are formed at the stage of the chemical adsorption of the OMC on the surface of the heterogeneous component of the catalyst from the corresponding PAC.[91,92]

of 1,4-*cis*-polydienes is energetically favourable, as observed in practice.[115] Growing MA with the 1,4-*cis*-configuration of the units show the least steric hindrance to the approach of the monomer to the catalytically active Ti atom.

A third type of AC (CAC-3, "wicket") (Fig.3*b*), practically indistinguishable from PAC-3 and characterised by a large coordination sphere volume, has been detected. These AC show a weak interaction between the components of the catalytic complex $M'X_n$ and the OMC. Analysis of the experimental data (Table 1) indicates that 1,2(3,4)-polydienes are most probably formed on CAC-3.

Thus CAC-1 are stereospecific in the polymerisation of α-alkenes and dienes, CAC-2 are not stereospecific in the polymerisation of α-alkenes, but give 1,4-*cis*-polydienes,

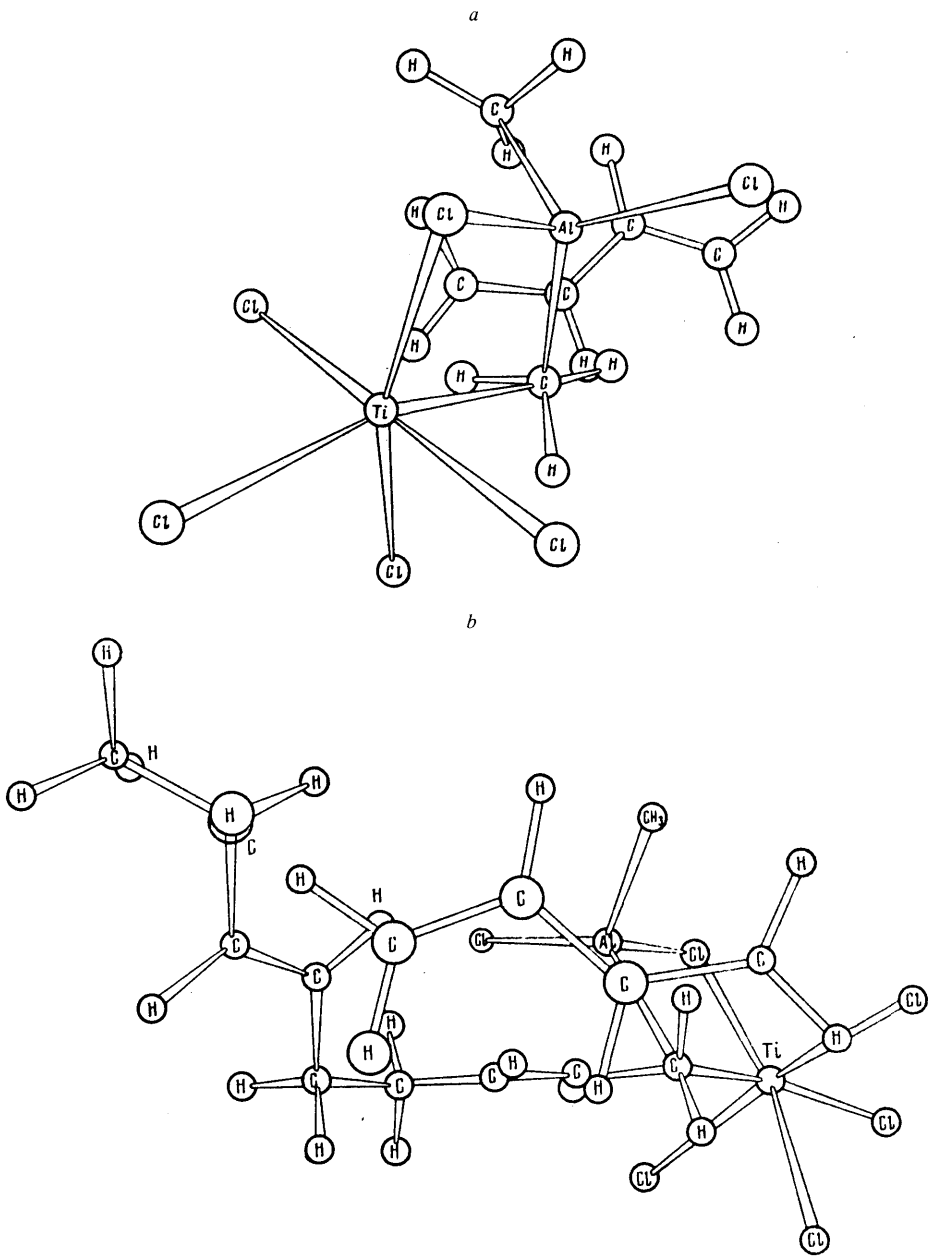


Figure 5. *a*) The coordination of butadiene with an active centre (stage of physical adsorption on the AC); *b*) physical adsorption of butadiene on an active centre with a growing 1,4-*trans*-polymer chain.

and CAC-3 bring about the non-stereospecific polymerisation of α-alkenes and dienes with the formation of atactic polyalkenes and 1,2(3,4)-polydienes. A theoretical base has been developed, which makes it possible, without carrying out tedious experimental searches, as has been done up to the present, to select in a first approximation (without allowance for kinetics) new Ziegler–Natta catalysts for the stereospecific polymerisation of α-alkenes and dienes.

IV. SUMMARY

Since the discovery of stereospecific polymerisation by Ziegler and Natta, a very large number of experimental and theoretical studies of the nature of the AC and the mechanism of stereoregulation have been published.

In the first twenty-year period (1954–75), a large number of hypothetical ideas were put forward, based on a limited amount of experimental material. It was shown that polymerisation on Ziegler–Natta catalysts is an ionic–coordination process in which the AC has a stereoregulating action on the micro-structure of the macromolecules. Two models of the AC, single-metal and two-metal, have been discussed. Although the polymerisation scheme on single-metal AC has been adopted by most workers, there are nevertheless many experimental data which are fundamentally inconsistent with this and similar theories. Polymerisation schemes involving AC with a two-metal structure are much more probable. The stereoregulating action of Ziegler–Natta catalytic systems is due to steric and (or) electrostatic factors.

The use of quantum-chemical calculations essentially has not led to an improvement in existing theories. They have merely confirmed various particular details of the process, or, at best, refined or slightly extended theories of the characteristic features of the electronic structure of AC. This at first sight unexpected result has a quite definite cause, namely the *a priori* selection of the structure of the AC in the quantum-chemical calculation, generally without allowance for the real structure of the $M'X_n$ and the OMC molecules, in accordance with the subjective sympathy of the authors for the single-metal or two-metal model of the AC.

At the same time, the comprehensive approach to the theoretical study and modelling of the process using semi-empirical and empirical methods of calculation and numerical experiment at all stages, from the physical adsorption of the homogeneous organometallic component on the real surface of the heterogeneous component of the Ziegler–Natta catalytic system to the formation of the AC and their participation in the process of polymerisation and stereoregulation, has enriched the theories with new and fruitful ideas, and hence made possible a new approach to the development of the theory of the processes of ionic–coordination stereospecific polymerisation of alkenes and dienes. In particular, the structure of the AC and the dynamics of their formation have been determined, and it has been shown that the stereospecificity of action of Ziegler–Natta catalysts is determined by the structure of the coordination sphere of the catalyst, and that stereoregulation takes place by a single common mechanism in the polymerisation of alkenes and dienes. Three types of adsorption centre differing in their three-dimensional structure have been identified: CAC-1, "tent" (isotactic polyalkenes and 1,4-*trans*-polydienes are formed), CAC-2, "flower" (atactic polyalkenes and 1,4-*cis*-polydienes), and CAC-3, "wicket" (atactic polyalkenes and 1,2(3,4)-polydienes).

Thus the traditional and up to the present the only empirical method for finding new effective Ziegler–Natta catalysts by tedious experimental searches can be replaced by numerical experiments involving the estimation of the proportion of stereoregulating AC determining the stereoisomerism of the MA formed.[87–92]

Naturally, there are a number of unsolved problems, such as the influence of various modifying additives on the rate of polymerisation and the properties of the AC, the detailed mechanism of the excitation of the polymerisation of alkenes and dienes, and the influence of the kinetics of polymerisation on the yield of the stereo-isomers of alkenes and dienes in the presence of specific Ziegler–Natta catalysts and monomers.

Another unresolved problem is the apparently fundamental question of the justification for classifying individual organometallic compounds of transition metals, showing stereospecificity in the polymerisation of dienes and cycloalkenes,[36–38] as Ziegler–Natta catalytic systems. The possible production of stereoregular polydienes in the presence of individual M′ compounds is the main argument used by supporters of the concept of single-metal catalysis. These compounds apparently represent a new generation of organometallic catalysts of the stereospecific polymerisation of dienes and cycloalkenes, and they should not be regarded as classical Ziegler–Natta catalysts. They apparently represent a unique new type of stereospecific catalyst. It is more correct to regard them as a separate class and to call them Dolgoplosk catalysts in honour of the leader of the school which has established priority in the development of the synthesis of individual transition metal OMC and the study of their catalytic activity and the mechanism of stereoregulation in stereospecific polymerisation, the copolymerisation of dienes, and metathesis (Refs.36–38, 62, etc.). This should lead in the near future to the general acceptance of the mechanism of two-centre catalysis in the stereospecific coordination–ionic polymerisation of alkenes and dienes on Ziegler–Natta catalysts. This, together with a deeper understanding of the processes of catalysis and stereoregulation, will provide a basis for the further development of improved methods for the directed control of the stereospecific polymerisation of alkenes and dienes.

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