On the Mechanism of Formation of Isotactic and Syndiotactic Polydiolefins

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SUMMARY: The mode of formation of isotactic and syndiotactic polymers from 1,3-dienes is examined in the light of the most recent results. An interpretation is given for the formation of trans-1,4 isotactic polymers from CH_2=CH-CH=CHR (R = Me, Et, Pr, etc.) type monomers with heterogeneous VCl_3-based catalysts. Evidence is reported showing that stereoregular 1,2 or cis-1,4 polymers derive from a growing polymer chain anti-η^3-bonded to the transition metal and a cis-η^4 coordinated monomer. The influence on stereoselectivity of the substituents at the central carbon atoms of the monomer is discussed. The peculiar behavior of (Z)-1,3-pentadiene and 4-methyl-1,3-pentadiene, which give 1,2 polymers with catalysts that give 1,4 polymers from other monomers, is attributable to the fact that they can coordinate trans-η^2, in addition to cis-η^4.

Introduction

Conjugated diolefins can give different types of monomer units, i.e., trans-1,4, cis-1,4, 1,2, and, for non-symmetric monomers, 3,4 as well. For this reason different types of iso- or syndiotactic polymers can be obtained from this class of monomers. Isotactic and/or syndiotactic polymers having a 1,2-structure have been obtained from butadiene, (E)- and (Z)-1,3-pentadiene, and 4-methyl-1,3-pentadiene.[1-6] Trans-1,4 isotactic polymers have been obtained from various monomers of general formula CH_2=CH-CH=CHR (R = Me, Et, Pr, etc.)[7-9], while cis-1,4 iso- and syndiotactic polymers have been obtained from (E)-1,3-pentadiene[10-11], (E)-2-methyl-1,3-pentadiene[12-13] and (E)-3-methyl-1,3-pentadiene[14]. The interpretation of the mode of formation of these polymers is not easy. However, as a result of the work carried out during the last decade, the main factors that determine steric control in diolefin polymerization have been identified. In the following pages we will attempt to review the current understanding of the mechanism of formation of iso- and syndiotactic polymers from 1,3-dienes.

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Some Peculiar Features of Diene Polymerization

There are some differences between the polymerization of 1-alkenes and that of 1,3-dienes. We shall briefly examine these differences before discussing the factors that determine steric control in diene polymerization.

1) The first difference concern the mode of monomer coordination to the transition metal (Mt) of the catalytic species. A 1,3-diene, at least in principle, can coordinate cis-η^4, trans-η^4, and trans-η^2. For simple dienes such as butadiene, isoprene and (E)-pentadiene the cis-η^4 coordination is by far the energetically most favored mode of coordination. The trans-η^4 coordination, although less common, has been observed in some complexes of Zr[15], Mo[16] and Hf[17], therefore one cannot exclude its intermediacy in the polymerization with some transition metal catalysts. Trans-η^2 coordination likely occurs when only one coordination site is available.
2) The second difference is the type of bond between the growing polymer chain and Mt. This bond is of the σ-type for monoalkene polymerization, while it is of the η^3-butenyl type, of syn or anti form, for diene polymerization. An η^3-butenyl-Mt group is chiral, as is the Mt-CH_2-CH(Me)- group in propylene polymerization. In the latter group, however, the asymmetric carbon atom is too far from Mt to exert an asymmetric induction on the incoming monomer. In addition, there is freedom of rotation around the Mt-C bond. The situation is different for an η^3-butenyl-Mt group, which is conformationally more rigid than the Mt-CH_2-CH(Me)- group and is capable of exerting asymmetric induction on the incoming monomer. This is the reason why isotactic polydienes can be obtained using soluble catalysts prepared from non-racemic precursors: 1,2 isotactic polybutadiene was obtained with catalysts based on $Cr(acac)_3$ or other non-racemic Cr compounds;[1] cis-1,4 isotactic poly[(E)-pentadiene] with catalysts based on $Ti(OR)_4$;[10] and cis-1,4 isotactic poly[(E)-2-methyl-1,3-pentadiene] with catalysts based on $CpTiCl_3$.[13] In diene polymerization, racemic catalytic species are formed after the first monomer insertion into the Mt-C bond of the complex derived from the aluminum alkyl and the non-racemic transition metal compound. Soluble catalysts for the isotactic or syndiotactic polymerization of propene have been obtained only by using racemic

metallocene precursors. It is well established[18] that in these catalysts the function of the cyclopentadienyl ligand is to give a chiral orientation to the last inserted unit. Metallocene catalysts have also been used for diene polymerization, but the function of the cyclopentadienyl ligand in these catalysts is not to give a chiral orientation to the last-inserted unit, because an η^3-butenyl-Mt group is by itself chiral. In metallocene catalysts for diene polymerization the cyclopentadienyl ligand has little influence, if any, on stereoselectivity; the importance of these catalysts lies in the fact that they are soluble and, in general, highly active because a high proportion of the transition metal participates in catalysis.

3) The third significant difference between the polymerization of monoalkenes and of dienes is that in diene polymerization the last-inserted unit has two reactive points, C1 and C3 of the butenyl group. Reaction of the incoming monomer at C1 gives rise to a 1,4-monomer unit (cis or trans, depending on whether the butenyl group has an anti or a syn structure), while reaction at C3 gives rise to a 1,2-unit, independent of the form, anti or syn, of the butenyl group.[19]

Trans-1,4 Isotactic Polymers

Several monomers of general formula $CH_2=CH-CH=CHR$ (R = Me, Et, Pr, *i*-Pr, Bu, *sec*-Bu) have been polymerized to trans-1,4 isotactic polymers using heterogeneous catalysts based on VCl_3 or $TiCl_3$ (violet modification)[7, 8]. Trans-1,4 isotactic polymers have also been obtained from the deuterated monomer (Z,Z)-CHD=CH-CH=CHD, using the same catalysts,[20] which means that the group R does not have a determining effect on stereoselectivity.

In the case of heterogeneous systems, in which only a very small proportion of the transition metal is active in polymerization, it is difficult to have a detailed information on the nature of the catalytic species and hence on the mechanism of steric control. It is possible, however, to arrive at plausible interpretations on the basis of the general information we now possess of the polymerization with transition metal catalysts.

With VCl_3- or $TiCl_3$-based catalysts, the chemoselectivity, that is the formation of trans-1,4 rather than cis-1,4 or 1,2 units, likely depends on the fact that only one coordination site is available for the monomer, which therefore coordinates trans-η^2.

A hypothetical schematic representation of the active site for a VCl_3-based catalyst is shown in Figure 1.

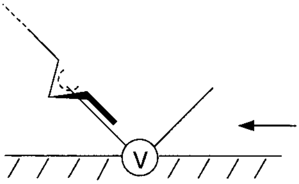

Fig. 1. Schematic representation of the active site for the VCl_3-$AlEt_3$ system, with the growing polymer chain η^3-bonded to vanadium.

For an isotactic polymer to be formed, the new monomer must always react on a catalytic center with the same enantioface during the growth of a macromolecule. The problem of enantioselectivity in propylene polymerization has long been debated and there is now a general agreement that it depends mainly on non-bonded interactions at the active site.[18] This conclusion is also valid for diene polymerization.

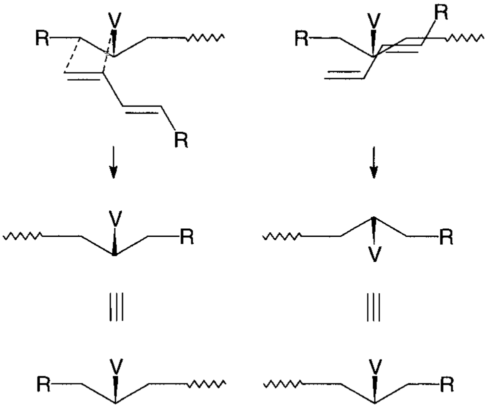

Fig. 2. Tentative interpretation of the mechanism of enantioselectivity in diene polymerization to trans-1,4 isotactic polymers with VCl_3-$AlEt_3$.

Figure 2 shows a tentative interpretation of the mechanism of monomer insertion with a VCl_3-based system, as seen by an observer along the direction of the arrow in Figure 1. The incoming monomer (above the plane of the figure) is trans-η^2 coordinated, the vanadium atom is in the plane of the figure, and the last-inserted unit, in the syn form, is below the plane. The new monomer can coordinate with either enantioface, as shown in Figure 2. Insertion of the monomer coordinated as in

Figure 2a will give rise to a new butenyl group of the same chirality as the previous one, whereas the monomer coordinated as in Figure 2b will give a new butenyl group of opposite chirality. The reason why insertion of the monomer coordinated as in **a** is favored is due to non-bonded interactions between the monomer itself and the last inserted unit. These interactions are stronger for the monomer coordinated as in **b**, and consequently insertion of this monomer is less favored.

Soluble catalysts have also been used for the polymerization of CH_2=CH-CH=CHR type monomers, but in general they give polymers of mixed 1,2/trans-1,4 structure. For instance, (E)-1,3-pentadiene gives polymers consisting of ca. 50% 1,2 and ca. 50% trans-1,4 units using the soluble system $VCl_3 \cdot 3THF\text{-}AlEt_2Cl$.[21]

The results obtained for the polymerization of pentadiene with LiBu in heptane are of some interest[9]. The (E)-isomer gives an amorphous polymer of mixed structure (ca. 80% trans-1,4, the other units being 1,2 and cis-1,4). The (Z)-isomer instead gives a product containing a fraction (ca. 30%, in polymerizations carried out at -30°C) consisting of a crystalline trans-1,4 isotactic polymer. The reason why the (E)-isomer gives a polymer of mixed structure is that, in addition to the trans-η^2 or trans-η^4 modes, this isomer can also coordinate to Li in the cis-η^4 mode . The formation of an isotactic fraction from the (Z)-isomer seems attributable to two factors: a) the cis-η^4 coordination is unfavored for this isomer, which explains why a 97-98% trans polymer is obtained; b) LiBu is associated in hydrocarbon solution, and a molecule of LiBu located on the outer part of a cluster behaves as a heterogeneous catalyst, in the sense that monomer approach is possible only from one hemisphere.

Cis-1,4 and 1,2 Stereoregular Polymers

Several pieces of evidence indicate that for most of the monomers (with a few exceptions, as will be indicated later) cis-1,4 and 1,2 stereoregular polymers (either with an iso- or a syndiotactic structure) all derive from the same situation: the growing polymer chain is anti-η^3-bonded to Mt, and the new monomer is cis-η^4 coordinated.

The new monomer can adopt two orientations with respect to the last-inserted unit, as shown in Figure 3a, b. In each orientation it can react either at C1 of the butenyl group, to give a cis-1,4 unit, or at C3, to give a 1,2 unit as can be seen from the schemes of Figure 3, these are the two factors that determine the formation of a new butenyl group of the same or opposite chirality with respect to the previous one.

With an orientation as in Figure 3a, reaction of the new monomer at C1 will, on insertion, give rise to a cis-1,4 unit and to a new butenyl group having the same chirality as the previous one; hence a cis-1,4 isotactic diad will be produced. On the other hand, reaction at C3 will give rise to a 1,2 unit and to a new butenyl group of opposite chirality with respect to the previous one; hence a 1,2 syndiotactic diad will be produced. Analogously, with a monomer orientation as in Figure 3b, a cis-1,4 syndiotactic and a 1,2 isotactic diad will be formed.

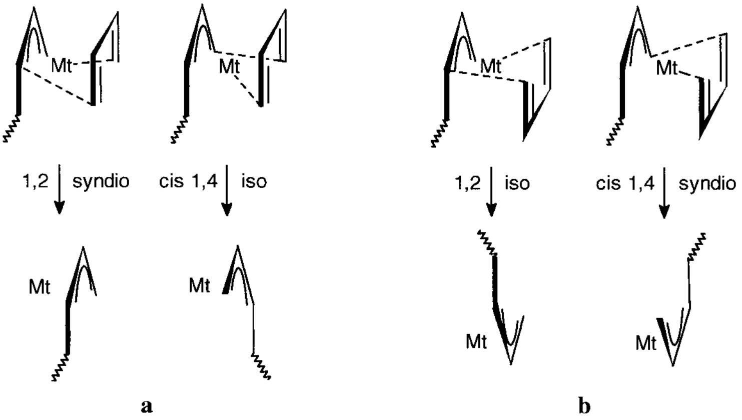

Fig. 3. Possible modes of formation of stereoregular 1,2 and cis-1,4 polydienes.

The validity of these schemes was checked with the use of deuterated monomers [(Z;Z)-CHD=CH-CHCHD; (E;E)-CHD=CH-CHMe] and it was found that the structure of the polymers obtained was that expected from the schemes of Figure 3.[19,20,22]

The work carried out during the last years has allowed us to identify some of the factors that determine A) reaction of the new monomer at C1 or C3 of the butenyl group, and B) the orientation of the new monomer with respect to the last-inserted unit.

A) The presence of substituents at C1 and C3 of the last-inserted unit is one of the factors that determine reaction of the new monomer at C1 or at C3. The soluble system $CpTiCl_3$-MAO is active for the polymerization of several 1,3-dienes. This system almost exclusively gives a cis-1,4 polymer from 2,3-dimethyl-butadiene, DMB, while it almost exclusively gives a 1,2 polymer from 4-methyl-pentadiene, 4MP.[13] The reason for this is that in the butenyl group derived from 2,3-DMB

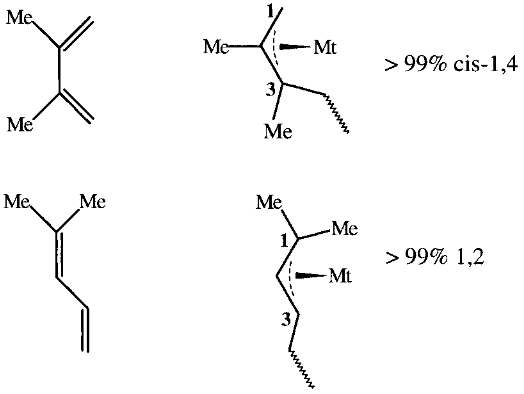

Fig. 4. η^3-Butenyl groups derived from 2,3-dimethyl-butadiene and 4-methyl-pentadiene.

(Figure 4) C1 is less substituted than C3, while in the butenyl group derived from 4MP C1 is more substituted. The monomer reacts more rapidly at the less substituted C atom, giving a cis-1,4 polymer from DMB and a 1,2 polymer from 4MP.

Another factor that determines reaction of the new monomer at C1 or C3 is the coordination geometry around the transition metal. Small variations in the relative position of the new monomer with respect to the last-inserted unit, which may depend on the type of ligand(s) bonded to Mt and on the type of monomer, may lead to the preferential formation of one type of unit (Figure 5). The results obtained with two soluble systems, $AlEt_3$-$Ti(OBu)_4$ and $(dmpe)_2CrCl_2$-MAO (dmpe = bis(dimethyl-

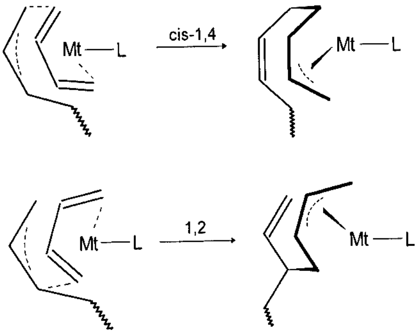

Fig. 5. Formation of cis-1,4 vs. 1,2 units in dependence of the coordination geometry around Mt. The incoming monomer is above the plane of the figure, the last-inserted unit is below, Mt is in the plane.

phosphino)ethane) are of interest with regard to this problem. Both systems polymerize butadiene to a 1,2 syndiotactic polymer, but give cis-1,4 isotactic polymers from (E)-pentadiene instead. The difference in chemoselectivities for butadiene and pentadiene polymerization is likely attributable to small variations in the position of the incoming monomer with respect to the last-inserted unit, as shown in Figure 5.

B) As to the factors that determine the mode of orientation of the incoming monomer with respect to the last-inserted unit, our interpretation is summarized in the schemes of Figure 6. If the growing polymer chain is the only ligand bonded to the transition metal of the catalytic center, the new monomer adopts an orientation as in Figure 6**a**, because of the steric interaction with the last-inserted unit. A situation of this type occurs with some nickel catalysts, e.g., Ni(acac)$_2$-MAO, [(allyl)Ni(COD)]$^+$[PF$_6$]$^-$ (COD = 1,5-cyclooctadiene), which have been used for the polymerization of some dienes to cis-1,4 syndiotactic polymers (Figure 7).[23]

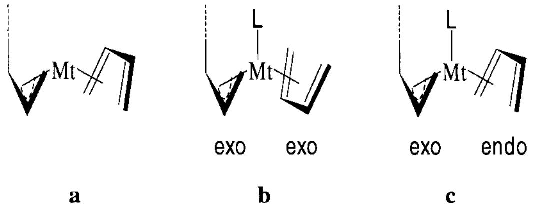

Fig. 6. Possible modes of orientation of the incoming monomer with respect to the last inserted unit.

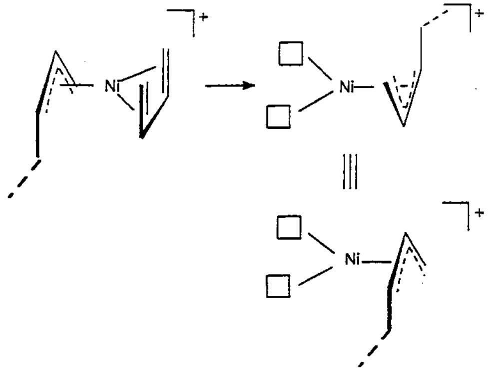

Fig. 7. Possible mode of formation of cis-1,4 syndiotactic polydienes with Ni catalysts.

If a generic ligand L is bonded to Mt (L = Cl, alkoxy group, Cp, etc), the last-inserted unit and the new monomer can adopt two arrangements, *exo-exo* and *exo-endo*, (Figure 6b,c), depending on the size of the ligand L and on the type of monomer. The following experimental results support this interpretation.

1) The (dmpe)$CrCl_2$-MAO catalyst system (dmpe = bis (dimethylphosphino)etane) polymerizes butadiene, at room temperature, to a 1,2-syndiotactic polymer that is crystalline as shown by x-ray analysis. The same system is also active for the polymerization of isoprene and gives, at room temperature, a polymer consisting predominantly of 3,4-units (> 92%), but shown to be amorphous by x-ray analysis, and atactic by NMR examination.[24]

2) While the (dmpe)$CrCl_2$-MAO catalyst system polymerizes butadiene to a crystalline 1,2-syndiotactic polymer, the (dmpm)$CrCl_2$-MAO catalyst system (dmpm = bis(dimethylphosphino)methane) polymerizes this monomer to an amorphous 1,2-polymer. However, NMR analysis indicates that isotactic triads predominate over the syndiotactic ones. This means that a simple modification in the bulkiness of the ligand (-CH_2-CH_2- replaced by -CH_2-) causes a remarkable effect on stereoselectivity.[25]

3) Soluble neodymium systems active for the cis-1,4 polymerization of butadiene have recently been reported.[26] We have polymerized (E)-1,3-pentadiene, EP, and 2-methyl-1,3-pentadiene, 2MP, with these catalysts. At room temperature, EP gives a polymer consisting of ca. 85% cis units, the other units being 1,2. At -20°C it gives a polymer ca. 94% cis, having an isotactic structure according to ^{13}CNMR

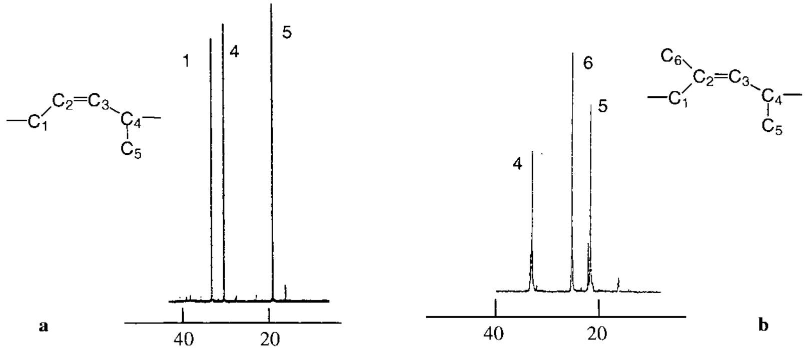

Fig. 8. ^{13}C NMR spectra (aliphatic region) of (a) poly(EP) and (b) poly(2MP).

analysis (Figure 8a). At room temperature, 2MP gives a polymer consisting of ca. 92-94% cis units, the other units being predominantly trans-1,4. The ^{13}CNMR spectrum (Figure 8b) indicates that the polymer has a predominantly syndiotactic structure, although isotactic triads are also present in minor amount.[25]

All the results reported under 1-3) can reasonably be accounted for according to the schemes of Figure 6. The formation of 1,2-syndiotactic polybutadiene with the (dmpe)$CrCl_2$-MAO system probably derives from an *exo-exo* arrangement, as in Figure 6b. Reaction of the incoming monomer at C2 of the last-inserted unit in fact gives a new butenyl group of opposite chirality with respect to the previous one.

Formation of a 3,4-atactic polymer from isoprene most likely depends on the fact that the Me group increases the steric interaction between incoming monomer and last-inserted unit, with the result that *exo-exo* and *exo-endo* arrangements become energetically similar for isoprene. This gives rise to iso- and syndiotactic diads during the growth of the macromolecules, hence to an atactic polymer.

The polymerization of butadiene with (dmpm)$CrCl_2$-MAO is of interest because it shows that by decreasing the bulkiness of L (a -CH_2- group instead of -CH_2-CH_2- in the phosphine ligand) the *exo-endo* arrangement becomes favored, with formation of an amorphous 1,2 polybutadiene, in which, however, isotactic triads prevail over the syndiotactic ones. This result too is in accordance with the schemes of Figure 6.

Polymerization of (Z)-1,3-Pentadiene (ZP) and 4-Methyl-1,3-Pentadiene (4MP)

These two monomers have a Me group in the cis position and for this reason the cis-η^4 coordination is not as favorable for them as it is for butadiene or isoprene. Both monomers have been polymerized with heterogeneous $TiCl_3$- or VCl_3-based systems. ZP gives trans-1,4 isotactic polymers, probably according to the mechanism previously outlined. 4MP gives 1,2-isotactic polymers; the mode of formation of these polymers has never been investigated.

Most of the soluble systems used for diene polymerization (e.g., $Al_2Et_3Cl_3$-$Co(OCOR)_2$, $Al_2Et_3Cl_3$-$V(acac)_3$) are practically inactive for ZP and 2MP polymerization. However, $CpTiCl_3$-MAO exhibits a good activity, and the results obtained with this system are of mechanistic interest.

Polymerization of ZP. At room temperature, the $CpTiCl_3$-MAO catalyst system gives a poly(ZP) which is ca. 85% cis and 15% 1,2, and has a predominantly cis-isotactic structure according to ^{13}C-NMR examination. However, the polymer obtained at -20°C is practically 100% 1,2, is crystalline and has a syndiotactic structure. In addition, the polymerization is faster at -20°C than at +20°C. The dependence of polymer structure on the polymerization temperature has been observed only for ZP; other monomers (butadiene; (E)-pentadiene; 2,3-dimethyl-1,3-butadiene; etc.) polymerized by the $CpTiCl_3$-MAO catalyst system give the same polymer at both +20°C and -20°C.

The formation of a cis poly(ZP) at +20°C and of a 1,2 syndiotactic poly(ZP) at -20°C cannot be attributed to a different oxidation state of Ti in the catalytic species (eg, Ti^{3+} at +20°C; Ti^{4+} at -20°C). Catalysts prepared at room temperature and used at -20°C give 1,2 poly(ZP), but if the polymerization temperature is brought to +20°C after ca. 30% monomer conversion, the polymer formed at +20°C is predominantly cis. This means that the same catalytic species gives polymers of different structure at +20°C and -20°C respectively.

Polymerization of 4MP. In the temperature range from +60°C to –70°C, $CpTiCl_3$-MAO gives a poly(4MP) consisting almost exclusively of 1,2 units, having a syndiotactic structure. The polymerization of 4MP is much faster than that of butadiene, under the same conditions (Table 1).

Table 1. Polymerization of butadiene and 4-methyl-pentadiene with $CpTiCl_3$-MAO. Influence of temperature on polymerization rate.

Polymerization temperature	TON *	
(°C)	Butadiene	4-Methyl-pentadiene
+ 20	233	2300
- 30	6	2230

* Number of monomer molecules polymerized per Ti atom per minute.

Useful information on the problem of ZP and 4MP polymerization comes from an investigation of the copolymerization of some dienes with $CpTiCl_3$-MAO at room temperature[27]. Butadiene and (E)-pentadiene give random copolymers, but butadiene and 4MP give block copolymers. Although 4MP polymerizes much more rapidly than B, the butadiene/4MP copolymerization with a feed molar composition 1/1 gives only polybutadiene. ZP and 4MP give random copolymers and in the copolymers containing less than 50% ZP units, these are 1,2 (they are predominantly cis-1,4 in ZP homopolymer obtained at 20°C).

In our interpretation, the particular features of ZP and 4MP polymerization with $CpTiCl_3$-MAO (formation of poly(ZP) of different structure at +20°C and -20°C respectively; very fast polymerization of 4MP to 1,2 polymers; the results of the copolymerization) are all related to the different coordination behavior of ZP and 4MP with respect to that of other dienes. For butadiene, isoprene, and (E)-pentadiene the mode of coordination by far energetically favored is cis-η^4. For ZP and 4MP the cis-η^4 coordination is not so energetically favored and an equilibrium between cis-η^4 and trans-η^2 coordination likely occurs.

The case of 4MP is simpler to explain. 4MP can coordinate cis-η^4 or trans-η^2, but since insertion of the monomer coordinated cis-η^4 is unfavored, because of the presence of two Me groups at C1 of the last-inserted unit, only 1,2 units are formed (Figure 9). In other words, kinetic factors determine the high chemoselectivity, either at +20°C or –30°C. ZP too can coordinate cis-η^4 and trans-η^2, but in this case C1 of the last-inserted unit bears only one Me group and therefore insertion of the cis-η^4 coordinated monomer to give cis-1,4 units is not so unfavored as for 4MP.

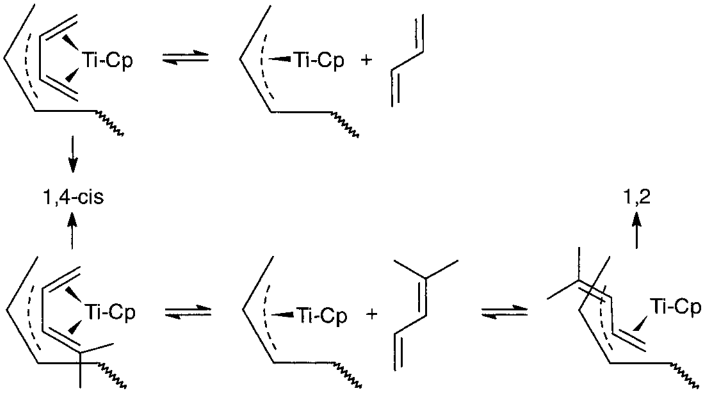

Fig. 9. Possible modes of coordination of butadiene and 4-methyl-pentadiene to the catalytic species in the $CpTiCl_3$-MAO catalyzed polymerizations. The last unit is below the plane of the figure, the incoming monomer is above, Ti is in the plane.

In the case of ZP, the formation of a predominantly cis polymer at +20°C and of an almost exclusively 1,2 polymer at -20°C may be accounted for if one assumes that a) the equilibrium between the trans-η^2 and cis-η^4 coordination is shifted towards the latter form at higher temperature, and b) that the activation energy for insertion of the cis-η^4 coordinated monomer is higher than for the monomer coordinated trans-η^2.

Other experimental data are needed to elucidate the chemo- and stereoselectivity of ZP and 4MP polymerization with $CpTiCl_3$-MAO, but according to the data so far available it seems that the mode of monomer coordination is the main responsible for their peculiar behavior.

Conclusions

The problem of chemoselectivity in diene polymerization is far from being fully clarified. Some simple cases, in which the chemoselectivity depends on the presence of substituents on C1 or C3 of the allyl group, are of simple interpretation. The cases in which the chemoselectivity depends on the coordination geometry of the catalytic species are difficult to interpret. The formation of 1,2-syndiotactic polybutadiene and of cis-1,4 isotactic polypentadiene with $(dmpe)_2CrCl_2$-MAO or $AlEt_3$-$Ti(OBu)_4$ are two interesting cases in this regard.

As to the stereoselectivity, the problem is fundamentally analogous in monoalkene and diene polymerization, in the sense that stereoselectivity is mainly dependent on non-bonded interactions at the active site. However, it is worth noting a significant difference between the polymerization of these two classes of monomers. In the iso- and syndiospecific polymerization of propene by metallocene catalysts, the cyclopentadienyl ligand has mainly the function to give a chiral orientation to the last-inserted unit, but has practically no influence on monomer orientation. The latter depends on non-bonded interactions between the incoming monomer and the last-inserted unit.

In diene polymerization, the ligand L may have a remarkable influence on orientation of the new monomer, as shown by the different results obtained respectively with $(dmpe)_2CrCl_2$-MAO and $(dmpm)_2CrCl_2$-MAO, and also by the effect, on stereoselectivity, of substituents on C2 of the monomer.

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