Macromolecules **1980**, *13*, 42-49

Reaction Mechanism for Syndiotactic Specific Polymerization of Propene

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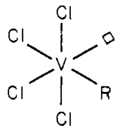
Received February 27, 1979

ABSTRACT: Pentacoordinated V^{III} catalytic complexes are proposed for the syndiotactic specific polymerization of propene, as carried out with homogeneous catalytic systems at low temperature. Polymerization is considered to occur via equatorial coordination of the monomer on the V atom, rotation of the coordinated olefin, and insertion on the reactive V–C bond. The stereochemical features of the polymerization are satisfactorily accounted for by considering the nonbonded interactions between the monomer molecule undergoing insertion and the ligands on the V atom, including the growing chain end, both in the actual complex and during the process of olefin coordination to the metal. Copolymerization of propene with different olefins is also interpreted within the proposed reaction scheme.

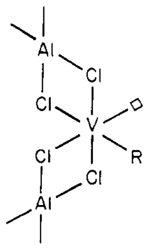
Much information has been accumulated concerning the stereochemistry of the syndiotactic specific polymerization of propene in the presence of homogeneous catalytic systems (e.g., VCl_4AlR_2Cl where R = alkyl group).[1-9] On the contrary, the studies dealing with the structure of the catalytic complexes are quite scanty[10-12] and for many respects are superseded because of the more accurate knowledge of the stereochemical polymerization mechanism achieved in the last few years.[1]

For instance, in an early paper[11] it was suggested that the syndiotactic specific catalytic complexes could be essentially hexacoordinated vanadium atoms[13] surrounded by four chlorine and one alkyl ligands and bearing a coordination vacancy (□) to ensure a preferential direction in the approach of the monomer to the growing chain end:



1

The V atom was considered to be in oxidation state 3, and at least part of the chlorine ligands were assumed to belong to bridge bonds with aluminum atoms.



2

At that time, it was assumed that the insertion of propene on the reactive vanadium–carbon bond was of the primary type

$$VR + C_3H_6 \rightarrow VCH_2CH(CH_3)R$$

Subsequent work showed that in the presence of homogeneous catalytic systems the syndiotactic chain propagation occurs via secondary insertion steps[3,4,9,14]

$$VR + C_3H_6 \rightarrow VCH(CH_3)CH_2R$$

Actually, the result is that the syndiotactic polymerization of propene is not completely regiospecific and that it must rather be formally considered as a binary copolymerization of head-to-tail and tail-to-head propylene units with $r_1r_2 > 1$, $k_{11} > k_{12}$, $k_{22} \gg k_{21}$:[4,6,7,15]

$$Mt\vdash\!\bullet \ldots + C_3H_6 \xrightarrow{k_{1.1}} Mt\vdash\!\bullet \;\; \vdash\!\bullet \ldots \quad (1.1)$$

$$Mt\vdash\!\bullet \ldots + C_3H_6 \xrightarrow{k_{1.2}} Mt\bullet\!\dashv\vdash\!\bullet \ldots \quad (1.2)$$

$$Mt\bullet\!\dashv \ldots + C_3H_6 \xrightarrow{k_{2.1}} Mt\vdash\!\bullet \;\; \bullet\!\dashv \ldots \quad (2.1)$$

$$Mt\bullet\!\dashv \ldots + C_3H_6 \xrightarrow{k_{2.2}} Mt\bullet\!\dashv\bullet\!\dashv \ldots \quad (2.2)$$

(where $\vdash\!\bullet = CH_2CH(CH_3)$ and $\bullet\!\dashv = CH(CH_3)CH_2$), step 2.2 being the only syndiotactic specific step.[1,3,4,7]

This experimental fact does not agree with the structure of the catalytic complexes assumed above. Actually one could easily convince himself by stick models that complex **2**, in particular, should rather be isotactic specific in step 2.2, because of the steric interactions between the approaching monomer molecule and the substituents of the Al atoms and considering the twofold symmetry relating the V–R bond and the vacancy. Actually, an analogous symmetry was assumed by one of us for the heterogeneous isotactic specific centers (i.e., Ti atoms of layered $TiCl_3$[16]).

In addition, considering that in step 2.2 the alkyl ligand is a secondary one, the approach of the monomer to the reactive metal–carbon bond should be severely hindered by nonbonded interactions with the ligands.

In this paper we want to show that if an essentially pentacoordinated V^{III} atom bearing three chlorine and one alkyl ligand is assumed in the catalytic complex, the previously discussed difficulties are avoided and much of the reaction stereochemistry concerning propene itself and other olefins can be accounted for.

On the other hand, pentacoordination of the V^{III} atom is suggested by the consideration that the bulky secondary alkyl ligand may favor a coordination number lower than six. As an example, pentacoordination around V^{III} is observed in $VCl_3(N(CH_3)_3)_2$, where the bulky amine ligands occupy the axial sites of a trigonal bipyramid (Figure 1).[17]

The Catalytic Model

The model for the syndiospecific catalytic complex assumed by us in order to account for the experimental observations reported in a following section will consist of a vanadium atom coordinated to three chlorine atoms, two of which could be bridge bonded to aluminum, to a sec-

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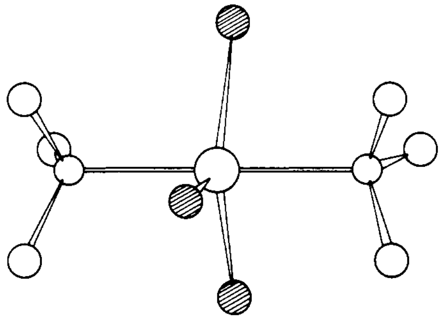
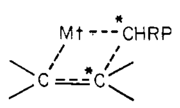


Figure 1. Geometry of the $VCl_3(N(CH_3)_3)_2$ molecule in the crystal[17] (axonometric projection: N, C, V atoms are indicated with increasing sizes, chlorine atoms are shaded, hydrogen atoms are omitted).

ondary carbon atom (i.e., the last atom of the growing chain end), and to a π-complexed olefin, considered as a monodentate ligand. On the other hand, the pentacoordinated complexes of transition metals containing a single olefin ligand usually display a trigonal bipyramidal structure, where the olefin occupies an equatorial site and its double bond is approximately placed in the equatorial plane.[18] Consequently we will assume the catalytic model shown in Figure 2a, where four different coordination modes of the olefin are shown; they correspond to four different steric orientations relative to the last secondary C atom of the growing chain. The possibility that this is a primary atom will also be considered later.

Our catalytic model will be further specified on the basis of the following assumptions:

(a) Olefin insertion proceeds via a four-center complex,

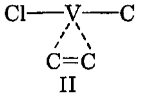


$$\begin{array}{c} Mt\cdots\overset{*}{C}HRP \\ | \quad\quad | \\ >C=\overset{*}{C}< \end{array}$$

I

the formation of which requires previous attainment of a short contact distance (i.e., less than 3 Å) between the starred C atoms (R may be either H or CH_3). After formation of the four-center complex, the growing chain acquires a new monomer unit via cis ligand insertion, which involves configuration retention of the C atom previously σ bonded to the metal.[1]

(b) The short C*···C* distance, required for the formation of the four-center complex, is obtained through a 90° rotation of the olefin around the axis V–(center of the C=C bond). The rotation leaves both the V···C distances and the olefin geometry unchanged. The resulting structure may be schematized as



$$\begin{array}{c} Cl\text{—}V\text{—}C \\ / \quad \backslash \\ C=C \end{array}$$

II

i.e., the Cl–V–C axis is parallel to the C=C bond. This will be assumed as the step with the highest energy through the whole process, and it will be denoted henceforth as the *active state*.

It should be clearly stressed at this point that the reaction cycle

olefin coordination →
catalytic coordination complex (see Figure 2a) →
olefin rotation to achieve active state (II) →
four-center complex (I) → olefin insertion

is understood to represent what is in our opinion the most plausible lowest free energy pathway. Although we consider the catalytic complex (with the olefin occupying a fixed position) as corresponding to a relative minimum of the free energy, in actual fact it might simply represent the first stage of olefin rotation.

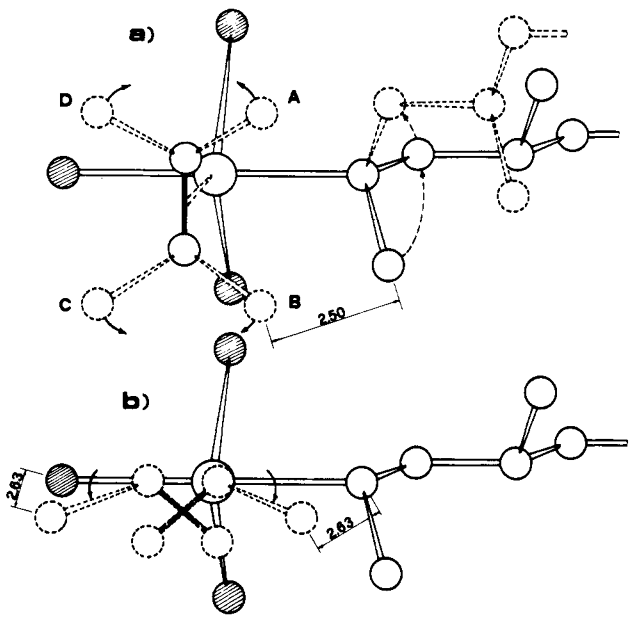


Figure 2. Four different modes of olefin coordination to the metal (A, B, C, D in dashed lines, see text). The heavy bar stands for the C=C bond. The arrows show the sterically allowed rotations around the (η-C=C)--V bond, as well as the rotation of the chain end around the σV–C bond required for coordination mode B (see text). (b) The alternative rotations of the olefin are hindered by short interactions involving the olefin methyl group (Axonometric projections: C, V atoms with increasing sizes, chlorine atoms dashed, H atoms omitted).

(c) The growing chain occupies an axial site (see Figure 2a) since no active state could form otherwise, according to assumptions (a) and (b); in fact, the distance between the C atom σ bonded to the metal and the closer unsaturated C atom would be more than 3.5 Å. The presence of aluminum atoms bridge bonded to the chlorines is not explicitly accounted for. They could be arranged in several possible ways; the only one which is inconsistent with our reaction model is given by coordination of one aluminum to both equatorial chlorine atoms. However, if a double bridge between an Al and the V atom occurs, it should preferentially involve the axial and one of the equatorial chlorines, because this is the only possibility consistent with the value of about 90° for the ∠Cl–Al–Cl bond angle with bridge Cl atoms observed by one of us in $(AlCl_2CH_3)_2$.[19] In conclusion, we have simply taken the V–Cl bond lengths as a rough average between the values pertaining to simple and bridge bonds (2.35 Å). As to the geometry of the coordinated olefin, it will be taken as analogous to that found in other methyl-substituted ethylenes π coordinated to transition metals (in particular we will adopt the parameters observed in Ni[1,2-bis(dicyclohexylphosphino)ethane]($Me_2C=CMe_2$)).[20] All of the geometrical parameters characterizing the catalytic complex (Figure 2a) are reported in Table I.

(d) After olefin insertion, the catalytic complex changes from penta- to tetracoordination (i.e., $Cl_3V(C_3H_6)_n\ldots$), where its structure may be reasonably assumed as tetrahedral (see Figure 4a). Considering the overall insertion process

$C_3H_6 + Cl_3V(C_3H_6)_n\ldots \rightarrow$
(coordination catalytic complex) $\rightarrow Cl_3V(C_3H_6)_{n+1}\ldots$

our scope will be to compare the activation energies, i.e., the energies of the active states as defined in II, for the

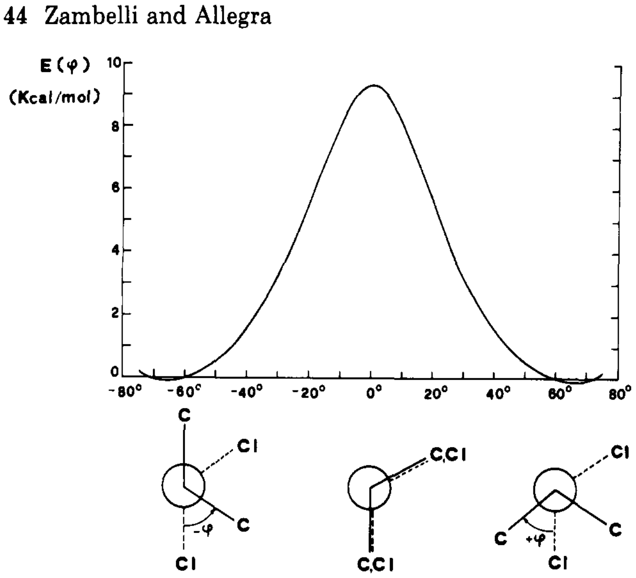


Figure 3. Nonbonded interaction energy vs. the rotation angle around the V–C bond in the catalytic complex. Interactions involving the coordinated olefin are not included (see text).

Table I
Geometrical Parameters of the Catalytic Complexes (see Figure 2a)

Bond Lengths, Å			
V—Cl	2.35	C=C	1.42
V—C	2.30	C—H	1.10
V· · ·C(olefin)	2.30	C—C	1.54

Bond Angles, deg			
$\angle Cl_{ax}$-V-Cl_{eq}	90	∠C-C-C	112
$\angle Cl_{ax}$-V-C	180	∠C-C-H	109
$\angle Cl_{ax}$-V-C(olefin)	90	∠H-C-H	109
∠C-V-C(olefin)	90	∠H-C(olefin)-H ∠H-C(olefin)-CH_3	114.6
$\angle Cl_{eq}$-V-Cl	120		
$\angle Cl_{eq}$-V-C	90	∠C=C-H ∠C=C-CH_3	120.5
$\angle Cl_{eq}$-V· · ·$\overset{C}{\underset{C}{\|}}$	120	∠V-C(olefin)-H ∠V-C(olefin)-CH_3	113.6
∠V-C-C	112		
∠V-C-H	109		

different insertion steps. In fact, the experimental evidence presently available essentially refers to the *ratios* between the kinetic constants k_{ij} (i, j = 1, 2, see copolymerization scheme). As a consequence, as long as k_{ij} may be expressed as (constant) $\exp(-E_{ij}/RT)$, *relative* values of the activation energy E_{ij} (i.e., $E_{ij}^{(r)} = E_{ij}$ + constant term) are sufficient for our purposes. In general, we will identify the relative activation energy of each insertion step as the sum of all the nonbonded interaction energies involving the olefin atoms in the active state. This is correct as long as we assume that (i) the electronic energy change is the same for all olefin coordination modes as well as for either type of V–C bond (i.e., primary or secondary C atom) on turning from tetra- to pentacoordinated complexes; (ii) the energy change due to the nonbonded interactions *not* involving olefinic atoms is also the same; and (iii) steric interference effects between the olefin approaching the tetrahedral complex and the growing chain are the same for all of the different modes of olefin coordination. Assumption (i) seems to be reasonable enough within the present approximate approach. Assumption (ii) is justified because the nonbonded interaction energy between the chlorine atoms and the growing chain end changes very little on turning from the tetracoordinated complexes to the reference conformation of the pentacoordinated complexes (i.e., staggered orientation between the VC< group and the VCl_3 bonds, see Figure 3). As for assumption (iii), it will be shown to hold for modes A, C, and D of olefin coordination only, while it appears to fail for mode B (see Figure 2a), which is subject to particularly severe steric hindrance with the chain during the olefin approach. Consequently, in the case of mode B, the relative activation energy $E^{(r)}$ obtained as a sum of nonbonded interactions in the active state will be increased by a term (Δ) having the character of a free-energy contribution.

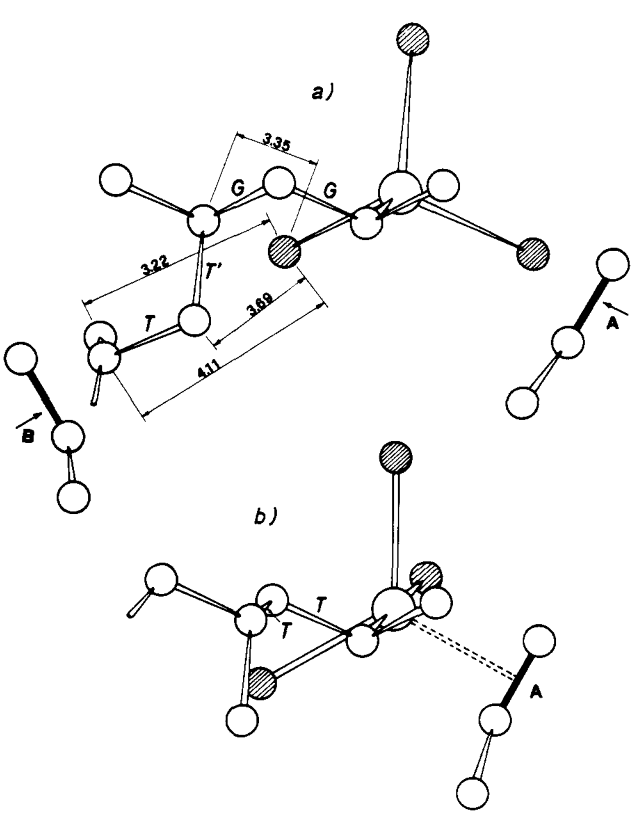


Figure 4. (a) In the tetrahedral V complex existing prior to olefin coordination, the GGTT... conformation of the chain end hinders olefin access toward coordination mode B (at left), unlike mode A (at right). (The skeletal bond labeled as T′ undergoes an internal rotation differing by 15° from the exact 180° angle. (b) After olefin coordination, the chain end turns to the TT. . . conformation. (Axonometric projections: atoms and bonds are represented as in Figure 2.)

Table II
Parameters for the Nonbonded Interaction Energies[a]

	A_{ab}	B_{ab}
C· · ·C	2.94×10^5	381
C· · ·H	3.97×10^4	134
H· · ·H	4.71×10^3	49
CH_3· · ·CH_3	5.64×10^6	2750
CH_3· · ·H	1.63×10^5	367
CH_3· · ·C	1.29×10^6	1024
CH_3· · ·Cl	3.93×10^6	2608
C· · ·Cl	9.01×10^5	980
H· · ·Cl	1.31×10^5	360

[a] $E_{ab} = A_{ab}/r_{ab}^{12} - B_{ab}/r_{ab}^{6}$; r_{ab} in Å; E_{ab} in kcal/mol.

For the sake of comparison, the energy of the catalytic complexes shown in Figure 2a will also be evaluated together with that of the active states following the same criteria. The nonbonded interaction parameters reported in Table II will be used adopting the Lennard-Jones potential function ($E(r) = a/r^{12} - b/r^6$). Within the limits of the present qualitative study, the methyl groups are treated as spherically symmetrical pseudoatoms[21] with a van der Waals' radius (r_{CH_3}) equal to 2 Å. The parameters corresponding to the methyl group, to the C and H atoms (r_C = 1.7 Å, r_H = 1.2 Å),[22] are identical with those adopted by one of us in a previous study on the unperturbed dimensions of polypropylene.[23] As for the interactions involving the chlorine atom, the corresponding b parameters are derived from the Slater–Kirkwood approximation,[24-26] a being chosen so that the minimum of the energy corresponds to the sum of the van der Waals' radii (r_{Cl} = 1.8 Å).[22] The interactions involving the metal atom will not be explicitly considered; on the other hand, within the nonbonded interaction scheme, they have an essentially constant value within each reaction step until formation of the active state.

Energetic Analysis of the Insertion Steps

It is convenient to represent at first the structure of the growing chain end during the process of the syndiospecific insertion step of propene (i.e., step 2.2), where the last chain atom is secondary.[3] Figure 3 shows the plot of the nonbonded interaction energy vs. the rotation angle around the V–C bond; the interactions involving the coordinated olefin are not explicitly evaluated at this stage. The methylene is assumed to be sterically equivalent to the methyl group, and the growing chain end is taken in the TT... conformation (see Figure 2; the first rotation angle defines the conformation of the V–C–C–C... sequence). The alternative GGTT... conformation, also accessible to the syndiotactic macromolecule in the free state,[27] is essentially forbidden by the nonbonded interactions either with the chlorine atoms or with the coordinated olefin or both. It is apparent that the chain orientation must be very close to either of the two (virtually equivalent) staggered conformations indicated in Figure 3; they will be taken as the *reference states* wherefrom the energy of the coordination complexes and of their active states is evaluated. The third staggered conformation will not be taken into consideration because it entails severe steric hindrance with the olefin during formation either of the coordination complex or of the active state, or both. If the last chain atom is primary (i.e., a methylene group), the most probable orientation (i.e., our reference state) of the (V)CH_2–C bond is half-way between the chlorine atoms, thus reducing to a minimum the steric interactions with the coordinated olefin. The energy difference between the eclipsed and the staggered orientation around the V–C bond is now about one-half of the value given in Figure 3.

Figure 2a shows that, unlike modes A, C, and D, the B coordination mode of the olefin does not permit the last chain methyl group to be oriented adjacent to the olefin itself, because of a methyl–methyl distance around 2.5 Å. This contact must be released through a rotation of 120° around the V–C bond (see dashed arrows in Figure 2a), bringing the chain methyl group opposite to the olefin and the rest of the chain end adjacent to it. However, it is interesting to examine the steric implications during the process of olefin coordination to the metal. Before olefin coordination, the V complex should be assumed as tetrahedrally coordinated; as a consequence, in addition to TT. . ., the chain end may now assume with no steric problems the GGTT. . . conformation (Figure 4a). Although this should be slightly unfavored with respect to TT. . . in the free syndiotactic chain,[27] in the V complex GGTT. . . may well be stabilized because of the four specific C. . .Cl interactions in the range 3.2–4.1 Å (see Figure 4a) that should entail a stabilizing effect of an electrostatic type, with no significant Lennard-Jones repulsion. Although it is difficult to give a quantitative evaluation of the corresponding Coulombic energy, it is expedient to consider the limiting case in which GGTT. . . is the only conformation accessible to the chain end. Let us focus our attention on coordination modes A and B. With respect to an observer looking along the V–C bond (see Figure 2a), the former mode may only be realized if the last chain methyl group is adjacent to the olefin and the latter if the methyl group points opposed to the olefin itself. Figure 4a shows that the chain end prohibits olefin access from the direction leading to mode B, while permitting the alternative access compatible with mode A. Modes C and D should also be obtained with no steric interference with the chain, i.e., along the same direction as that shown for mode A. In actual fact, the GGTT. . . and the TT. . . conformations should be in dynamical equilibrium, so that the B coordination mode is not completely forbidden, although contrasted by the flipping motions of the chain end. Another dynamical effect to be considered in principle is a rotation by 120° around the V–C axis during olefin approach (Figure 4a); if fast enough, the rotation could make modes A and B equivalent in a dynamic sense. Although the level of approximation of the present discussion does not permit any quantitative answer, we may say that any such rotation would appear to be slow compared with the diffusional motion of the olefin toward the metal, insofar as it should involve the concerted displacement of several chain atoms. When olefin coordination to the V atom is achieved, the complex acquires the trigonal-bipyramidal structure, and the chain end shifts to the TT. . . conformation (Figure 4b).

We are now able to evaluate the nonbonded energy content both of the catalytic complexes and of the corresponding active states. Let us first point out that each of the four coordination modes shown in Figure 2a is only compatible with one definite sense of rotation toward the active state (see arrows). In fact, the alternative rotations lead to either a CH_3···Cl or to a CH_3···CH contact distance of about 2.6 Å (see Figure 2b), corresponding to an interaction energy above 12 kcal/mol. In contrast, the allowed rotation does not entail significant steric interference, provided in cases B and C the chain is also rotated by 120° around the V–C bond as indicated in Figure 2a; the presence of the coordinated olefin does not interfere with such a rotation. As long as the methylene and the methyl groups are assumed to be equivalent from the nonbonded interaction viewpoint and the chain end is in the TT. . . conformation, the above rotation leads the chain into an equivalent energy minimum. On the other hand, under the same assumption it is also apparent that the above chain rotation makes coordination modes A and B energetically equivalent to each other; modes C and D are also equivalent to each other. Consequently, *after olefin coordination is achieved*, the four coordination modes will be considered in pairs, i.e., (A,B) on one side and (C,D) on the other. However, it is worth stressing once again that, *during the coordination process*, mode B is contrasted by steric interference with the chain as previously discussed.

If the last chain atom is a methylene carbon (i.e., after primary insertion), distinction either between A and B or between C and D may still be made with reference to the configuration of the previous tertiary C atom (see Figures 5 and 6, left side). However, since the most favored chain orientation is opposed to the coordinated olefin, no appreciable difference exists within either pair in terms of nonbonded interactions. In addition, contrary to the case with a secondary C atom σ bonded to the metal, in this case steric effects involving the chain end during olefin approach to the catalytic center do not appear to be noticeably different among the four coordination modes. They will be denoted as A′, equivalent to B′, and as C′, equivalent to D′, and may be visualized in Figure 2a if the

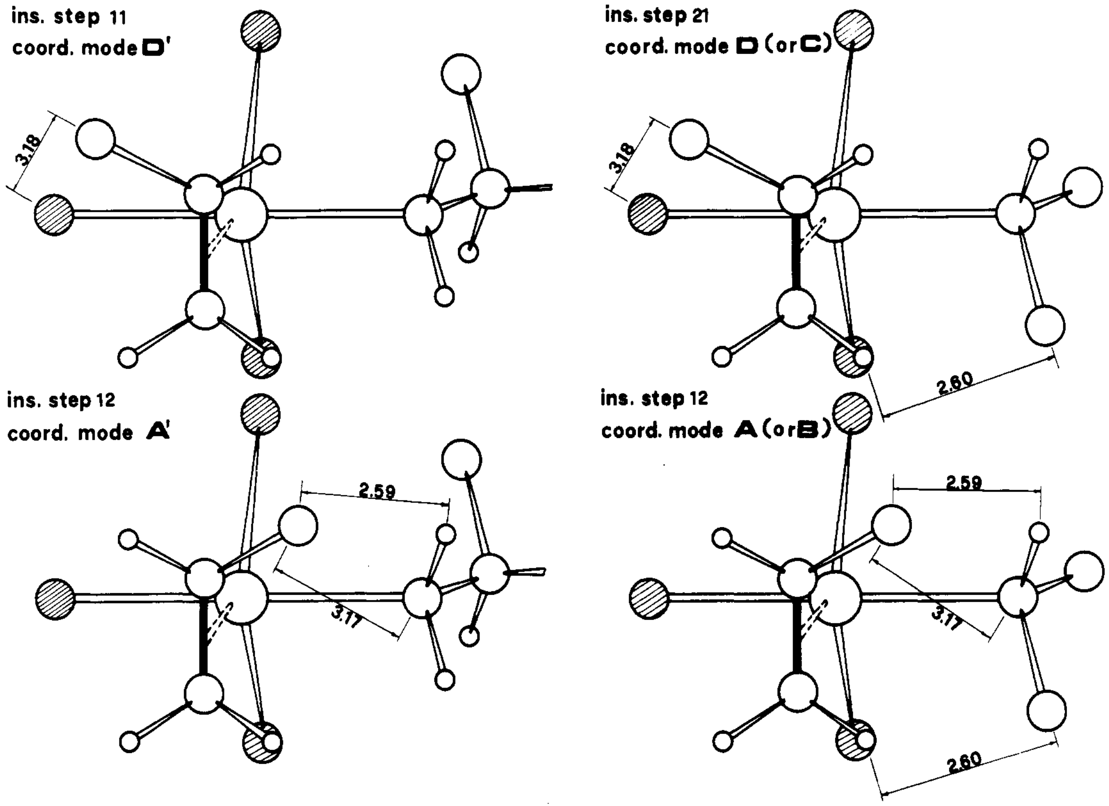


Figure 5. Geometry of the catalytic complexes corresponding to different olefin coordination modes (see Figure 2a) and for the V–C bond with primary (at left, modes D′ and A′) and with secondary carbon atoms (at right). Modes C′ and B′ are respectively derived from D′ and A′ after interchange between H and CH_3 on the last tertiary C atom of the growing chain. Unlike modes C and B, modes D and A (at right, from top to bottom) correspond to the last chain methyl group being closer to the olefin. No distinction between the last methyl and the last methylene chain carbon atom is made, considering analogous nonbonded interactions (see text). The rotation angle around the V–C bond is 60° in all cases (see Figure 3). (Axonometric projections: atoms and bonds are represented as in Figure 2, except for H atoms, smallest spheres.)

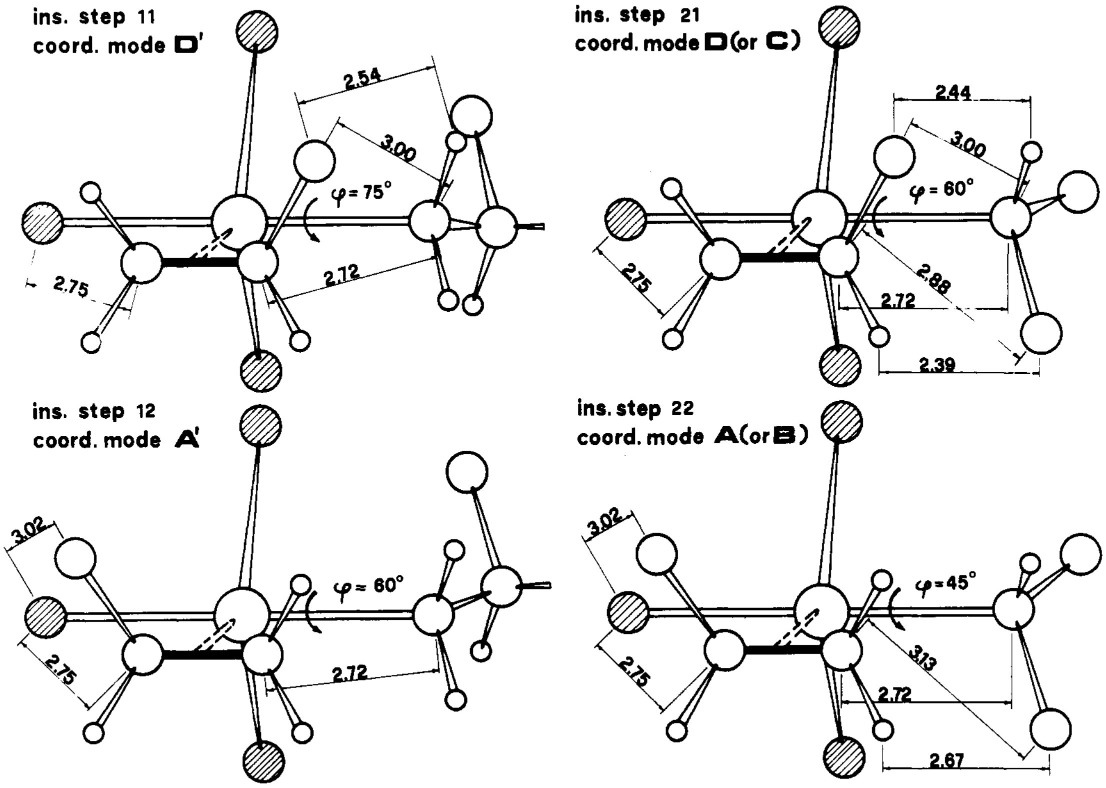


Figure 6. Geometrical representation of the active states corresponding to the catalytic complexes represented in Figure 5.

last methyl substituent of the chain is displaced from the last to the next to last skeletal C atom.

Figure 5 shows in some detail the geometry of the catalytic complexes with coordination modes A′, D′, A, and

Table III

a	*b*	*c*	*d*	*e*	*f*
1.1	C′	isotactic	0.4	4.8	stereoirregular
	D′	syndiotactic			
1.2	A′	erythro	0.0	6.1	stereoirregular
	B′	threo			
2.1	C	erythro	1.2	11.4	stereoirregular
	D	threo			
2.2	A	syndiotactic	0.8	8.0	predominantly syndiospecific
	B	isotactic	$0.8 + \Delta^g$	$8.0 + \Delta^g$	

[a] Insertion step, see copolymerization scheme. [b] Coordination mode of the olefin (see Figures 2a and 5). [c] Steric configuration relative to the previous tertiary C atom after insertion subsequent to the coordination mode. [d] Calculated energy of the catalytic complex (kcal/mol). A constant contribution has been added to all entries to avoid negative figures. [e] Calculated energy of the active state ($E_{ij}^{(r)}$, kcal/mol). The same constant contribution has been added to all entries as in column *d*. [f] Overall stereospecificity of the insertion step. [g] Δ arises from steric interference with the growing chain during olefin approach to the catalyst (see text and Figure 4a).

D, while the corresponding active states are reported in Figure 6. The above discussed pairwise equivalence between coordination modes (A,B) and (C,D) is reflected in the formal equivalence between the last methyl and the last methylene groups of the chain; the first few atoms further away from the metal along the chain do not give rise to appreciable nonbonded interaction energies with the olefin. The distances between nonbonded atoms corresponding to energy contributions more than 0.5 kcal/mol above their van der Waals' minimum are shown in the two figures.

Table III gives the energy results for the catalytic complexes as well as for their active states; correspondence between coordination modes, insertion steps, and their stereospecificity is also reported in the table. The energy of the active states is minimized for a rotation angle around the V–C bond close to that of either reference state shown in Figure 3. Small deviations have been found for (see Figure 6) (i) the active state of the A and B coordination modes where the lowest energy is achieved after a rotation of about 15° that releases the contacts between the olefin and the adjacent carbon atom of the chain end and (ii) the active state of the C′ and D′ coordination modes where a rotation of about the same magnitude is implied. Obviously enough, the corresponding nonbonded energy between the chlorine and the chain atoms has been taken into account.

The energy of the catalytic complex is not really important in the present context except to prove that it is remarkably lower than that of the active state, so that the reaction pathway assumed by us is reasonable.[28] Incidentally, π coordination of the olefin to the metal on a site adjacent to the M–C bond, with the C═C bond perpendicular to it, was also assumed by one of us in a study of the mechanism of isotactic polymerization of propylene.[16]

In the next section we will proceed to a systematic comparison of the results reported in Table III with the available experimental data.

Comparison with Experiment

At least qualitatively, the model proposed above accounts for several experimental observations concerning the homo- and copolymerization of propene and other olefins in the presence of the homogeneous syndiotactic specific catalytic systems under consideration. We will refer throughout to the insertion steps reported in the copolymerization scheme and to the data given in Table III.

(1) The overall stereochemical mechanism of addition to the double bond has been found to be of the cis type.[2]

(2) Step 2.2 has been shown to be the only syndiospecific step in propene polymerization.[3,4,6,7] Inspection of Table III shows that: (i) unlike the case of primary insertion, once a secondary insertion takes place it tends to persist because the energy of step 2.2 is much smaller than that of step 2.1 (by 3.4 kcal/mol); (ii) within each step 2.2, the probability of syndiotactic insertion is larger than that for isotactic insertion because of the steric hindrance with the growing chain experienced within mode B during the coordination process. Although we are unable to associate a free energy value to the resulting difference between an iso- and a syndiotactic step (Δ in Table III, experimental figure <2 kcal/mol[8]), our results appear to be in qualitative agreement with experimental observation.

(3) During propene polymerization, step 2.1 gives comparable amounts of erythro and threo placements of the vicinal methyl groups. This may be directly interpreted in terms of the previously discussed steric equivalence of coordination modes C and D, both in the catalytic complex and in the active state, and of the absence of any specific steric hindrance with the growing chain during olefin coordination.

(4) Experimentally, step 1.1 in propylene polymerization is found to be essentially nonstereospecific.[4,7,9] This is also in agreement with our model because of the steric equivalence between coordination modes C′ and D′.

(5) Still referring to propene homopolymerization, another experimental result is $k_{1.1} > k_{1.2}$ (k_{ij} = (constant) $\exp(-E_{ij}/RT)$); in other words, once the primary insertion is formed it tends to repeat, although with a smaller probability than in the case of secondary insertion.[4,6,7,9] This is also in agreement with the results of Table III; a quantitative evaluation of the activation free energy differences gives about 1.6 kcal/mol in favor of step 1.1,[15,29] to be compared with 1.3 kcal/mol as given in the table.

(6) According to our model, copolymerization of ethylene with propylene should turn the propylene blocks from the preferential 2.2 insertion mode (as observed in the homopolymer) to the preferential 1.1 mode, because the formation of a last primary carbon on the chain end, caused by insertion of an ethylene unit, favors the 1.1 compared with the 1.2 step (remember that $k_{1.1} > k_{1.2}$). Consequently, we should expect two effects: (i) the stereoregularity of the propylene blocks should be strongly depressed, because the atactic 1.1 sequences become more frequent; and (ii) since our model also predicts $k_{1.1} > k_{2.2}$, the average rate of polymerization within the propylene sequences should be increased. The first effect was observed by Bovey, Sacchi, and Zambelli:[4] small amounts of ethylene units dramatically decrease the stereoregularity of the polymer.

(7) Let us suppose that a butene-1 molecule undergoes coordination with the vanadium atom (Figure 7). If the previous unit inserted into the chain is propylene, it is quite obvious that the nonbonded interactions arising in the complex do not differ from the case of propylene complexation. In fact, the extra methyl group points just opposite to any possible steric interference if the usual *skew* rotation angle around the CH–CH_2 bond is adopted. For the same reason, the active state should not entail any additional energy. It is quite a different matter if the methyl group in the last (secondary inserted) chain unit is substituted by an ethyl group. Confining our analysis to staggered rotations both around the V–C bond and around C–C bonds, we see in Figure 7 the three shortest interatomic distances involving the last methyl group of the side chain. If the chain were rotated by 120° around

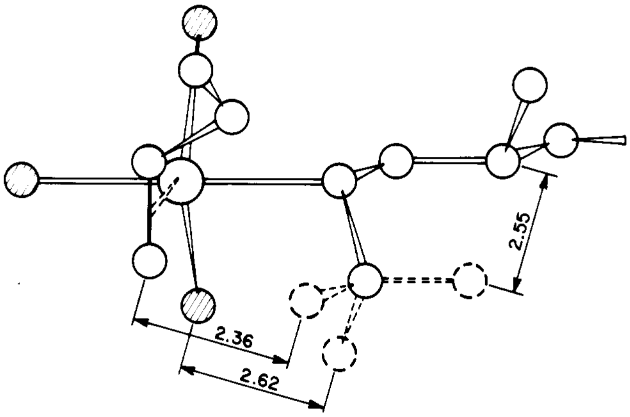


Figure 7. A butene-1 molecule coordinates to the V atom with the same nonbonded interactions as a propene molecule if the last inserted unit is propylene. If the last secondary inserted unit is butylene (the extra methyl group is represented in dashed lines for three possible conformations), very short nonbonded distances are unavoidable (see text). (Axonometric projections: atoms and bonds are represented as in Figure 2.)

the V–C bond so that the side chain pointed half-way between the equatorial chlorine atoms, the same methyl group would still interfere either with the chain C atom separated by four bonds or with either chlorine, the C···C or C···Cl distances being the same as the corresponding ones in Figure 7. As a consequence, although butene-1 should enter the chain with no difficulty, after a propylene unit, it should inhibit the next insertion step for either monomer, according to our model.

This is what is actually observed: butene-1 homopolymerizes very slowly and strongly reduces the polymerization rate when copolymerized with propylene, although $r_1 \simeq r_2 \simeq 1$.[5]

(8) It is easy to see from Figure 2 that our model predicts strong steric hindrance for the insertion step of a *cis*-butene-2 molecule. In fact, although this molecule could give rise to the catalytic complex keeping its methyl groups in sites C and D (see Figure 2a), any rotation toward the active state would be severely hindered by the nonbonded interactions of the type shown in Figure 2b. This prediction is in essential agreement with experiment. In fact, no matter how small the ethylene concentration in the reacting mixture is, a substantial proportion of ethylene sequences is always observed when copolymerization of *cis*-butene-2 with ethylene is attempted with the catalytic system under consideration. On the contrary, alternating copolymers have been obtained with other Ziegler-Natta catalysts.[32]

(9) As a final consideration, it is reasonable to predict that a further decrease of the coordination number around the V atom in the catalytic complex should lead to a faster, nonstereospecific propagation rate. In fact, the V–Cl bonds of the coordination catalyst act as steric constraints that both orient and slow down the polymerization reaction at the same time. As a matter of fact, when VCl_4 + $AlEt_3$ or $GaEt_3$ catalytic systems are used, instead of the one considered in this paper which essentially derives from VCl_4 + $AlEt_2Cl$, stereoirregular polymers are formed, and a very high propagation rate is observed.[12,33] The experimental facts may be related with a more pronounced displacement to the right of the dissociation equilibrium

$$VCl_2R{\cdot}MR'_nX_{3-n} \rightleftharpoons VCl_2R + MR'_nX_{3-n}$$

(M = Al or Ga; X = Cl), when less basic ligands or a less acidic metal atom are used for catalyst preparation.

Conclusions

Direct evidence on the structure of the catalytic complexes syndiotactic specific in propene polymerization has not been obtained so far. The structure proposed in this paper is based on the following considerations and assumptions.

(1) In the case of the homogeneous catalyst systems obtained from vanadium salts and aluminum alkyl chlorides, the catalytic complexes basically consist of VCl_2R.[10]

(2) VCl_2R expands its coordination number through complexation with other ligands present in the system. Cl atoms bridging V and Al are an example, but other possibilities can be conceived as well, e.g., dimerization of the VCl_2R itself.

(3) The polymerization is assumed to occur by addition of the monomer to the σ-alkyl–vanadium bond, and the rate of the four addition steps envisaged in the paper is assumed to be controlled by the nonbonded interactions between the monomer to be added and the vanadium ligands.

(4) Coordination number 5 for vanadium is chosen to justify the more relevant data concerning the propene polymerization and ethylene, butene-1, butene-2 cis copolymerization, i.e., all the stereochemical details of the polymer structure known so far and some kinetic data.

At last, we observe that the above discussed experimental data concerning polymerization are numerous enough as to provide very encouraging internal checks of the likelihood of our model.

Acknowledgment. This work was supported for one of us (G.A.) by a research contribution from Consiglio Nazionale delle Ricerche (CT.77.00628.03)

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Polyelectrolyte "Catalysis" on the Interionic Reactions between Similarly Charged Polyvalent Ions[‡]

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ABSTRACT: The influence of polyelectrolytes on the rate of the interionic reactions between similarly charged polyvalent ions was studied. As expected, the overall reaction between U^{4+} and Tl^{3+} was accelerated with an anionic polymer, i.e., sodium poly(ethylene sulfonate), at most by a factor of 10^4 accompanied by an increase in the entropy of activation and in the volume of activation. The results indicated that the activated complex was dehydrated by the macroions to a much larger extent than the reactants. Of the two reaction pathways, it was found that the route via a hexavalent intermediate was accelerated by the anionic macroions to a larger extent than that via a pentavalent one, indicating that the stabilization of the activated complex was important in polyelectrolyte catalysis. The reaction between $Fe(CN)_6^{4-}$ and $S_2O_8^{2-}$ was accelerated by a factor of about 10^5 by cationic polymers, i.e., polybrene and poly(4-vinyl-*N*-ethylpyridinium bromide). The entropy and volume of activation also increased with the addition of the polymers. The role of the desolvation effect by polyelectrolyte of the activated complex was suggested.

Intensive studies have been reported on the catalytic influence of macromolecular substances on various kinds of chemical reactions.[1-3] We ourselves have been engaged in kinetic investigations of interionic reactions in the presence of ionic macromolecules or polyelectrolytes.[4-6] The essential results are that (1) interionic reactions between similarly charged ionic species can be accelerated efficiently by macroions of the opposite charge, (2) reactions between oppositely charged species were retarded by both cationic and anionic macroions, and (3) forward and backward processes are influenced independently by macroions, suggesting that the polyelectrolytes do not fulfil the basic conditions required for catalysts. These results were accounted for in terms of the extended primary salt effect on the basis of the Brönsted–Bjerrum–Manning theory fairly successfully.[6] More recently, we pointed out on the basis of the activation volume data that the stabilization of the activated complex, which gave rise to acceleration, was caused also by dehydration induced by added macroions.[7,8]

In order to make a scrutiny into the true cause of the polyelectrolyte catalysis, it would be highly interesting to study reactions between polyvalent ionic species and the polyelectrolyte influence thereupon. In the present paper, we report data on inorganic reactions between U^{4+} and Tl^{3+} and between $Fe(CN)_6^{4-}$ and $S_2O_8^{2-}$.

Experimental Section

Materials. The aqueous solution of U^{4+} was obtained by electrolytic reduction.[9] Aqueous $Tl(ClO_4)_3$ solution was prepared by dissolving Tl_2O_3 (guaranteed grade) in a $HClO_4$ solution. The concentrations of U^{4+} and Tl^{3+} ions were determined by chelate titration with EDTA, using thorine and xylenolorange as indicators, respectively. $K_4Fe(CN)_6$ and $K_2S_2O_8$ were guaranteed grade reagents commercially available. The concentrations were determined by the gravimetric method and iodometry, respectively.

Sodium poly(ethylene sulfonate) (NaPES) was purchased from Polysciences, Inc. (Warrington, Pa.). The sample was purified by repeated precipitation, using methanol as the precipitant. Then the solution was dialyzed against deionized water. Further purification was carried out by ion exchange through columns of Amberlite IRA-400 and IR-120B.

Polybrene (cationic 3,6-ionenpolymer, 1,5-dimethyl-1,5-diazaundecamethylene polymethobromide) was purchased from Aldrich Chemical Co. Milwaukee, Wis. This polymer was purified by repeated precipitation, using acetone as the precipitant. The details of the preparation of poly(4-vinyl-*N*-ethylpyridinium bromide) (C_2PVP) have been described elsewhere.[10] Deionized water obtained with cation- and anion-exchange resins was further distilled for the preparation of solution.

Kinetic Measurements. The reaction rates of U^{4+} with Tl^{3+} were determined from the absorption decrease at 650 nm ascribed to U^{4+}, using a high-sensitivity spectrophotometer (Type SM-401) of the Union Engineering, Hirakata, Osaka-fu. The conversion of the UO_2^{2+} to U^{4+} by the electrolysis was approximately 85%. Further, we could not exclude the contamination of UO_2^{2+} from the reaction solution. However, we note that the presence of UO_2^{2+} does not affect the rate constants, according to Harkness and Halpern.[11] The reaction of $Fe(CN)_6^{4-}$ and $S_2O_8^{2-}$ was followed by the absorption increase at 420 nm ascribed to $Fe(CN)_6^{3-}$, using the above spectrophotometer and a stopped-flow spectrophotometer (Model RA1100, Union Engineering). EDTA was added in the reaction mixture in order to obtain reliable kinetic data, following the procedure of Kershaw and Prue.[12] The details of the apparatuses were described in a previous paper.[13] A high-pressure spectrophotometer (Union Engineering) was used at

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[‡] This work was partly presented at the IUPAC Symposium on Macromolecules, Mainz, 1979.

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