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The Trigger Mechanism for Polymerization of α-Olefins with Ziegler–Natta Catalysts: A New Model Based on Interaction of Two Monomers at the Transition State and Monomer Activation of the Catalytic Centers

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The trigger mechanism involves a two-monomer transition state, where the entering of a new monomer unit triggers the insertion of the already complexed monomer. The catalytic center is activated through the insertion of the first monomer, and a reaction scheme (the dynamic steady-state approach) for a repeated activation/deactivation of the active center is formulated. The model explains kinetic phenomena as a reaction rate order vs monomer concentration between 1.0 and 2.0, the complex kinetics of ethene/α-olefin copolymerization, and phenomena observed when reaction parameters are changed during the polymerization. If the catalytic center is an octahedral titanium complex with three facial ligands bridging a support surface, an isospecific insertion is predicted as a result of the interaction between the two monomers and between the monomers and the surface. The model predicts a very high and self-correcting microisotacticity, self-correcting stereoselectivity, and a lower regularity for the first insertion. A reaction rate higher for the isospecific centers compared to that of nonspecific centers is rationalized. Syndiospecific polymerization is predicted for nonchiral homogeneous catalysts. © 1991 Academic Press, Inc.

INTRODUCTION

It has been more than 35 years since Ziegler first polymerized ethene to a linear polymer (*1*), and Natta produced the first isotactic polypropene (*2*) using Ziegler–Natta catalysts. Furthermore, it has been more than 25 years since Cossée formulated his well-known mechanism for the insertion of the monomer, employing an alkene complex intermediate (*3, 4*).

But too many questions remain unanswered, and too many results are not explained. A main problem is that even if all reasonable ideas are accepted, there are still some important phenomena that defy explanation. By far the most important of these are the intimate mechanism of stereoregulation during the propene polymerization, and the different kinetic behavior of atactic and isotactic centers. Other such phenomena include several reports of a monomer reaction rate order higher than 1.0 (*5–12*), and a reaction rate that is higher for copolymerization than for homopolymerization of either of the two monomers (*12–15*).

Not all the ideas presented in this paper are new. Tait has raised the possibility that some of the active centers may be propagative only part of the time (*16*). Chien *et al.* (*17*), Tait (*18*), Burfield (*19, 20*), Ver Strate *et al.* (*21*), and Henrici-Olive and Olive (*22*), among others, have indicated that the monomer may take part in the activation of catalytic centers.

Just recently Ewen (*11*) and Karol *et al.* (*12*) have proposed, on the basis of their kinetic results, that there are two sites for the monomer on the catalytic active center. Earlier formulations of two-monomer mechanisms have been given by Fellmann *et al.* (*23*) and McKinney (*24*), the latter also supported by quantum mechanical calculations. Strong evidences for two-monomer interac-

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tions have also been given for oligomerization catalysts related to Ziegler–Natta catalysts (*25, 26*). Finally a ligand-assisted insertion mechanism, which has much in common with the trigger mechanism presented here, has been proposed to explain the stereochemical behavior of the carbonyl insertion in pentacarbonylmethylmanganese (*27, 28*).

It is therefore time for a thorough analysis of the ideas, and for the fundaments and consequences thereof to be formulated.

In the following I refer to experimental results from different Ziegler–Natta catalysts, both homogeneous and heterogeneous. Most of the results are for titanium-based catalysts, but some results for vanadium-based catalysts are referred to. It seems highly unlikely that there should be several different mechanisms for the stereoregular polymerization of α-olefins, and that these mechanisms should appear for catalysts that by chance had very similar structures. It is therefore assumed that the main principles of the mechanism should apply for all these catalysts. The mechanism must therefore be compatible with every major phenomenon observed for either of the catalysts, although further sophistication is necessary to describe each and every catalyst system in detail.

Throughout the paper I consequently use the term "center" meaning a titanium complex of the catalyst that may or may not be catalytically active. The term "site" will always refer to a position on the complex. That is, a six-coordinated center has six sites.

FUNDAMENTAL PROBLEMS WITH THE TRADITIONAL COSSEE MECHANISM

It is well known that isotactic and atactic polypropene are formed at separate centers (*15, 29–34*), here called the isospecific and the nonspecific centers. There may be several mechanisms leading to atactic polymers, but the mechanism for formation of isotactic polymer is probably unique. A convincing model for the isospecific polymerization of propene should therefore be able to explain, or at least be compatible with, all results related to isospecific polymerization of α-olefins.

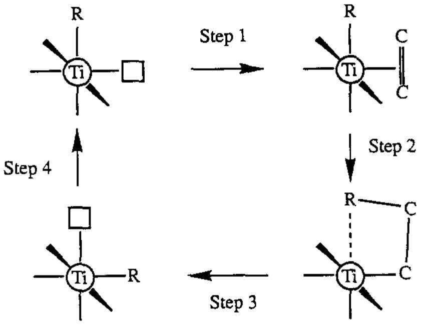

FIG. 1. The four steps of the Cossée mechanism for polymerization of olefins. R is any alkyl group. The square represents a free acidic site.

Figure 1 gives an overview of the Cossée mechanism (*3, 4*) for polymerization of propene. The model emphasizes the complexion of the monomer prior to the insertion, and is the basis for most models presented today (*35–41*).

However, the mechanism rests on several unstated assumptions that are not supported by theoretical or experimental evidence. A thorough analysis of these assumptions reveals several problems, and shows that the Cossée mechanism is apt to be revised. From the evaluation of the problems I have formulated certain requirements a proper mechanism must fulfill.

Problem 1. In order to explain isotacticity, it was assumed that the polymer chain should flip from one position to the other (step 4) (*36, 42*). Few scientists in the field of Ziegler–Natta catalysis believe that this flipping is possible, but the flipping is a consequence of the model, and cannot simply be erased. It must be explained, or the model must be modified.

Requirement 1. A proper reaction mechanism must be able to explain how the polymer ligand maintains its position in the complex after each insertion.

Problem 2. Structures (c) and (d) in Fig.

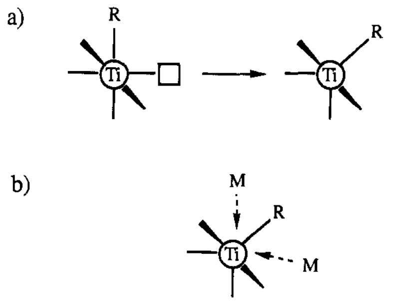

FIG. 2. A six-coordinated complex with one ligand missing is virtually a five-coordinated complex, and should be expected to relax to a less strained configuration. As shown this will give two equivalent sites for attack by a monomer (M).

1 are assumed to be octahedral, and the free site is visualized as a square. This presentation is deceiving, as one intuitively regards the free site as a something, whereas it virtually is a nothing, an empty space. Some of the ligands are bridged to the surface of the support, but at least the polymer chain is free to move. A rearrangement as given in Fig. 2 should therefore be regarded as a minimum. This conclusion is strongly supported by quantum mechanical calculations (*43*).

For the rearranged five-coordinated active center there are at least two sites that can be attacked by the next monomer. It seems exceedingly difficult to design a stereoregulating mechanism that allows insertion randomly from two different sites.

Requirement 2. A proper mechanism must either avoid the formation of a five-coordinated intermediate, or explain why the five-coordinated complex should maintain its octahedral geometry, and not relax to a less strained geometry.

Problem 3. In step 1 it is assumed that a monomer will complex to the free site. There may be several other Lewis bases in the slurry which will compete for the acidic free site, in fact these may form very stable complexes (*44, 45*). Although the monomer may be in the majority with a factor of 10–50:1, it is statistically impossible to get thousands of monomer complexions without intervention of the other bases, unless some kind of preference for the monomer is assumed. The Cossée mechanism gives no clues to assume such a preference.

Requirement 3. A proper mechanism must be able to explain the preference of monomers to Lewis bases on the monomer site.

Problem 4. The most unusual and characteristic property of the Ziegler–Natta catalysts is their ability to polymerize propene to a very isotactic polymer. The isospecific polymerization of propene is in fact the most stereoregular, nonenzymatic chemical reaction known (*46*). It is therefore exceedingly frustrating that this, the most important aspect of the catalyst, has not been properly described yet. Several models have been proposed (*33–37*), but none of the models seem able to explain a rapid polymerization to a highly isotactic polymer (*30, 47–50*), or to rationalize why the formation of atactic polypropene is slower than the formation of the isotactic polymer (*29–34*).

The formation of isotactic polyolefins requires a chiral active center. Models based on the Cossée mechanism (*3, 4*) have used one of two concepts to explain the chirality: The chirality is caused by the active catalytic complex itself (*35–41, 51*), or by the sidegroups on the growing polymer chain (*41, 42*).

The first concept is the least controversial, but does not explain why the first monomer is inserted with a far lower stereoregularity than the rest of the polymer chain (*52–55*). Furthermore, calculations of nonbonding interactions have shown that one should not expect isotacticity by this mechanism (*56*) without the help of external Lewis bases or without assuming very specific structures for the active center (*57*). But it is possible to make isotactic polypropene with no Lewis base present (*59*), and there is nothing in the models that indicates that the given structures should be the most active or the most abundant.

The second concept cannot explain a self-correcting isotacticity or stereoselectivity or why the chirality is not lost when ethene is inserted (*59–61*).

None of the concepts explain why propagation is far more rapid at stereospecific centers than at nonspecific centers (*15, 29–34*).

Requirement 4. The mechanism must be able to explain the high isotacticity found in the polypropene chains and all the other aspects of the stereochemistry of the polymerization.

Problem 5. The propagation mechanism after Cossée (*3, 4*) can be divided into two distinct steps, the complexion and the insertion. One should expect a rapid complexion, with a low activation energy, while the insertion should be the rate-determining step. Quantum mechanical calculations (*62–64*) indicate that the metal–alkyl complex should be favored energetically, and that there should be a very low, if any, activation energy for the complexion. On the other hand, there should be a considerable activation energy (50–150 kJ/mol) (*63–65*) for the insertion of the monomer into the polymer–metal bond.

Most papers on the kinetics of the polymerization assume a first-order reaction rate with respect to monomer concentration. However, this would require that the monomer complexion is rate determining or in equilibrium with free monomer, and hence only a minor fraction of the monomer sites should be occupied. In other words, after each insertion the monomer site should on the average have to be a free site for longer periods of time and be occupied by a monomer only seldom. It is very difficult to see how this could be compatible with a rapid polymerization in the presence of Lewis bases.

Furthermore, there are several reports on reaction rate orders higher than 1.0; in fact, all the way up to 2.0 have been reported (*5, 11, 12*). These results constitute another challenge that the Cossée mechanism fails to meet.

Requirement 5. A proper mechanism must be able to explain why the reaction rate order vs monomer concentration is at least 1.0, and may be as high as 2.0.

Polymerization according to the Cossée mechanism may still be possible. But according to the discussion above, one should expect a slow, atactic polymerization, giving polymers with relatively short chain lengths, at centers that should be easily blocked by addition of Lewis bases. Hence, the unmodified Cossée mechanism will predict the formation of atactic polypropene.

But the five problems obviously make it necessary to modify the mechanism if one wants to explain the rapid formation of long chains of isotactic polymers at centers not easily quenched by Lewis bases.

THE TRIGGER MECHANISM

Figure 3 illustrates the "monomer triggered insertion mechanism" or simply the "trigger mechanism." Figure 4 gives perspective ball and stick models of the active complex, and an early intermediate of the triggered insertion. The structures are idealized, the details are open for discussion. The main characteristics of the trigger mechanism compared to the Cossée mechanism are as follows:

— The monomer is never a free site during the propagation, as a new monomer will enter the monomer site at the same time that the first monomer is inserted.

— The insertion of the first monomer will not proceed (or will proceed very slowly) if no new monomer is available. That is, the new monomer triggers the insertion of the first monomer.

— The transition state is a pseudo-seven-coordinated complex with two monomers interacting with each other and with the central titanium atom.

It is assumed that the complexed monomer, and not the incoming monomer, will be inserted, as a rather firm π-complexion of both monomers at the same time seems improbable from steric reasons. This as-

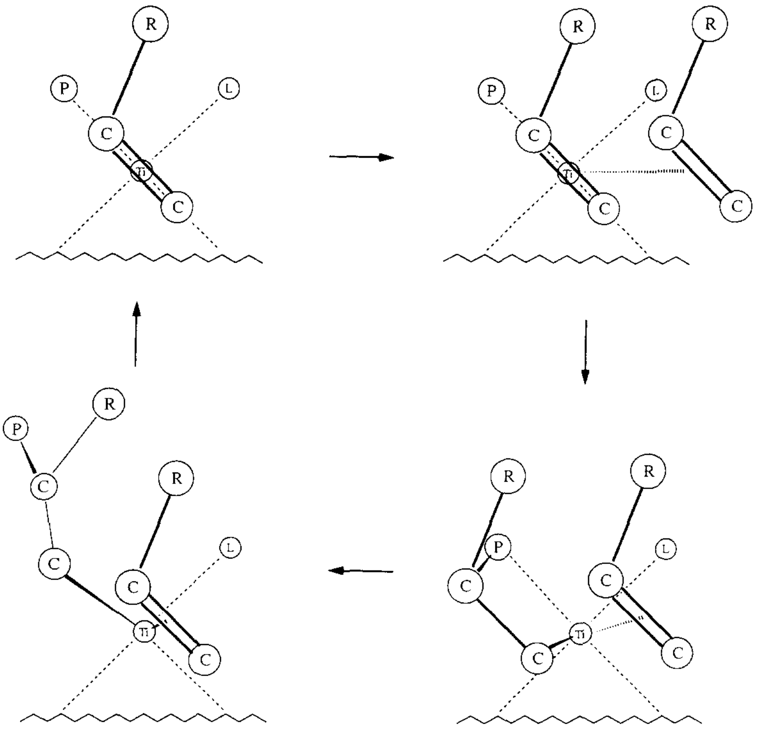

FIG. 3. Visualization of the trigger mechanism. Four different stages of the triggered insertion. The lower right structure is probably close to the transition state. The complex is viewed along the alkene–metal axis, and one of the ligands is hidden beneath the metal atom. The entering monomer will transiently expand the coordination sphere. L is an inert ligand, and is here a chlorine atom, an ester, or an alkoxy group. P is the polymer chain and R is the alkyl sidegroup of the alkene. The zigzag ribbon indicates the support surface.

sumption is also supported by the reported syntheses of alternating polymers (*66, 67*), which would be impossible if one given monomer unit should be stationary at the active center. The alternating polymers were made by homogeneous vanadium-based catalysts, but it seems improbable that titanium-based catalyst systems should work by a very different mechanism.

The trigger mechanism will meet all five requirements:

1. As the monomer site is never a free site but always occupied by a monomer, the polymer chain is forced to stay in its position. There is no flipping of the polymer chain within the trigger mechanism. Except for the inserted monomer, none of the ligands can change their positions during any stage of the triggered insertion.
2. The active complex is never five-coordinated; hence the ambiguity of the monomer site is avoided.
3. The monomer site is always occupied, and a monomer is needed for the triggering effect. The monomer will therefore be preferred over other Lewis bases, and a large number of consecutive insertions may appear.
4. The detailed analysis of the stereospecificity control is outlined separately below.
5. As stated in conjunction with the "dynamic steady-state approach," the formation of the active center must involve a monomer, i.e., $C^* = C^*([M])$. The propa-

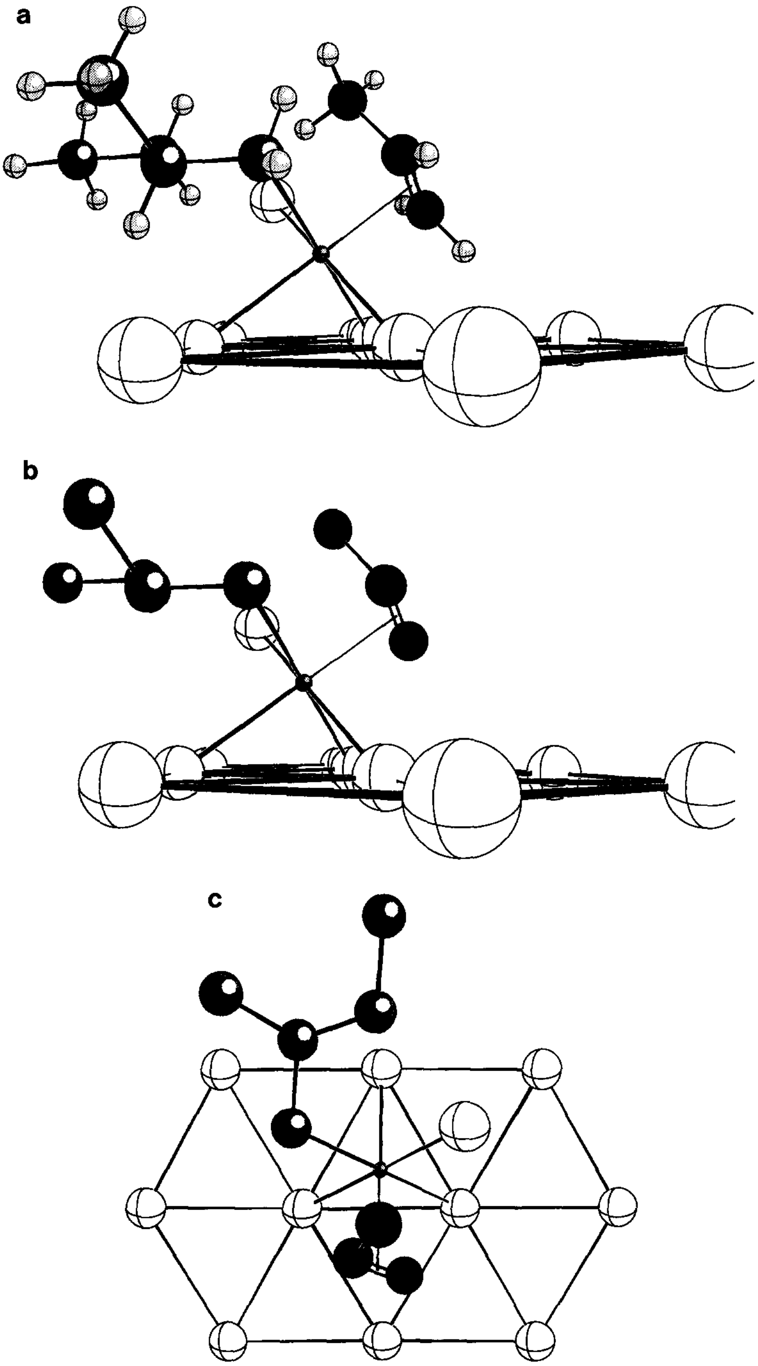

FIG. 4. Ball and stick perspective models for the active catalytic complex (*65*). The support surface is visualized as an array of chlorine atoms. The polymer chain is seen after insertion of the first monomer in an ethyl–titanium bond. The polymer chain has been given idealized tetrahedral carbons and staggered configurations. The orientation of the chain is chosen to give the minimum steric repulsion from the monomer and the support surface. In Fig. 4 the free ligand (L) is taken as a chlorine atom. (a) The active complex, side view. (b) Same as (a), but hydrogens removed for clarity. (c) Top view of (b), showing the details of the polymer chain. (d) Same as (a), with a second triggering monomer entering. The structure is idealized with the two monomers parallel and coplanar, and the position of the first monomer unaffected. (e) Gives a front view of (d) with the hydrogens removed for clarity. (f) Gives the view of (e) seen along the monomer–titanium axis, the same view as given in Figs. 3, 5, 6, and 8. (f) Same as structure H in Fig. 6.

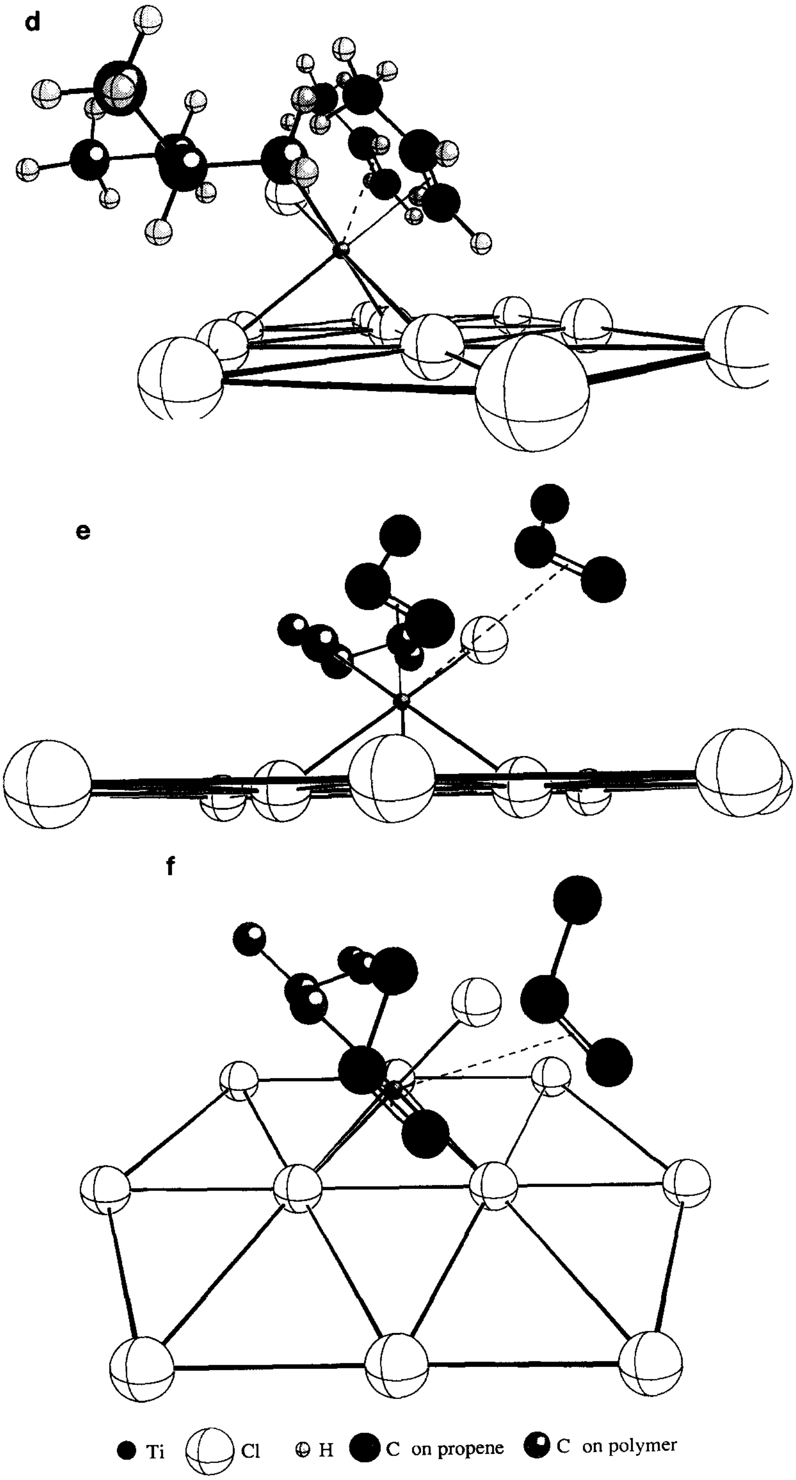

FIG. 4—*Continued*

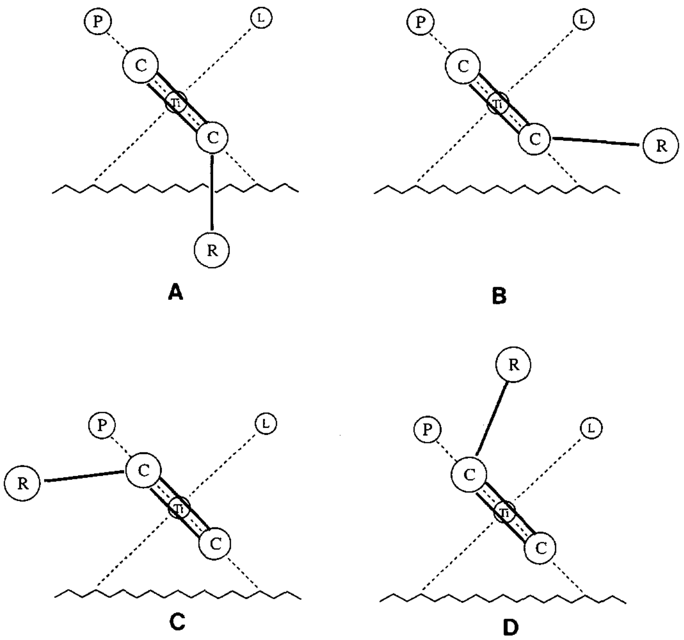

FIG. 5. Schematic structure of the stereospecific active center on a supported Ziegler–Natta catalyst for polymerization of propene. The active titanium complex is octahedral, and shares three ligands (one face) with the support. One of the three bridges extends backward from the titanium atom; hence it is not shown on the figure. Four different orientations of a monomer on the active center are shown.

gation must be of first order with respect to monomer concentration, i.e., $d[M]/dt = kC^* ([M])M$. The trigger mechanism therefore predicts a minimum 1.0 reaction rate order, and maximum 2.0 rate order with respect to monomer concentration.

THE STEREOCHEMISTRY OF THE POLYMERIZATION

Isospecific Polymerization on Heterogeneous Catalysts

The isospecificity of the monomer insertion is easily explained by the trigger mechanism if one assumes that the titanium complex is octahedral and shares one face with the catalyst surface. The presence of such complexes has earlier been proposed based on IR spectra of the catalyst (*43*). In this complex three sites will be available, one for the polymer chain (P), one for the monomer, and one for an inert ligand (L), which could be a terminal chlorine atom or any other Lewis base.

In Fig. 5., this complex is viewed along the alkene–metal axis (Cf. Fig. 4f)). One of the chlorine bridges is hidden beneath the titanium atom. The monomer can take four different orientations if the alkene C–C bond is forced to be parallel to the metal–alkyl bond. (The monomer can also be oriented orthogonally to the metal–alkyl bond, but in this case there will be no insertion before the monomer is rotated 90°.)

Of the four possible structures, A and B will have a higher energy because of the steric repulsion between the alkyl sidegroup (R in Fig. 5) and the bulky chlorine ligands, as has been shown by calculation of nonbonding interactions (*56*). Structure A seems to be even more unlikely, as the alkyl sidegroup is close to the support surface.

Structures C and D are both more stable, and structure D may be slightly more stable than C due to interaction with the support surface. However, if the free ligand (L in Fig. 5) is a chlorine atom, this terminal chlorine should be bonded closer to the titanium

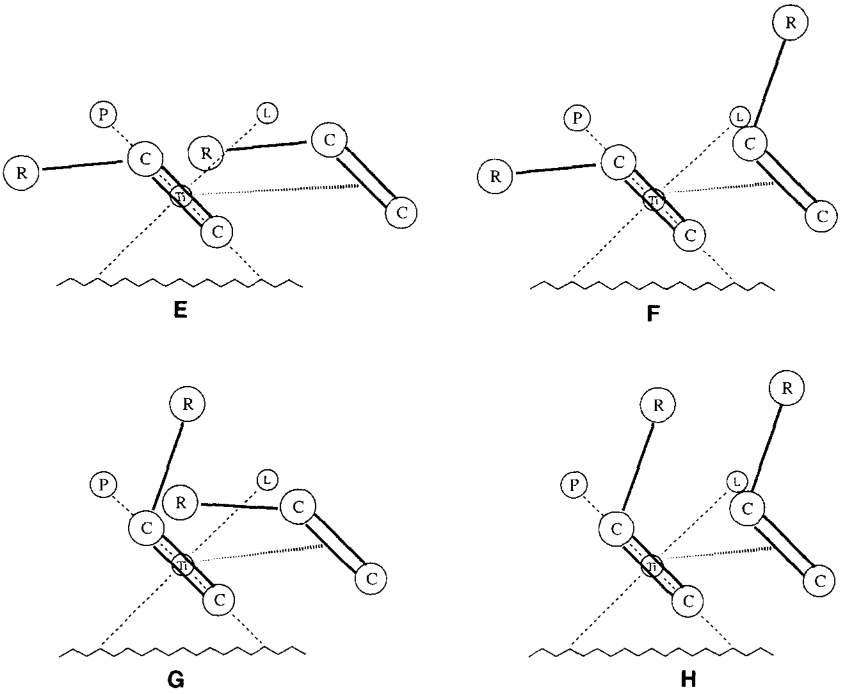

FIG. 6. Schematic structure of four transition states derived from structures C and D in Fig. 5.

atom than the bridging chlorine (*43*), and this effect would facilitate structure D.

Note that when a complex of structure C or D is formed, it cannot be easily transformed into the other, as there is no free rotation along the alkene double bond.

In Fig. 6 four structures, E, F, G, and H, are given for a transition state with two monomers. For structure E and G there will be a steric repulsion between the sidegroups of the two monomers that will increase the energy of the transition state. In both cases the repulsion will be easily removed by rotation of the incoming monomer around the alkene bond. As the incoming monomer at this point is only weakly bonded to the central titanium atom, the rotation will proceed with almost no barrier. The rotation will produce transition state F or H, and these two transition states should therefore be expected to be dominating. (For transition state E one could possibly get a triggering by the incoming monomer, if the latter moves closer to the polymer chain. However, in this case the sidegroup of the incoming monomer would come between the inserting monomer and the growing polymer chain, which would increase the energy of the transition state.)

A transition state H is derived from complex D, and will give a complex D. H will therefore reproduce itself every time a new monomer enters, and hence give an isotactic polymer. Transition state F will also give a complex of structure D, which shows that one erroneous insertion will not affect the stereochemistry of the following insertions.

Nonspecific Polymerization on Heterogeneous Catalysts

It is assumed that the atactic polymer is formed at nonspecific centers with lower coodination, centers which may be described as five-coordinated or centers with two monomer sites or free sites. The most important clue of this assumption is the ob-

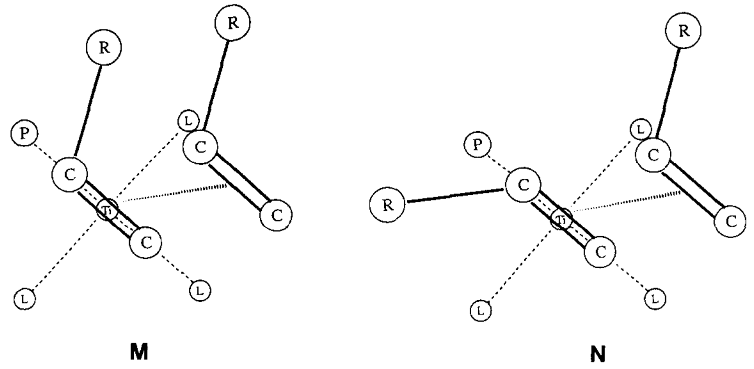

FIG. 8. Schematic structure of two possible transition states for a homogeneous catalyst, showing why syndiotactic polymerization should be favored.

shown that the titanium atoms will be surrounded by six ligands, which in several cases requires the formation of dimeric or polymeric units with chlorine bridges (*45, 71–78*). (This should be compared with the tendency for $TiCl_4$ to stay monomeric, except maybe at cryogenic temperatures (*79*), which could indicate that four-coordinated Ti(IV) is *less* acidic than five-coordinated Ti(IV).)

The first step is the alkylation of the titanium tetrachloride complex. There are three free ligands that can be alkylated; the other three are assumed to be irreversibly linked to the magnesium chloride support. One may therefore expect both mono-, di-, and trialkylation. Two sites are needed to create an active center; hence, the monoalkylated centers can immediately be labeled as inactive.

A full treatment of the trialkylated species is very complex, and will be discussed separately (*80*). However, if one assumes that the third site is occupied by an inert ligand (a Lewis base), the trialkylated complexes will mainly lead to the same conclusions as the scheduled reactions for the dialkylated complexes.

The starting point in Fig. 9 is the dialkylation of the initial complex, and formation of what is called a "latent center." Reaction 2 is a spontaneous splitting of one alkyl–metal bond to form a vacant site. The mechanism for the splitting is not known, although probably the aluminum alkyl compound is involved in the reaction. The undersaturated center is illustrated as an octahedral complex with one free site, but the dynamic steady-state approach as formulated here is indifferent to the detailed structure of this intermediate.

In reaction 3 the free site reacts with a Lewis base or a monomer. The reaction is very rapid, and may be on a "first come, first served" basis, although there may be some preference for one or the other. If the free site reacts with a monomer, the center will be activated to a propagating active center. If the site reacts with a Lewis base, the center will be temporarily deactivated, or become a "sleeping center." The same sleeping center will be formed when the propagative center eventually is terminated by a Lewis base (reaction 4).

Finally, the sleeping centers may be reactivated to "latent centers" by alkylation (reaction 5).

In Fig. 9 all probable reactions are indicated, and the lengths of the arrows indicate the estimated importance of each of the reactions of the specified catalyst system under normal polymerization conditions. For other catalytic systems the reaction scheme may be different, but the principles of alkyl-

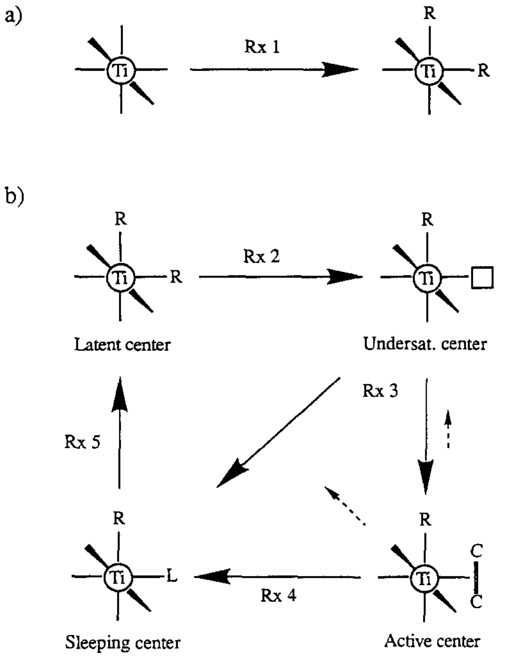

FIG. 9. Schematic representation of the "dynamic steady-state approach" for a supported $TiCl_4$ catalyst. (a) Dialkylation of the catalytic complex. Monoalkylation and trialkylation will also occur, as described in the text. (b) The repeated activation–deactivation–reactivation of the catalytic centers. The large arrows show the main reactions, while reactions according to the smaller arrows may also occur. The undersaturated center is as by the Cossée mechanism. However, the free site appears only once in this model, whereas according to the Cossée mechanism the free site is formed after every insertion. For reaction 3 there are two possible paths, either toward formation of an active center, or to direct formation of a sleeping center. The deactivation (reaction 4) may proceed via the undersaturated complex.

ation, splitting of the alkyl bond, monomer activation, and blocking by Lewis bases should still apply.

PREDICTIONS FROM THE MODELS COMPARED WITH EXPERIMENTAL EVIDENCES

Reaction Rate Order

Prediction. The reaction rate dependence upon monomer concentration should be of minimum first order, maximum second order, with intermediate orders possible.

Observations. Keii *et al.* (*5*) report that the maximum reaction rate was proportional to the square of the monomer concentration when the catalyst was activated without propene present. When the monomer was present during the activation, only a first-order dependence was observed (*81*).

Kissin (*82*) claims an almost complete consensus of a first-order kinetics. However, for some catalysts a higher rate law order (up to 2.0) was found at very low propene concentrations (*8*).

Pino *et al.* (*9*) reports proportionality between yield and monomer concentration for a given supported catalyst when no external Lewis base is used, but a higher order (ca.1.3) when methyl *para*-toluate is used as external base.

Second-order reaction rates have also been reported by Berger and Grieveson (*10*), Ewen (*11*), and Karol *et al.* (*12*). Other reports on significant increase in activity of a catalyst with increasing monomer concentration include Keii (*6*), Follestad and Larsen (*7*), Dyachkowskii *et al.* (*83*), Chien and Salajka (*84*), and for the peak rate by Nirisen (*85*).

These observations cover a broad range of catalysts from homogeneous catalysts in solution to heterogeneous catalysts for gas-phase polymerizations. There should be no doubt that a second-order reaction rate occurs at least under some circumstances.

Shielding of the Monomer Site

Prediction. The monomer site is protected. Hence, any addition of Lewis base, catalyst poison, or any other compound, should have a delayed effect, unless the Lewis base or poison is able to trigger the monomer insertion. In the latter case the effect should be almost immediate.

The molecules which are able to trigger the insertion should share a common characteristic feature.

Observations. The most obvious evidence of shielding of the monomer site is that it is possible to polymerize propene even when Lewis bases are present (*86*). If there was no shielding, one should expect a reduction in the molecular weight upon adding Lewis bases. In fact a slight increase is normally observed (*69, 86–91*).

A rapid effect on the reaction rate is observed upon addition of carbon monoxide (*92–94*), allene (*16, 94–96*), or ethene during propene polymerization (*97, 98*). Monomers, allene, and carbon monoxide are all π-acceptor ligands, and similar rapid effects should be expected upon addition of phosphines and cyanides. On the other hand, addition of water, oxygen, silanes, and esters seems to give a much slower effect (*99*).

Continuous Alkyl and Monomer Activation of the Active Center

Prediction. Alkyl and monomer are required for continuous reactivation of the catalytic centers.

Observation. The necessity of a continuous presence of aluminum alkyl has been elegantly proved by Keii et al. (*81*). Work is in progress to study the effect of alkyl and monomer activation, and the results will be published in due time (*100*).

Active Center Counting

Prediction. The number of metal–polymer bonds should be larger than the number of centers which are propagative at a given moment.

Observations. Several methods have been used to count the number of active centers, usually by counting the number of metal–polymer bonds, through quenching and radiotagging techniques. Generally the individual methods give very different result (*15, 16, 101–105*). The chemical methods correspond to propagation rates up to 200 insertions per second and per center for a 1 *M* propene solutions at 50°C (*31–33*).

Several recent studies with very short polymerization times (tens of seconds to fractions of a second) show a considerably higher propagation rate than that obtained from chemical methods. Typical values for k_p ($dm^3\ mol^{-1}\ s^{-1}$) are in the range of 2000–9000 for temperatures between 40 and 60°C (*30, 47–50*). These results indicate that the number of propagative active centers is far less than found by the chemical methods (*15, 16, 101–105*).

The results from Keii *et al.* (*49*) suggest an extremely high reaction rate. The k_p is calculated from the M_n. If one assumes that some of the chains are at least two times the MW, one ends up with a k_p of ca. 10,000 insertions per second or more for at least some of the centers in a 1 *M* propene solution at 20°C!

Copolymerization

Prediction. Different monomers should be expected to have (a) different propagation rates, (b) different abilities to activate the catalytic centers, and (c) different abilities to make the active center withstand deactivation.

Observations. The phenomena related to copolymerization are too many and too diversified to be discussed in extensio here. I therefore concentrate on a few very pronounced phenomena. If, during ethene polymerization, a small amount of propene is added, one will observe a slow but significant and persisting increase in catalyst activity (*98*). On the other hand, if during propene polymerization a small amount of ethene is added, there will be a rapid increase in the polymerization rate, but the effect lasts only as long as the ethene is present (*97, 98*).

The increase in reaction rate in the latter case is evidently a result of higher propagation rate for the ethene monomer, as the effect is immediate and ends when all ethene is consumed.

The increase in ethene polymerization rate upon addition of propene must be due to an increase in the number of the active centers, and can be explained if propene has a higher ability than ethene to activate catalytic centers. This explanation is supported by studies showing a high number of active centers during polymerization of 4-methylpent-1-ene (*106*).

Similar explanations can be given for several other observations of a higher polymerization rate for the copolymerization than for homopolymerization of either of the comonomers (*12, 14, 15, 107–109*).

Formation of a Titanium–Alkene Complex

Prediction. The metal–alkene complex has a lifetime which is at least equal to the time needed for the formation of one polymer chain. More than a prediction, this is a fundamental requirement for the trigger mechanism.

Observations. No direct proof for this complex has been presented yet, but there are several observations that evidence its existence.

Burfield (*110*) claims to have observed the complexion of propene with a homogeneous vanadium catalyst at −78°C by IR spectroscopy. The compound was catalytically active at room temperature.

Grubbs and Miyashita (*26*) reported reactions with dicyclopentadienyl titanocyclopentane which requires an intermediate with at least one monomer complexed to the titanium atom. This intermediate has a structure very similar to modern homogeneous Ziegler–Natta catalysts.

By addition of monomer to an activated catalyst, the EPR signal is markedly changed (*111*), or even intensified (*112*).

When ethene is introduced to an active $TiCl_3$ catalyst, the surface available for CO absorption is reduced (*113*).

The retardation of the polymerization by internal olefins (*12, 19, 22*) is difficult to explain unless by assuming that these nonpolymerizing olefins are able to complex to and block the active center.

Stereochemistry of Isospecific Polymerization

Predictions. An isotactic polymer should be formed and the discrimination should be high enough to provide a very high isotacticity even at moderately high temperatures. Also regioirregular entities should be expected to be predominantly isotactic. The isospecificity should be self-correcting.

The isospecificity should be far less for the first monomer than for the following, as the isospecificity is caused by the interaction of two monomers. Except for this first insertion, the microtacticity of the polymer chain should be only marginally affected by the insert ligand.

Comonomers, i.e., other α-olefins or ethene, should not affect the isotacticity of the polypropene blocks.

The active center should be chiral enough to yield a significant and self-correcting stereoselectivity.

Observations. The isotacticity of the polymer is very high. No one knows yet how perfect the isotacticity can be, but there are reports of polymer chains with less than one erroneous insertion per hundred insertions (*114, 115*). Isotactic polymerization of α-olefins is a unique example of stereospecificity in organic nonenzymatic reactions (*46*).

It is possible to obtain a polymer with a 97% isotacticity (measured as percentage *mmmm* pentads) at 240°C, which requires an isospecific discrimination of at least 15 kJ/mol (*116*).

The isospecificity is self-correcting; i.e., an erroneous insertion will not change the chirality of the active center (*51, 117–122*).

Regioirregularly inserted monomers also seem to be predominantly isotactic (*123–125*).

The stereoregularity of the first inserted monomer is very low compared to the overall isotacticity (*52–55*).

Addition of small amounts of ethene does not seem to affect the isotacticity of the polypropene blocks of the copolymer (*59–61*).

When racemic mixtures of monomers with chiral sidegroups are polymerized, chains enriched in R and S enantiomers are formed (*126*). This stereoselectivity is rather moderate, and must therefore be self-correcting, or the polymer chains would be racemic on average.

Formation of Atactic Polymer by Heterogeneous Catalysts

Predictions. If the nonspecific polymerization proceeds without triggering (i.e., Model 1) the nonspecific centers will be easily blocked by Lewis bases, also during the polymerization. This will in turn lead to a low molecular weight for atactic polypropene, and the chain length should be decreased by addition of external bases. There should be a maximum first order reaction rate, and therefore the relative amount of atactic polymer should be reduced by increased monomer pressure, and one should expect a much slower reaction rate, as the triggering is assumed to increase the propagation rate.

Observations. The blocking (*31–34, 69, 86, 88, 91, 122, 127–131*) and the low molecular weight (*29, 30, 49, 69, 130–133*) are observed by several authors, and there are reports on increased isotacticity index upon increasing monomer concentration (*85, 134*). We have experienced that the atactic polymer produced in the presence of external Lewis base is more short chained than when no external base is present, but there are reports that claim that external Lewis bases do not effect chain length significantly (*69*). The low propagation rate for nonspecific polymerization compared to isospecific polymerization is also well documented (*29–34*).

Even though the interpretation of these observations is less straightforward for Models 2 and 3 (see above), where the nonspecific polymerization also proceeds by a triggering mechanism, these models should not be ruled out on the basis of the present kinetic results.

Formation of Syndiotactic Polymer by Nonchiral Homogeneous Catalysts

The very low discrimination for the syndiospecific insertion should indicate a rather moderate syndiotacticity which will only be obtained at low temperatures. These predictions are in agreement with previous observations (*135–137*).

The model also predicts that syndiotactic polymerization should not be self-correcting and that the chirality should be lost when an ethene monomer is inserted, and both these predictions are verified (*60, 119*).

FINAL COMMENTS

It has been shown that the Cossée mechanism for isospecific polymerization of α-olefins is apt to be revised. Furthermore I have proposed a significant modification of the mechanism by introducing the trigger mechanism, based on an interaction of two monomers in the transition state. Based on this mechanism and an assumed reaction pattern for the formation of the active center, the dynamic steady-state approach, a number of predictions are given, which are significantly different from those given by the traditional Cossée mechanism. A large number of these predictions are observed, and several of the observed phenomena seem to be contradictory to the standard models.

It should be stressed that the stereochemical model is preliminary, as it is based on visual inspection of a simple molecular model. No quantum mechanical calculations or calculation of nonbonding interactions or molecular dynamics have been performed. Such calculations, when eventually performed, may force adjustments in the details of the model for the transition state, especially for the orientation of the incoming monomer. However, I do not foresee that such refinements should lead to major changes in the predictions outlined above.

The kinetic model, too, is only qualitative, and will not be quantitative before much work is done to experimentally determine the magnitude of several involved parameters. One should also be aware that other than pure chemical effects may influence the observed kinetics. The kinetics will also be influenced by such effect as transport limitations of any component in the system (*138, 139*) and fracturing of the catalyst to display new active centers (*45, 140*), as well as other foreseen or unforeseen phenomena.

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