# Notes

## The Influence of Back-Biting Interaction on the Polymerization of Conjugated Dienes in the Presence of Ziegler−Natta Catalysts

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### Introduction

There is substantial evidence that in the polymerization of conjugated dienes by Ziegler−Natta catalysts the growing polymer chain (P) plays a role both in determining the position of insertion of the incoming monomer (M) (1,2 vs 1,4 polymerization) and the energetics of the propagation reaction.[1] An example is provided by isoprene and butadiene copolymerization in the presence of $CpTiCl_3$−MAO (Cp = cyclopentadyenil, MAO = methyl aluminoxane), which copolymerize almost randomly, despite the large difference that the two monomers exhibit in homopolymerization experiments.[2−4] Such behavior can only be rationalized by assuming that the rate of the whole propagation reaction is determined to a larger extent by P rather than by M.[5−7] Besides, in the copolymerization of butadiene and isoprene in the presence of $Co(acac)_2-H_2-AlEt_2Cl$ (acac = acetylacetonate, Et = ethylate), the chemoselectivity appears to be strongly affected by the nature of the ending units of R.[8−10] In fact, $Co(acac)_2-H_2-AlEt_2Cl$ yields polybutadiene containing more than 99% of 1,4 units,[8] whereas for polyisoprene[9] and poly-2,3-dimethyl-butadiene,[10] the amount of 1,4 units is less than 70%. However, when butadiene is copolymerized with isoprene, the butadiene units become partly 1,2 in a proportion that increases with the content of isoprene,[8] and correspondingly, the amount of cis 1,4 isoprene units increases with the butadiene content in the copolymer. Besides, in butadiene-2,3-dimethyl-butadiene copolymerizations, the 1,2 butadiene units are always preceded by 2,3-dimethyl-butadiene units.[10]

To better understand the role played by the growing polymer chain, we have studied, by means of ab initio calculations and orbital interaction diagrams, the active species for the homopolymerization and the copolymerization of butadiene and isoprene in the presence of $CpTiCl_3$−MAO. Since it is possible that in the presence of many Ziegler−Natta based catalysts P folds on itself, forming a bonding interaction with the metal center (back-biting interaction),[11−15] we have modeled P by considering both of the two ending repeating units.

Assuming that the active catalytic species is the organotitanium $[CpTi-P]^+$ cation, as suggested by several experimental evidence,[16−18] we have analyzed the nuclear configurations and the electronic distributions of the four $[CpTi(R)]^+$ active species involved in the copolymerization of butadiene-isoprene, namely those with R = octo-2,6-diene(1-yl) (**Bb**), R = 2,6-dimethyl-octo-2,6-diene(1-yl) (**Ii**), R = 6-methyl-octo-2,6-diene(1-yl) (**Bi**), and R = 2-methyl-octo-2,6-diene(1-yl) (**Ib**), Figure 1.

All of the allylic units of R are in the anti form, in accordance with the fact that both homo- and copolymerization of butadiene and isoprene give cis polymers[1−4] and that previous ab initio UHF/MP2 computations predicted that the anti form is slightly more stable than the syn one.[6]

As concerns the mutual orientation of the two ending units of R, there are four possible minimum energy conformations, according to whether the open side of the two monomeric units are oriented toward the Cp ring (exo orientation) or in the opposite direction (endo orientation). The term conformation could be misleading here, because, in the presence of the back-biting interaction, the carbon skeleton of R is rigidly fixed to Ti, so that interconversion between different conformers cannot occur by simply rotating about a single bond but requires at least the breakage of the back-biting interaction, (roughly 10 kcal/mol, see infra) and perhaps also the switch of the allylic coordination mode from the $\eta^3-\pi$ to the $\eta^1-\sigma$ one.

Among the four possible combinations, only two appears to be compatible with the observed stereotacticity of the products, namely those resulting from the endo/endo and the exo/exo insertion of M into the Ti−$R_1$ bond ($R_1$ = ending unit of P).[1,19] However, the exo/exo orientation is ruled out both because it gives a comparatively longer distance between the two carbons that have to form the new C−C bond[20] and because of the very high barrier predicted by DFT computations, which is 15 kcal/mol higher than its counterpart for the endo/endo insertion.[21] Thus, we have analyzed only the active species resulting from the endo/endo insertion.

Finally, to have an energy estimate of the back-biting interaction, we have also considered the active species $[CpTi(2\text{-buten(1-yl)-2butene})]^+$ (**Bb′**) with the 2-buten-(1-yl) ending unit in the syn conformation, since in that case the back-biting interaction is indeed not possible.[1]

All computations have been performed by GAMESS package,[22] using the ROHF approximation and the 3-21G split valence basis set.[23] No constraints have been imposed in the optimization runs. A few test computations, carried out using a much larger basis set, with a triple-$\zeta$ valence[24] on Ti and 6-31 g* for carbons and hydrogens,[25] testify to the reliability of the adopted computational methods. The importance of the electronic correlation has been tested by performing DFT computations with the nonlocal B3LYP exchange cor-

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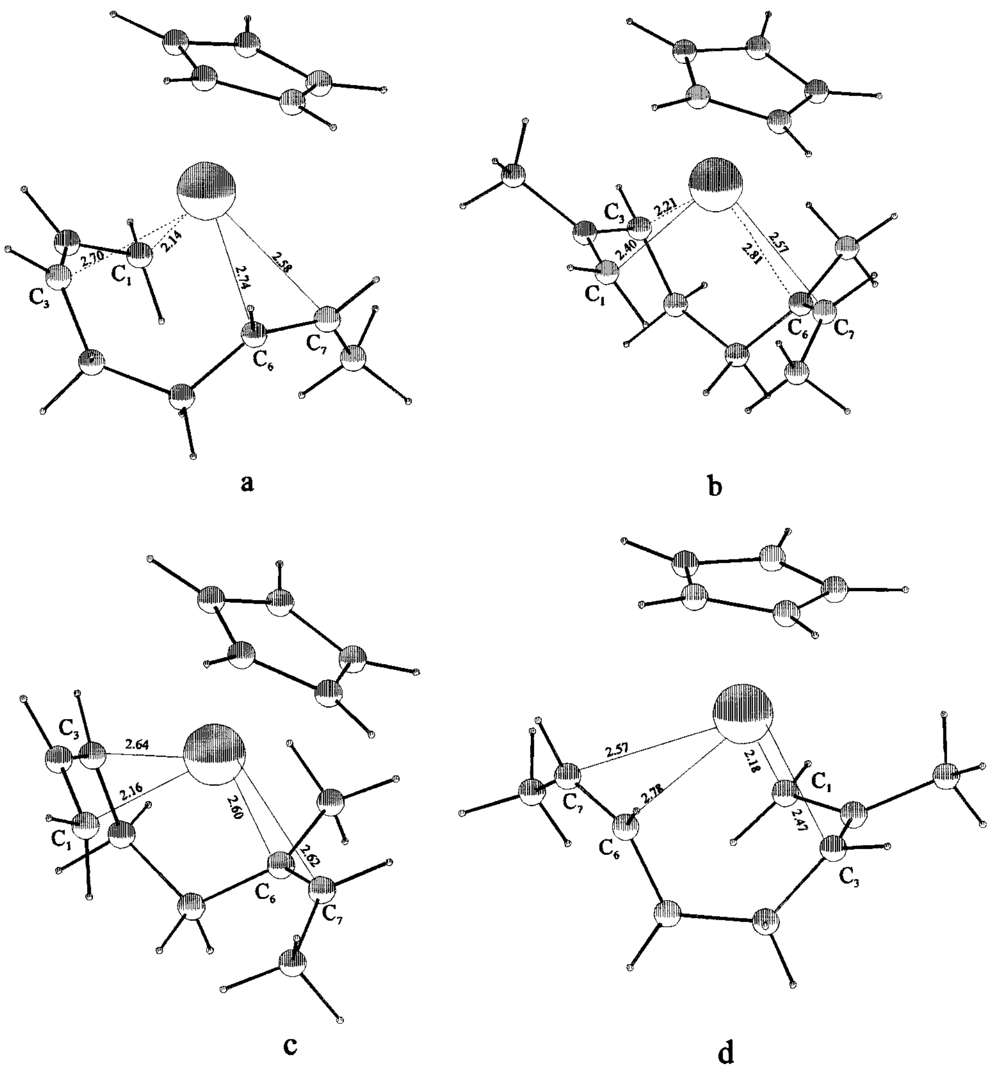

**Figure 1.** Optimized structures of the active species: **Bb** (a), **Ii** (b), **Bi** (c), and **Ib** (d), at ROHF/3-21 g level.

relation potential[26] and the land2z split valence basis.[27] DFT computations have been performed with the Gaussian94 package.[28]

## Results

The computed minimum energy geometries of the four active species are shown in Figure 1. All of them have been obtained starting from the transition state for the endo/endo insertion,[5] and optimizing all geometrical parameters until all gradients are less than $1 \times 10^{-4}$ hartree/bohr. For each minimum energy configuration, the Hessian matrix has only positive eigenvalues. In all the species examined, R forms two dative bonds with the metal center, being coordinated to Ti both with $R_1$ and with the penultimate unit ($R_2$). The distances between the sp carbons of $R_2$ and the metal center lie in the range 2.6−2.8 Å, and the $\pi$ orbitals are oriented in the ideal way to interact with the *d* orbitals of Ti, lying in the plane parallel to the cyclopentadienyl ring.

Selected geometrical parameters and relative energies are reported in Table 1. Inspection of Table 1 shows that for $R_1$ = butenyl the back-biting interaction causes a weakening of the Ti−butenyl bond, which is somewhat distorted from the usual $\eta^3-\pi$ coordination mode toward a $\eta^1-\sigma$ one. On the contrary, when $R_1$ is an isoprenyl unit, the Ti−$R_1$ bond is very similar to that expected for an ideal $\eta^3$ allylic coordination.

Comparison of the energies of **Bb** and **Bb′** (Table 1) shows that the energy gained from the back-biting interaction is roughly 14 kcal/mol. In the absence of back-biting, the $\pi$ allylic coordination of $R_1$ in **Bb′** is almost ideal,[29] very similar to that predicted by computations and $C_6-C_7$ bond distance (see Figure 1) is slightly shortened.

It is remarkable that, in the presence of the back-biting interaction, the coordination mode of $R_1$ is affected by the nature of the penultimate unit of P. The influence of $R_2$ is more clear-cut when $R_1$ is an isoprenylic unit: in that case, the methyl group of $R_2$ changes the way in which the $\eta^3-\eta^1$ distortion occurs. In fact, in **Ii**, the $R_1$ carbon nearest to Ti is $C_3$, ($Ti-C_3$ = 2.21 Å and $Ti-C_1$ = 2.40 Å), and correspondingly, the $C_1-C_2$ bond distance is shorter than that of $C_2-C_3$ (1.38 vs 1.44 Å). In **Ib**, the situation is reversed: $C_1$ is closer than $C_3$ to the metal center (2.18 vs 2.48 Å), whereas the $C_1-C_2$ distance is 1.45 Å and that of $C_2-C_3$ one is 1.38 Å.

The orbital interaction diagram, Figure 2, drawn using the fragment orbitals obtained with the well-known EHT method,[30] using Hoffmann's standard parameters, can explain the above finding. There are three important electronic interactions associated with the back-biting interaction: an attractive one (**2**), which involves the $\pi$ bond of $R_2$ and the $\delta$ orbitals of Ti, and two repulsive ones, **1** and **1′**, which are between the

**Table 1. Computed Geometrical Parameters of Minimum Energy Configurations for Species Bb, Ii, Bi, Ib, Bb**[a−c]

| | **Bb** | | | | **Ii** | | **Bi** | **Ib** | **Bb′** |
|---|---|---|---|---|---|---|---|---|---|
| | 3-21G | TZV[d] | TZV*[e] | DFT | 3-21G | TZV[d] | 3-21G | 3-21G | 3-21G |
| $C_1$−Ti | 2.14 | 2.16 | 2.18 | 2.14 | 2.40 | 2.45 | 2.16 | 2.18 | 2.25 |
| $C_2$−Ti | 2.37 | 2.39 | 2.37 | 2.32 | 2.37 | 2.41 | 2.36 | 2.36 | 2.35 |
| $C_3$−Ti | 2.70 | 2.75 | 2.70 | 2.64 | 2.21 | 2.23 | 2.64 | 2.47 | 2.26 |
| $C_4$−Ti | 3.34 | 3.45 | 3.42 | 3.36 | 3.14 | 3.19 | 3.38 | 3.25 | 2.64 |
| $C_6$−Ti | 2.74 | 2.75 | 2.78 | 2.55 | 2.81 | 2.71 | 2.60 | 2.78 | 4.68 |
| $C_7$−Ti | 2.58 | 2.65 | 2.65 | 2.64 | 2.57 | 2.87 | 2.62 | 2.57 | 5.82 |
| $C_{Cp}$−Ti[g] | 2.42 | 2.43 | 2.42 | 2.40 | 2.42 | 2.43 | 2.41 | 2.42 | 2.39 |
| $C_1$−$C_2$ | 1.47 | 1.46 | 1.46 | 1.46 | 1.38 | 1.38 | 1.46 | 1.45 | 1.42 |
| $C_2$−$C_3$ | 1.36 | 1.36 | 1.36 | 1.40 | 1.44 | 1.45 | 1.36 | 1.38 | 1.39 |
| $C_3$−$C_4$ | 1.52 | 1.52 | 1.52 | 1.53 | 1.55 | 1.55 | 1.53 | 1.54 | 1.54 |
| $C_6$−$C_7$ | 1.34 | 1.35 | 1.34 | 1.37 | 1.34 | 1.35 | 1.34 | 1.34 | 1.32 |
| $C_1$−$C_2$−$C_3$ | 122.7 | 128.9 | 129.2 | 127.2 | 117.8 | 120.7 | 126.2 | 122.2 | 120.3 |
| $C_2$−$C_3$−$C_4$ | 126.5 | 131.8 | 131.8 | 130.8 | 122.3 | 122.9 | 128.7 | 128.6 | 122.0 |

[a] ROHF calculations. [b] Bond distances in angstroms, angles in degrees, energies in atomic units. [c] Atom numbering is shown in Figure 1. [d] TZV= Triple $\zeta$ valence on Ti, 6-31G on C, H. [e] TZV*= Triple $\zeta$ valence on Ti, 6-31G* on C,H. [f] Energies: **Bb** −1344.1113 (3-21G), −1350.7836 (TZV), −1351.0632 (TZV*), 563.9911 (DFT); **Ii** −1421.7586 (3-21G), −1428.8246 (TZV); **Bi** −1382.9329; **Ib** −1382.9361; **Bb′** −1344.0886. [g] Average distance.

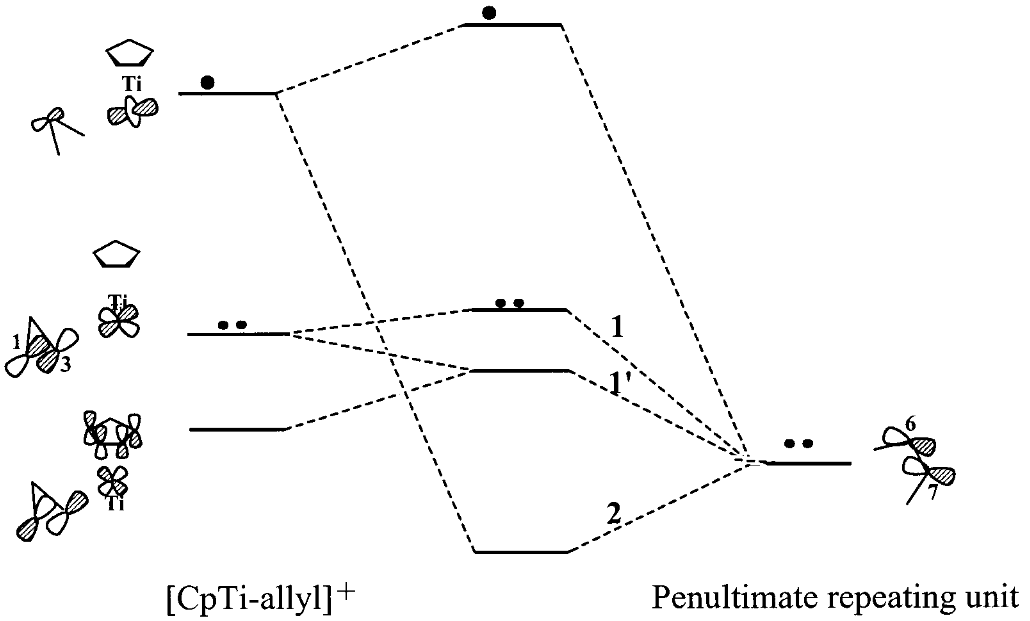

**Figure 2.** Orbital interaction diagram performed on the equilibrium geometry of **Bb**.

filled $\pi$ orbitals of $R_1$ and $R_2$. The strongest electronic repulsion, **1′**, mainly involves the $C_3$ and $C_6$ carbons and can be minimized by increasing the $C_3$−Ti bond distance and decreasing that of Ti−$C_1$. The methyl group at $C_6$ lowers the contribution of $C_6$ to the $\pi$ molecular orbital (MO) of $R_2$, weakening the electronic repulsion **1′**. Therefore, in **Ii**, $C_3$ is closer to Ti than to $C_1$ to minimize the repulsion (**1**) between $C_1$ and $C_7$ carbons, whereas in **Ib** the converse is found.

The influence of the $R_2$ substituents on repulsion **1′** is confirmed by the comparison of the equilibrium geometries of **Bb** and **Bi**: a methyl group at $C_6$ decreases **1′**, leading to a shorter Ti−$C_3$ bond distance (2.64 vs 2.70 Å).

## Discussion and Conclusion

The results presented so far show that the back-biting interaction significantly stabilizes the active species for the polymerization of conjugated oleofins in the presence of $CpTiCl_3$−MAO, even though it causes the distortion of the $\pi$ allylic coordination of $R_1$ because of the electronic repulsion sketched in Figure 2. There are several factors which play a part in determining the way in which the $\eta^3 \rightarrow \eta^1$ rearrangement occurs: usually, the most substituted double bond and the less substituted carbanion is formed, but steric hindrances and electronic repulsions between the filled orbitals of $R_1$ and $R_2$ may also play a role, which could become significant when the other factors do not strongly favor the formation of the Ti−C $\sigma$ bond at one carbon over the other. For $R_1$ = butenyl, the $\eta^3 \rightarrow \eta^1$ distortion always occurs with a shortening of the Ti−$C_1$ bond distance, but for an isoprenylic ending unit, the presence of a methyl group on $C_2$ makes the formation of the $C_1$−$C_2$ double bond less disfavored so that the two possible $\eta^1$ configurations become close in energy. In that case, computations suggest that the back-biting interaction can be important. In fact, the $R_2$ substituents can affect the strength of the electronic repulsion **1′**, reversing the direction of the $\eta^3$−$\eta^1$ rearrangement: if $R_2$ bears electron donor substituents at $C_6$, the probability that the $\eta^3$−$\eta^1$ switch occurs with a shortening of the Ti−$C_3$ distance increases.

In the presence of a coordinated monomer, the situation is of course more complicated. For the $CpTiCl_3$−MAO catalytic system, the back-biting interaction is probably lost[5] before M insertion, and therefore, its influence on the formation of the Ti−C $\sigma$ bond disappears. However, it is worth noting that, in polymerization runs performed at room temperature, the percentage of 1,2 unit is higher in polyisoprene than in polybutadiene,[4a] confirming that the presence of a methyl substituent on the $C_6$ of $R_2$ increases the yield of 1,2 units.

In the presence of different catalysts, the back-biting could be retained upon coordination of the monomer (see, for instance, Tobisch et al. and references therein), and then it could play a more important role in determining the product of the polymerization reactions. That could be the case of $Co(acac)_2-H_2-AlEt_2Cl$,[8−10] whose puzzling behavior has been cited before. In fact, the findings that the amount of 1,4 units increases with increasing amount of butadiene and that, in the butadiene and 2,3-dimethyl-butadiene copolymerization, the 1,2 butenylic units are always preceded by the 2,3-dimethyl-butenylic are evidence of the effect of the back-biting interaction in determining the reactivity of the last repeating unit. Of course, transfer of results from one catalytic system to another is not straightforward and requires much caution, but in light of the results discussed here, the possibility that the back-biting interaction can play a role in determining the observed chemoselectivity for that catalytic system is worth investigating.

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