Mechanism of Stereocontrol in Methyl Methacrylate Polymerization Promoted by C_1-Symmetric Metallocenes

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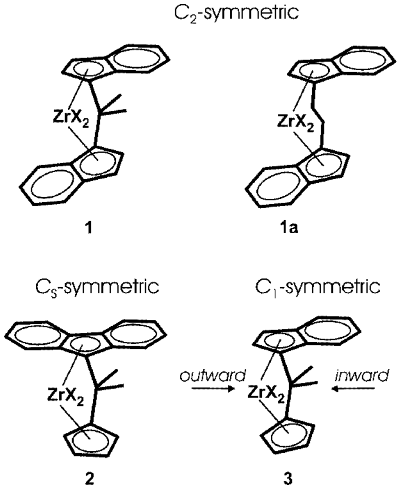
ABSTRACT: The mechanism of stereoselectivity in methyl methacrylate (MMA) monometallic polymerization promoted by the C_1-symmetric *ansa*-$Me_2C(Cp)(Ind)Zr$-based zirconocene, presenting two diastereotopic coordination sites, was investigated within density functional theory. At variance from the case of propene polymerization, our results suggest that MMA addition is stereoselective when the growing chain is in the more hindered as well as in the more open diastereotopic coordination site. In both cases the same enantioface of the enolate bond of the ester enolate growing chain is selected, although selectivity is higher when the growing chain is in the more hindered diastereotopic coordination site. Further, there is no substantial energy difference between these two situations, which indicates that the moderate isotacticity of the produced PMMA is consistent with an almost regular chain-migratory mechanism. The different stereoselectivity of the two diastereotopic sites is due to different steric interaction between the growing chain (chain effect) or MMA (monomer effect) with the indenyl ligand. This decomposition of stereoselectivity into chain and monomer effects is used to reinvestigate the stereoselectivity of strictly related C_2- and C_s-symmetric zirconocenes.

Introduction

Group 4 *ansa*-metallocenes have been thoroughly investigated during the past decades for stereoselective 1-olefins polymerization, and combined experimental/theoretical studies allowed to achieve an incredible knowledge of these systems.[1,2] This understanding definitely contributed to accelerate the pace at which these systems have been developed and used in the synthesis of new polymeric materials, with beneficial consequences in terms of investments, atom economy, waste of material, and time.[3] Recently, the same metallocenes have been employed as catalysts in the stereoselective polymerization of methyl methacrylate (MMA),[4–12] and it is tempting to extend the knowledge acquired on propene polymerization to MMA polymerization. Indeed, some aspects of MMA polymerization, for example that the active species is monometallic and cationic for both monomers,[1,2,11] show meaningful analogies with 1-olefins polymerization, but the stereoselectivity of a given metallocene in MMA polymerization cannot be easily rationalized using concepts developed for propene polymerization. Nevertheless, for the sake of completeness we recall that in the case of catalytic systems including neutral zirconocenes, which are not investigated in this work, a bimetallic active species should be considered.[5,13]

Chart 1



For example, C_2-symmetric *ansa*-metallocenes, such as the *rac*-$C_2H_4(1\text{-Ind})_2Zr$-based systems, **1a** of Chart 1, produce both highly isotactic PP[1,2,14–18] and PMMA[5–7,11] (iPP %*mm* = 95 and iPMMA %*mm* 95, at room temperature), and the presence of isolated *rr* stereomistakes is consistent with an enantiomorphic-site stereocontrol. Similarly, C_s-symmetric *ansa*-metallocenes, such as the $Me_2C(Cp)(9\text{-Flu})Zr$-based systems, **2** of Chart 1, produce both syndiotactic PP[1,2,14,19,20] and PMMA[12] (sPP %*rr* = 90 and sPMMA %*rr* = 64, at room temperature). However, analysis of the produced polymers shows the substantial presence of *mm* stereomistakes, consistent with enantiomorphic-site stereocontrol, only in the case of sPP. In fact, in the case of sPMMA the majority of the stereomistakes correspond to isolated *m* diads, which is surprisingly consistent with chain-end stereocontrol, although very recently it has been reported that highly stereoregular sPPMA (%*rr* = 95, at room temperature) presenting *mm* stereomistakes typical of enantiomorphic-site stereocontrol can be obtained with $Ph_2C(Cp)(9\text{-Flu})Zr$-based systems.[21] Finally, the more complicated C_1-symmetric metallocenes, such as the $Me_2C(Cp)(1\text{-Ind})Zr$-based systems, **3** of Chart 1, which lead to a PP whose tacticity strongly depends on the polymerization conditions,[2,22–24] lead to substantially stereoregular iPMMA (%*mm* = 84) via enantiomorphic-site stereocontrol in a large range of polymerization conditions.[9] These experimental facts indicate that 1-olefin and acrylate polymerizations have to be compared with caution.

The mechanism of chain growth operative with olefins involves displacement of the counterion by a coordinating olefin, followed by olefin insertion into the M−(growing chain) bond through a *cis* opening of the monomer double bond (see Scheme 1a).[25–27] Differently, the mechanism of chain growth operative in MMA polymerization involves displacement of a coordinated ester group of the growing chain by a coordinating MMA molecule, followed by MMA addition via an ester enolate intermediate,[13,28] analogous to that proposed for MMA polymerization initiated by neutral lanthanocenes (see Scheme 1b).[29,30] Further, while a chain-migratory mechanism is well established in 1-olefins polymerization, it is unclear whether a chain-

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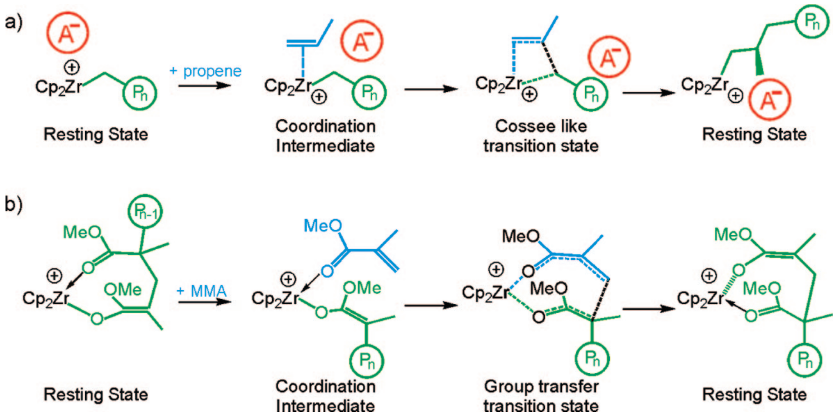
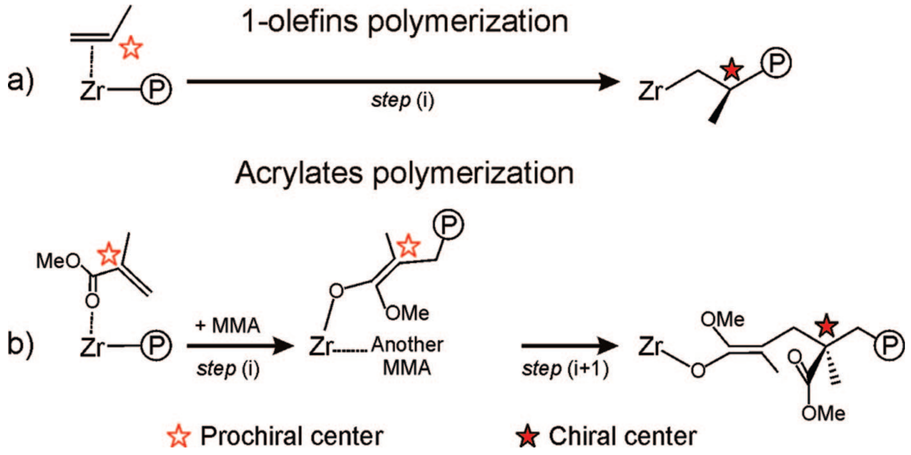
Scheme 1



Scheme 2



migratory or a chain-retention mechanism is operative with acrylates polymerization.[31]

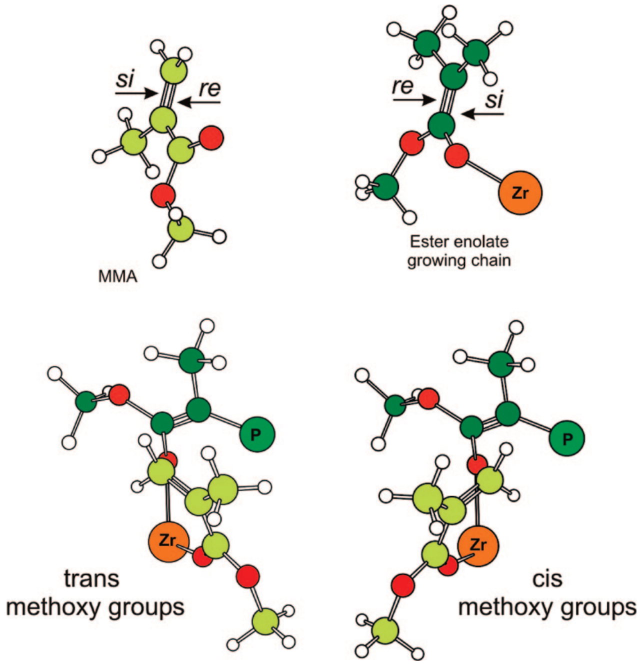
As stereoselectivity is concerned, in a previous paper we investigated the origin of stereoselectivity in the chain growth step of MMA polymerization with the C_2-symmetric system **1** and the C_s-symmetric system **2**.[32] We remarked that MMA is prochiral in the same sense of propene, since it has one prochiral C atom. However, in propene polymerization the prochiral sp^2 C atom of the monomer becomes a chiral sp^3 C atom immediately after monomer insertion into the M−(growing chain) bond, and thus stereoselectivity is connected with a selection of which enantioface of the monomer reacts preferentially (see Scheme 2a). Differently, the prochiral sp^2 C atom of MMA remains prochiral after MMA addition, since it is "transformed" into the prochiral sp^2 C atom of the ester enolate growing chain (see Scheme 2b). In short, the ester enolate growing chain is prochiral like propene and MMA, and during MMA addition it is the prochiral sp^2 C atom of the ester enolate growing chain that becomes a chiral sp^3 C atom. Thus, in MMA polymerization stereoselectivity is connected with a selection of which enantioface of the ester enolate growing chain reacts preferentially (see Scheme 2b).

Besides these differences, in both propene and MMA polymerization with C_2- and C_s-symmetric metallocenes stereoselectivity originates mainly from steric interactions between the metallocene skeleton and the growing chain. However, in propene polymerization it is well accepted that the growing chain, chirally oriented by the chiral site, selects between the two enantiofaces of the incoming propene molecule,[33–36] while we suggested that in MMA polymerization the chirally oriented growing chain autoselects between its own two enantiofaces.[32] On the basis of this mechanism, C_2-symmetric systems, such as **1**, are necessarily isospecific, whereas C_s-symmetric systems, such as **2**, can yield sPMMA only within a chain-migratory mechanism. We recall that the isolated *m* diads of sPMMA from **2**, consistent with chain-end stereocontrol, are also consistent with enantiomorphic site stereocontrol and site epimerization after a stereomistake.[31,37,38]

To get further insights on the origin of stereoselectivity in MMA polymerization, we study here MMA polymerization with the C_1-symmetric zirconocene **3**. In a previous study it was proposed that MMA addition takes place only with the ester enolate growing chain residing in the more open coordination site (hereafter defined as outward site, see Chart 1), with the MMA molecule coordinated in the more hindered coordination site (hereafter defined as inward site).[9,39] MMA addition with the growing chain and the monomer in the inward and outward coordination sites, respectively, being disfavored by steric interactions between the growing chain and the ligand. Of course, in the framework of an almost regular chain migration, this mechanism requires that after each chain growth step the steric pressure of the ligand on the growing chain induces a site epimerization reaction.

In this work we offer an alternative perspective to rationalize the stereoselectivity of the C_1-symmetric systems. Indeed, we anticipate that the group transfer reaction can take place with the ester enolate growing chain in both the inward and the outward coordination positions. Both situations are stereoselective, and the same enantioface of the growing chain is favored, although the geometry with the growing chain in the inward coordination position is more stereoselective. Thus, our results suggest that the stereoregularity of PMMA obtained with C_1-symmetric metallocenes can be also rationalized within a prevalent chain-migratory mechanism.

Scheme 3



Models and Computational Details

Models. On the basis of the nomenclature adopted in the case of propene polymerization, we define the two enantiofaces of the MMA and of the enolate bond of the growing chain *re* and *si* (see Scheme 3).[32] Further, we distinct the relative orientation of the −OMe groups of MMA and of the ester enolate growing chain in the transition states by using the trans and cis nomenclature. Trans indicates that the −OMe groups of the monomer and of the growing chain are located on opposite sides of the metallocene equatorial belt, while cis indicates that these two groups are on the same side.[32] To discriminate between diastereotopic situations in which the coordination positions of the growing chain and of the MMA molecule are exchanged, in all the geometries we specify the coordination position of the growing chain, and which enantioface of the enolate bond is facing the MMA molecule. Thus, we will use labels such as out-*re*/trans or out-*si*/trans to specify the transition states with the growing chain in the outward[40] coordination position, with a trans orientation of the methoxy groups of the monomer and the chain, and with the *re* and *si* enantiofaces of the enolate bond of the growing chain facing the MMA molecule, respectively. Labels such as in-*re*/cis and in-*si*/trans are used similarly.

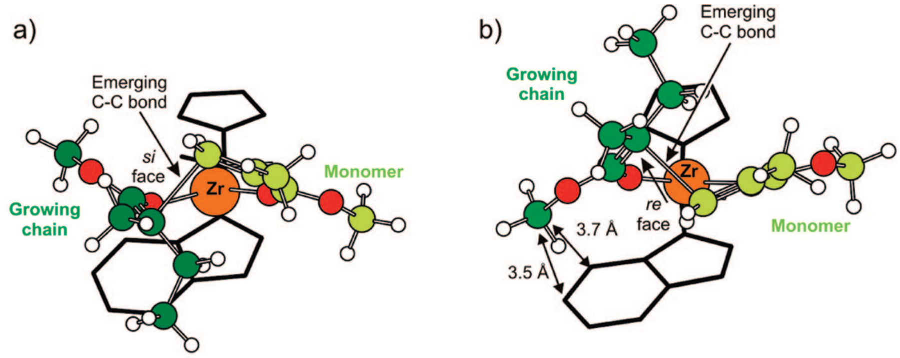
Computational Details. The Amsterdam Density Functional (ADF) program was used to obtain all the results discussed herein.[41,42] The electronic configuration of the molecular systems was described by a triple-ζ STO basis set on zirconium for 4s, 4p, 4d, 5s, 5p (ADF basis set TZV).[41] Triple-ζ STO basis sets, augmented by one polarization function, were used for C and O (2s, 2p) and H (ADF basis sets TZVP).[41] The inner shells on zirconium (including 3d), carbon and oxygen (1s), were treated within the frozen core approximation. Energies and geometries were evaluated using the local exchange-correlation potential by Vosko et al.,[43] augmented in a self-consistent manner with Becke's[44] exchange gradient correction and Perdew's[45,46] correlation gradient correction.

Both the inward and outward transition states were approached from the transition states we previously reported for the C_{2v}-symmetric $Me_2C(Cp)_2Zr$-based system, by appropriate modification of the metallocene skeleton. These approximate transition states were first relaxed by keeping the forming C−C bond fixed. This partial geometry optimization was required to relax steric stress introduced by modification of the metallocene skeleton. Full transition state searches were started from these preoptimized geometries. As in similar papers,[31] transition states were not validated by vibrational analysis due to the extreme computational cost. All geometries were localized in the gas phase. However, since MMA polymerization is usually performed in a rather polar solvent, such as CH_2Cl_2, we performed single-point energy calculations on the final geometries to take into account solvent effects. The ADF implementation of the conductor-like screening model (COSMO)[47,48] was used. A dielectric constant of 8.9 and a solvent radius of 2.94 Å were used to represent CH_2Cl_2 as the solvent. The following radii, in angstroms, were used for the atoms: H 1.16, C 2.00, O 1.50, and Zr 2.40. All the reported energies include solvent effects.

Results and Discussion

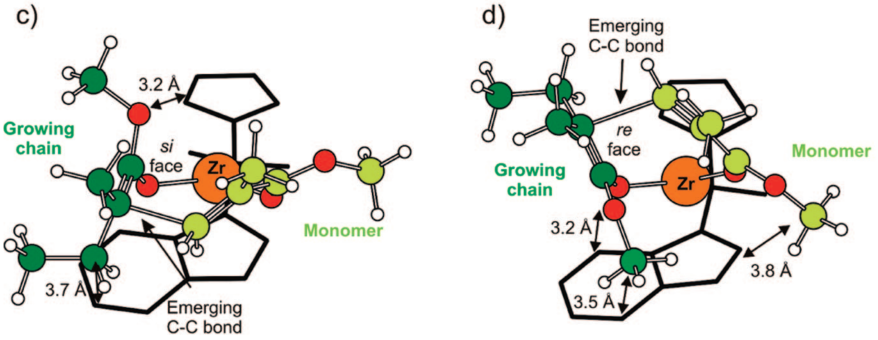
MMA Polymerization with the C_1-Symmetric Zirconocene 3. The four transition states lowest in energy for MMA addition with the growing chain in the inward coordination position are reported in Figure 1. Two of them (in-*re*/cis and in-*si*/cis, see Figure 1c,d) present a relative cis orientation of the methoxy groups of the growing chain and of the monomer and, in agreement with previous calculations,[32] are of quite higher energy and thus are not discussed any further. The other two transition states (in-*re*/trans and in-*si*/trans, see Figure 1a,b) present a relative trans orientation of the methoxy groups of the growing chain and of the monomer and, in agreement with previous calculations,[32] are quite more stable. The lowest in energy is the in-*si*/trans transition state of Figure 1a, which presents the methoxy group of the growing chain in an open part of space, that is, away from the 6-membered ring of the indenyl ligand. This chiral orientation of the growing chain automatically places the *si* enantioface of the ester enolate growing chain toward the monomer. The other transition state with a trans disposition of the growing chain and of the monomer, in-*re*/trans of Figure 1b, is disfavored by the steric interactions evidenced by the short distances between the methoxy group of the growing chain and the 6-membered ring of the indenyl group. The transition state in-*re*/trans, which is 2.7 kcal/mol higher in energy relative to transition state in-*si*/trans, corresponds to a chiral orientation of the growing chain that automatically places the *re* enantioface of the ester enolate growing chain toward the monomer. In short, when the growing chain is in the most hindered inward coordination site, the chain growth step is stereoselective ($\Delta E_{\text{stereo}} = 2.7$ kcal/mol),[49] and for a metallocene with a (*S*)-coordinated indenyl ligand the *si* enantioface of the ester enolate growing chain reacts preferentially.

We now focus on the four transition states lowest in energy for MMA addition with the growing chain in the outward coordination position (see Figure 2). Again, the two transition states with a relative cis orientation of the methoxy groups of the growing chain and of the monomer (out-*si*/cis and out-*re*/cis, see Figure 2c,d) are of quite higher energy and thus are not discussed any further. The transition state lowest in energy is out-*si*/trans of Figure 2a, which presents the methoxy group of the monomer in an open part of space, that is, away from the 6-membered ring of the indenyl ligand. This chiral orientation of the monomer automatically selects the *si* enantioface of the enolate bond, in order to achieve the preferential trans disposition of the growing chain and of the monomer. The other transition state with a trans disposition of the growing chain and of the monomer, out-*re*/trans of Figure 2b, is disfavored by the steric interactions evidenced by the short distances between the methoxy group of the monomer and the 6-membered ring of the indenyl group. The transition state out-*re*/trans is 1.0 kcal/mol higher in energy relative to transition state



in-si/*trans; E* = 0.0

in-re/*trans; E* = 2.7



in-*si*/*cis; E* = 3.8

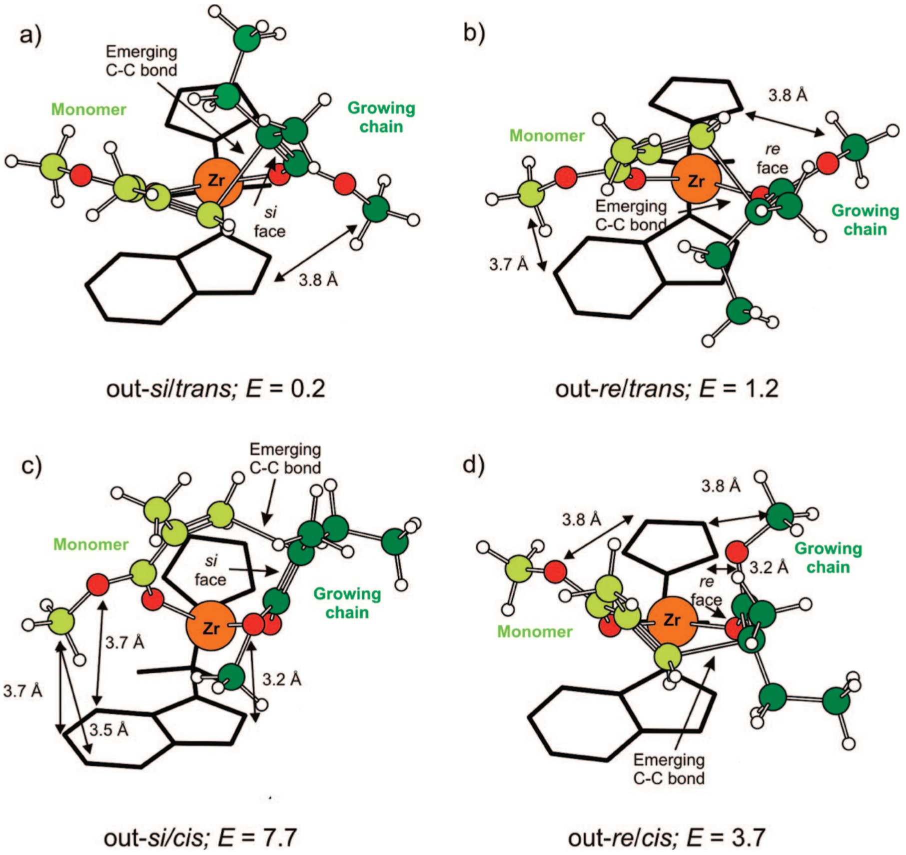
in-*re*/*cis; E* = 6.3

Figure 1. Transition states for MMA addition with the growing chain in the inward coordinated position of the C_1-symmetric $Me_2C(Cp)(Ind)Zr$ zirconocene with a (*S*)-coordinated indenyl ligand. Near to each structure is reported the energy, in kcal/mol, relative to the most stable transition state in-*si*/trans.

out-*si*/trans and corresponds to a chiral orientation of the monomer that automatically selects the *re* enantioface of the enolate bond in order to have a trans disposition of the growing chain and of the monomer. In short, also with the monomer in the most hindered inward coordination site the chain growth step is stereoselective ($\Delta E_{\mathrm{stereo}} = 1.0$ kcal/mol), and for a metallocene with a (*S*)-coordinated indenyl ligand the *si* enantioface of the ester enolate growing chain reacts preferentially.

Comparison of the results reported in Figures 1 and 2 indicates that both for the inward and outward coordinated growing chains the *si* enantioface of the enolate bond reacts preferentially. This rationalizes formation of iPMMA in the framework of both almost regular chain-migratory or chain-retention mechanisms. Nevertheless, it is worth noting that the stereoselectivity of MMA addition with the growing chain in the inward coordination position, $\Delta E_{\mathrm{stereo}} = 2.7$ kcal/mol, is higher than that of MMA addition with the growing chain in the outward coordination position, $\Delta E_{\mathrm{stereo}} = 1.0$ kcal/mol. Further, there is no substantial energy difference between the most favored *si*/trans transition states, since the in-*si*/trans geometry is only 0.2 kcal/mol more stable than the out-*si*/trans geometry, which implies that even in the case of a chain-migratory mechanism there is no driving force for a site-epimerization (or growing chain back-skip) reaction.[50] Thus, in the framework of an almost regular chain-migratory mechanism, the resulting iPMMA should present a homogeneous microstructure with intermediate stereoregularity (~65% *mmmm,* calculated at 25 °C from a regular alternance of $\Delta E_{\mathrm{Stereo}} = 1.0$ and 2.7 kcal/mol), which is in qualitative agreement with the experimental value of 74% *mmmm* a 30 °C. Differently, in the framework of an almost regular site-retention mechanism, the resulting iPMMA should present a microstructure consistent with stereoblocks of different stereoregularity: higher when the growing chain is in the inward coordination position (~95% *mmmm*, calculated at 25 °C from a $\Delta E_{\mathrm{Stereo}} = 2.7$ kcal/mol); lower when the growing chain is in the outward coordination position (~43% *mmmm*, calculated at 25 °C from a $\Delta E_{\mathrm{Stereo}} = 1.0$ kcal/mol). Of course, any kind of site-isomerization reaction would switch the stereoselectivity of MMA addition from higher to lower or vice versa.[51]

To have further support for a monomer effect on stereoselectivity of MMA polymerization when the monomer is in the inward site, we investigated the stereoselectivity of propene polymerization with the C_1-symmetric metallocene **3**,[52] and we focused on the two transition states corresponding to inward propene coordination. As expected, when the growing chain is in the outward coordination position, there is no meaningful energy difference between the two transition states (0.4 kcal/mol only). Comparison between the two disfavored transition state geometries with the propene (Figure 3a) and MMA (Figure 3b) molecule in the inward coordination site clearly indicates that in the compact four-centers transition state for propene polymerization the methyl group of the monomer is pointed away from the metal and away from the indenyl skeleton. That is, the propene molecule does not interact significantly with the metallocene. On the contrary, in the bulkier eight-centers transition state for MMA polymerization, the methoxy group of the monomer is pointed inside the metallocene belt, and in the disfavored out-*re*/trans transition state it repulsively interacts with the six-membered ring of the indenyl ligand. In summary, the stereoselectivity of both propene and MMA polymerizations with zirconocenes is mainly determined by severe steric interaction between the metallocene skeleton and the growing chain (strong chain effect). However, in the case of MMA polymerization some steric interactions between the monomer and the ligand play a role in determining stereoselectivity (weak monomer effect).



out-*si*/*trans; E* = 0.2 out-*re*/*trans; E* = 1.2

out-*si*/*cis; E* = 7.7 out-*re*/*cis; E* = 3.7

Figure 2. Transition states for MMA addition with the growing chain in the outward coordinated position of the C_1-symmetric $Me_2C(Cp)(Ind)Zr$ zirconocene with a (*S*)-coordinated indenyl ligand. Near to each structure is reported the energy, in kcal/mol, relative to the most stable transition state in-*si/*trans of Figure 1a.

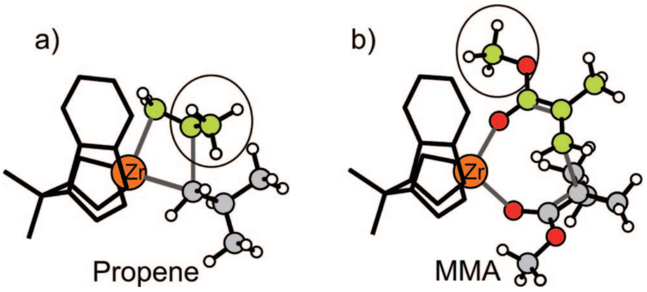


Figure 3. Transition states for the chain growth reaction involving a propene (a) and a MMA molecule (b) in the inward coordination position of the C_1-symmetric $Me_2C(Cp)(Ind)Zr$ zirconocene.

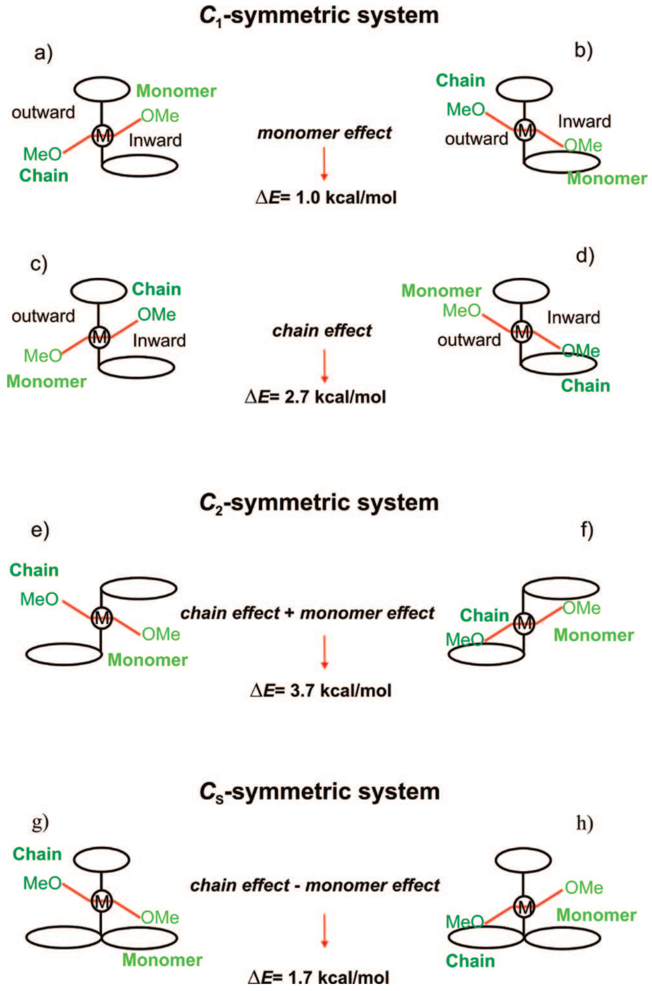
Stereoselectivity in MMA Polymerization with C_2- and C_s-Symmetric Zirconocenes. . In this section the mechanism of stereocontrol in MMA polymerization catalyzed by the C_2- and C_s-symmetric zirconocenes **1** and **2** is revised in light of the results achieved with the C_1-symmetric zirconocene **3**. In fact, the $\Delta E_{\mathrm{Stereo}}$ calculated with the growing chain or the monomer in the inward coordination position, that is 2.7 and 1.0 kcal/mol, respectively, can be assumed as a rough estimate of the amount of steric interaction between the growing chain (strong chain effect) or the monomer (weak monomer effect) and the 6-membered ring of the ligand in the unfavored in-*si/*trans and out-*si*/trans transition states, respectively. This assumption is based on the fact that substantial steric interactions in the unfavored transition states occur with the 6-membered ring only, since steric interaction on the outward side of the metallocene can be assumed to be substantially the same in both the favored and unfavored transition states, due to the absence of any local asymmetry in the outward side of the metallocene.

On this basis, the $\Delta E_{\mathrm{Stereo}}$ of the C_2-symmetric zirconocene **1** can be empirically estimated as the additive contribution of a chain effect of 2.7 kcal/mol and of a monomer effect of 1.0 kcal/mol, for a total of 3.7 kcal/mol. The chain and the monomer effects are additive because in the unfavored transition state both the monomer and the growing chain sterically interact with different 6-membered rings of the C_2-symmetric zirconocene (see Scheme 4f). In our previous study we reported a $\Delta E_{\mathrm{Stereo}}$ of 5.3 kcal/mol for **1**, which is quite higher than the value of 3.7 kcal/mol predicted on the basis of the empirical rule just described. For this reason we endorsed in a series of calculations to check for any mistake in our previous calculations,[32] and indeed we found a better conformation of the growing chain in the unfavored transition state, which reduces the $\Delta E_{\mathrm{Stereo}}$ of **1** from 5.3 to 4.2 kcal/mol, in better agreement with the 91% *mmmm* experimentally observed[5–7,11] and in qualitative agreement with the value obtained with the empirical rule.

On the other hand, the $\Delta E_{\mathrm{Stereo}}$ of the C_s-symmetric zirconocene **2** can be empirically estimated as the result of a chain effect of 2.7 kcal/mol that is counterbalanced by an opposite monomer effect of 1.0 kcal/mol, for a total of 1.7 kcal/mol. The chain and the monomer effects are in opposite directions because in the favored transition state the monomer sterically interacts with a 6-membered rings of the C_s-symmetric zirconocene (see Scheme 4g), while in the unfavored transition state it is the growing chain that sterically interacts with a 6-membered rings of the C_s-symmetric zirconocene. The value predicted with the empirical rule is in good agreement with the 64% *rr* experimentally observed[32] and with the $\Delta E_{\mathrm{Stereo}}$ of 1.9 kcal/mol for **2** we previously reported.[32]

In conclusion, the stereoselectivity of MMA polymerization with group 4 metallocenes is the result of steric interactions between both the growing chain (strong chain effect) and the

Scheme 4



monomer (weak monomer effect) with the metallocene. Thus, at variance from propene polymerization, our results suggest that to rationalize in detail the relationship between the structure of a give *ansa*-metallocene and the microstructure of the produced PMMA, beside fundamental steric interaction between the growing chain and the metallocene, steric interactions between the monomer and the ligand have to be considered. In the case of C_2-symmetric zirconocenes this interaction increases stereoselectivity of MMA polymerization, whereas in the case of C_s-symmetric zirconocenes it decreases stereoselectivity.

Conclusions

The origin of isospecificity in MMA polymerization promoted by the C_1-symmetric *ansa*-$Me_2C(Cp)(Ind)Zr$ zirconocene was studied by means of DFT calculations. Our results indicate that MMA addition with the growing chain both in the more hindered inward and in the more open outward site selects between the two enantiofaces of the enolate bond of the ester enolate growing chain. In both cases the same enantioface of the enolate bond are selected, which explains the isotacticity of the produced PMMA, and for a (*S*)-coordinated indenyl group the *si* enantioface of the enolate bond reacts preferentially. When the growing chain is in the hindered site selectivity is higher ($\Delta E_{\text{Stereo}} = 2.7$ kcal/mol) and originates mainly from steric interactions between the methoxy group of the growing chain and the indenyl ligand (chain effect), while selectivity is lower ($\Delta E_{\text{Stereo}} = 1.0$ kcal/mol) and originates mainly from steric interactions between the methoxy group of the monomer and the indenyl ligand when the growing chain is in the outward site (monomer effect). Finally, there is no substantial energy difference, 0.2 kcal/mol only, between the best transition states with the growing chain in the inward or in the outward site, which means that there is no driving force that would push the growing chain always in the same coordination site. As a consequence, an almost regular chain-migratory polymerization mechanism satisfactorily explains the moderate isospecificity experimentally observed in PMMA produced with the C_1-symmetric $Me_2C(Cp)(Ind)Zr$-based system.

In light of these results, we reinvestigated the stereoselectivity of MMA polymerization promoted by the C_2- and C_s-symmetric systems to elucidate the role of the chain and of the monomer effect in determining the overall stereoselectivity. Our results suggests that the stereoselectivity induced by the C_2-symmetric $Me_2C(1\text{-}Ind)_2Zr$-based system is higher that that induced by the strictly related C_s-symmetric $Me_2C(Cp)(9\text{-}Flu)Zr$-based system because in the former the chain and the monomer effects synergically contribute to select the same enantioface of the enolate bond, whereas in the latter the two effects oppose each other.

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Supporting Information Available: Cartesian coordinates and energy of all the structures considered. This material is available free of charge via the Internet at http://pubs.acs.org.

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(49) $\Delta E_{\mathrm{Stereo}}$ is the energy difference between the lowest in energy transition states leading to opposite configurations of the chiral C atom in the polymer.
(50) To verify for a possible preference of the polymer chain for the open outward site, we compared the situations corresponding to coordination of the chain in the outward and in the inward sites of **3** in the absence of a monomer molecule. The geometry corresponding to the growing chain in the outward site is preferred by only 0.4 kcal/mol. This further indicates that there is no driving force for a site epimerization (or growing chain back-skip) reaction.
(51) As final remark, we note very recently it has been reported the synthesis of highly stereoregular sPPMA presenting *mm* stereomistakes typical of enantiomorphic-site stereocontrol, which supports the an almost regular chain-migratory mechanism (see ref 21).
(52) In the literature (see ref 2) only MM calculations on the two TSs of propene polymerization with the C_1-symmetric system **3** in the propene polymerization are reported.

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