Group Transfer Polymerizations of Acrylates Catalyzed by Mononuclear Early d-Block and f-Block Metallocenes: A DFT Study

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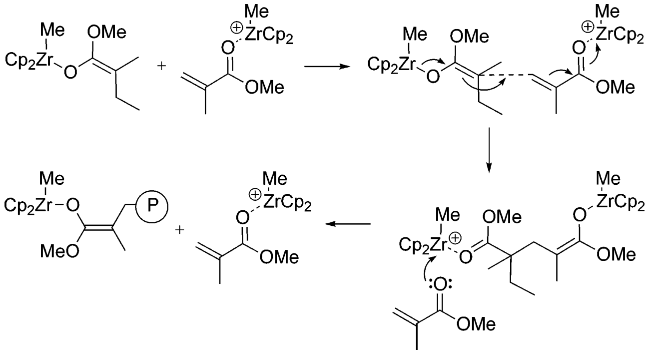
We present a DFT study of the monometallic group transfer polymerization (GTP) of methyl acrylate (MA) catalyzed by Sm-based and Zr-based metallocenes. The processes examined are the generation of the catalytically active species, the subsequent C−C coupling reaction, and the ring opening of a metallacyclic stable intermediate, resting state of the polymerization process, obtained from the C−C coupling. The mechanism for a neutral zirconocene, a cationic zirconocene, and a neutral samarocene are compared. The isoelectronic neutral samarocene and cationic zirconocene systems share many features, which explains their similar behavior in both the C−C coupling (no energy barrier on the potential energy surface) and the MA-assisted opening of the metallacycle. An analysis of the factors driving polymer stereoregularity in the processes catalyzed by the neutral samarocene and the cationic zirconocene has led to identifying a relationship between stereoregularity and the relative disposition of the acrylate and enolate ligands, as well as the direction of the incoming MA molecule in the opening of the metallacycle resting state. On the basis of these discoveries a kinetic model has been developed, which has proved successful in qualitatively predicting stereoregularity.

Introduction

The synthesis of high molecular weight and low polydispersity polymers from acrylic and methacrylic monomers has long been an elusive goal that is still challenging chemists. The traditional way of obtaining poly(acrylates) and poly(methacrylates) involves radical initiators and affords polymers having rather broad molecular weight distributions; therefore since the beginning of the 1990s the attention of many researchers has been drawn to living polymerization.[1−4] Particularly, numerous metallocene systems based on early d-block and f-block metals have shown very interesting properties in catalyzing polymerizations of acrylates and methacrylates with a group transfer mechanism (GTP).[5,6] Although several metallocenes have been tested, the most successful systems are based on Zr and Sm.

While it has been shown that a relatively straightforward mononuclear GTP is taking place with Sm-based systems, a very effective binuclear mechanism has been demonstrated to be responsible for the polymerization of acrylates and methacrylates with the Zr-based bicomponent systems proposed by Collins et al.[7,8] Under these conditions the so-called bimetallic mechanism is preferred to the standard GTP. Monocomponent cationic zirconocenes are also capable of catalyzing the polymerization following the usual GTP mechanism, albeit generally at a slower rate.

Scheme 1. The Bimetallic Mechanism



Both mechanisms have in common a metal enolate attacking an acrylate molecule activated toward nucleophilic attack by having its carbonyl oxygen coordinated to an electrophilic metal center.

The difference between the mono- and binuclear mechanism is that in the standard, mononuclear systems the activation of the acrylate molecule is done by the same metal center to which the enolate is linked, whereas in the bimetallic mechanism there are two metal centers, one linked to the enolate and the other activating the acrylate, which leads to the peculiar and elegant “swinging” role of the metal centers (see Scheme 1).

There are no reports on stereoregular polymerizations using bimetallic systems, whereas depending on the reaction condi-

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tions and the ligands, syndio- or iso-poly(acrylates) and poly(methacrylates) have been obtained with neutral systems based on Sm or cationic species based on Zr.

The aim of this work is to explore the forces driving mononuclear group transfer polymerizations, as well as the factors that determine whether a stereoregular polymer is obtained, by means of density functional calculations. Under these assumptions, it may be useful to explore also mononuclear mechanisms that are less likely experimentally, such as the GTP catalyzed by neutral zirconocenes.

Computational Details

Density functional theory (DFT) calculations on the systems of interest were carried out with the program ADF,[9,10] version 2004.01,[11] using the Becke−Perdew exchange−correlation functional (BP86).[12−14]

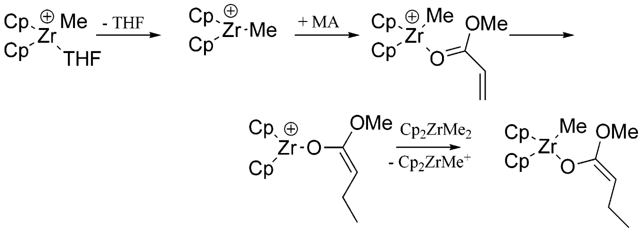
Double-ζ STO basis sets with polarization function were employed for H, C, and O atoms, while for Zr and Sm atoms triple-ζ STO basis sets with one p-type polarization function were employed. The 1s electrons of C and O as well as the 1s−3d electrons of Zr and the 1s−4d electrons of Sm were treated as frozen core. First-order scalar relativistic corrections were applied to the systems studied.[15−17]

The f electrons in the partially occupied 4f shell of Sm have required particular attention in order to ensure SCF convergence. Since in all the systems studied Sm is in the +3 oxidation state, an ionic Sm^{3+} ion fragment was created with a restricted calculation, in which a fractional, even occupation of the 4f orbitals was imposed (5 electrons in 7 orbitals). Therefore all calculations on systems containing Sm were based on atomic fragments, plus a Sm^{3+} ion fragment. Please note that the choice of fragments might help the SCF convergence, but it has no influence on the final outcome of the calculation.

Additionally, again to achieve SCF convergence, it was necessary to turn off the DIIS procedure[18] and to reduce the mixing parameter from the standard value to values ranging from 0.02 to 0.1.

All calculations were carried out in the gas phase without any symmetry constraint. Approximate transition states were located through reaction coordinate studies in which all degrees of freedom were minimized, while keeping a specific internal coordinate, or linear combination of internal coordinates, fixed. In the case of the C−C coupling reaction in all the mechanisms studied (Zr-based, both neutral and cationic, as well as Sm-based) the coordinate in question is the distance between the α-carbon of the enolate and the β-carbon of the acrylate. In the case of the ring-opening reactions, the coordinate chosen was the difference between the distances between the metal center and the carbonyl oxygen of the incoming acrylate and of the leaving ester group, respectively. The leading coordinate for the backbiting reactions was the distance between the α-carbon of the enolate and the carbon atom in the ester group not interacting with the central metal atom. All stationary points were then fully optimized as minima or transition states, starting from the constrained geometries. The systems studied are very floppy, especially the transition states in the ring-opening reactions, and frequency calculations have yielded a very high number of low-frequency modes. Under these conditions the harmonic oscillator approximation, under which vibrational frequencies are calculated, fails, thus affording unreliable values for the corrections to Gibbs free energies. For this reason reaction energies and not free energies are reported throughout the paper.

Scheme 2. The Zirconocene Initiation Step



No counteranions are present for the neutral zirconocene and samarocene systems. Compared to the metallocene-catalyzed polymerization of olefins, the anion plays a much less important role in the GTP of acrylates, since the two available metal coordination sites are occupied at all times by oxygen-based strong σ-donor ligands and the anion, if existing, is always relegated to an outer shell. In light of such considerations, and in order to be able to compare more directly the results, also the study with cationic zirconocenes was conducted without considering the counteranion (which experimentally is BPh_4^-).

All energies are given in kcal/mol relative to the parent reactants ($Cp_2ZrMeTHF^+$, Cp_2ZrMe_2, MA, THF, $Cp_2SmMeTHF$).

Discussion

Initiation: Formation of a Metallocene−Enolate Complex. In many cases the precursors of the catalytically active species is a metallocene to which a molecule of tetrahydrofuran (THF) is complexed. Removal of the THF molecule frees a coordination site, which can accommodate an acrylate molecule and activate it for an internal 1,4-conjugated nucleophilic attack, yielding an enolate (Scheme 2). The removal of the THF molecule is most likely the rate-determining step for the initiation.

Computations performed in vacuo on the neutral samarocene system $Cp_2SmMeTHF$ and on the cationic $Cp_2ZrMeTHF^+$ (the counteranion, which experimentally is BPh_4^-, has not been considered here) show as expected that the positively charged zirconium center interacts much more strongly with THF than the corresponding samarium species (41.5 kcal/mol dissociation energy compared to 18.6 kcal/mol).

The energy loss for the dissociation of THF is almost completely recovered upon complexation of methyl acrylate (MA); therefore the formation of the metallocene−MA complex is in both cases only a few kcal/mol endothermic, as shown in Table 1. Formation of the zirconocene−MA cationic complex is less endothermic than that of neutral samarocene−MA because the positively charged zirconium center is capable of a stronger interaction with MA. The substitution of THF by MA might take place by a low barrier associative mechanism, but this has not been explored here.

At this point of the study, rather than exploring the details of the initiation mechanism, which would require searching TS structures, we are more interested in the energies of the local minima along the reaction path. Transfer of the methyl group attached to the metal center to the β-carbon of the α,β-unsaturated MA yields a neutral enolate for the Sm-based system

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Table 1. Energies of the Species Involved in the Formation of the Samarocene and Zirconocene Enolates (initiation reactions)

species	E_{rel}[a]
MA	0
THF	0
$Cp_2ZrMeTHF^+$	0
Cp_2ZrMe_2	0
Cp_2ZrMe+	41.5
$Cp_2ZrMeMA^+$	2.4
Cp_2ZrEno^+	−15.8
$Cp_2ZrMeEno$	−32.0
$Cp_2SmMeTHF$	0
Cp_2SmMe	18.6
$Cp_2SmMeMA$	5.5
Cp_2SmEno	−28.4

[a] Relative energies in kcal/mol.

and a cationic enolate for the Zr-based complex. The latter can under the appropriate reaction conditions (i.e., the presence of Cp_2ZrMe_2, as done by Collins et al.)[7,8] react further to produce a more stable neutral zirconocene enolate, which besides having a role in the bimetallic mechanism, has been considered in previous experimental and computational studies to be potentially active on its own. Although it has been proven that under the conditions mentioned above the bimetallic mechanism is preferred over the neutral mononuclear one, the mononuclear mechanism involving a neutral zirconocene species can proceed (at a lower rate) as already shown by Sustmann et al.,[19] and it can serve as a useful reference point for a comparison with the Sm-based GTP catalyst.

Conformations of the Metallocene−Acrylate−Enolate Complexes. Once the metallocene−enolate is generated, it can form a complex with a MA molecule present in the medium, which can then undergo a coupling reaction in which the polymer chain is increased by one unit. Different conformations are possible for metallocene−enolate−MA complexes (Scheme 3). It is important to identify which geometries are possible because the side of the enolate facing the MA ligand determines the configuration of the stereocenter formed in the coupling reaction (vide infra).

Neutral Zirconocene−Acrylate−Enolate Complexes. Starting from the neutral zirconocene enolate, three different arrangements of the MA, Me, and the enolate substituents can be thought of, depending on the direction from which the incoming MA approaches the neutral zirconocene enolate.

Four stable complexes of different conformations have been found in the case that the incoming MA coordinates to the zirconium atom between the methyl and enolate groups, i.e., in the equatorial position, as shown in Scheme 3, structures Ia−Id. The conformations are determined by the relative positions of the substituents of the α-carbons of the acrylate and enolate groups. In the scheme and in the following discussion, “up” refers to a methoxy group above the plane defined by Zr, Me, O, and O, when the molecule is seen in such a way that the methyl group is away from the viewer (the enolate is in the foreground), whereas “down” refers to the opposite situation. In such complexes the Zr−O(acrylate) bond is slightly longer (up to 0.24 Å) than the Zr−O(enolate) bond, in agreement with the fact that the enolate ligand has a stronger donor capability than MA.

Similar conformations (structures IIa−IId) can be defined in the case of MA approaching the neutral zirconocene enolate from the side of the enolate, that is, in an axial position, but in this case it has been found that the Zr−O(acrylate) distance is very large (between 4.2 and 5.3 Å) and comparable to what was previously found by Sustmann et al.[19] Also, in the central (equatorial) position the binding of the enolate to the zirconium center in general is stronger, as witnessed by shorter Zr−O(enolate) distances (2.05−2.06 Å as compared to 2.18−2.27 Å when the enolate is on one side), as shown in Table 2.

The result of MA coming from the side of the methyl group (structure III) would be a complex with a methyl group in the equatorial position, and between MA and the enolate, both of which occupy axial positions. This configuration would greatly hinder the subsequent nucleophilic addition of the enolate to the acrylate. Actually, no local minimum corresponding to this arrangement has been found, due to the unfavorable steric interactions between the larger acrylate and enolate substituents and the Cp rings.

Formation of complexes from the neutral zirconocene enolate with the enolate ligand in the axial position is an endothermic process by 7.3−14.4 kcal/mol with respect to the neutral zirconocene enolate and MA at infinite separation, as shown below in Table 3. Entropic effects would make this process less favorable by another 9−12 kcal/mol.[20]

The formation of loose complexes with MA in the axial position ranges from slightly endothermic to somewhat more exothermic (complexation energies vary from 1.9 to −5.5 kcal/mol, see Table 3), as opposed to being endothermic when MA coordinates at the equatorial position (however, it should be remembered that entropic effects have not been taken into account; such an effect would cost an additional 9−12 kcal/mol).[20] Complexes with the enolate ligand in the equatorial position are more stable than those with MA in the same position by 5.4−19.9 kcal/mol. This can be explained in terms of destabilization by repulsive steric interactions and by electronic factors. Although MA binds more strongly to Zr when in the equatorial position, the increased proximity also involves overcrowding around the Zr center, which happens to a much lesser extent in the weakly interacting complexes with MA in the axial position. Even more important is the fact that the enolate is capable of binding more strongly than MA because it is a stronger donor. The strongest interaction is in the equatorial position, so structures with the enolate ligand in the equatorial position are expected to be more stable than those in which that position is occupied by MA.

Except for one case, complexes with MA in the axial position have the π-system of MA roughly perpendicular to the equatorial plane of the complex and to the π-system of the enolate.

In all these complexes the distance between the MA carbonyl oxygen and the Zr center is more than 4 Å, well above that of a covalent bond. The interaction of MA with the Zr center is quite weak, and elongation of the C═O bond (compared to the isolated MA) does not occur as it did at the equatorial position. On the contrary, the enolate ligand interacts more strongly with Zr when it is in the equatorial position. Consistently with a more pronounced electron density shift toward the metallic center, the enolate O−Zr distance is shorter than in the axial position. At the same time, the larger charge transfer from the enolate to the Zr center causes the enolate O−C distance to increase.

Tetracoordinated Cationic Zirconocene or Neutral Samarocene Enolate−MA Complexes. In the case of cationic, tricoordinated metallocene−enolates, a tetracoordinated complex is formed upon coordination of a MA molecule. In the absence of the methyl ligand there is only one configuration whose

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Scheme 3. Configurations and Conformations of Possible Neutral Zirconocene−Acrylate−Enolate Complexes

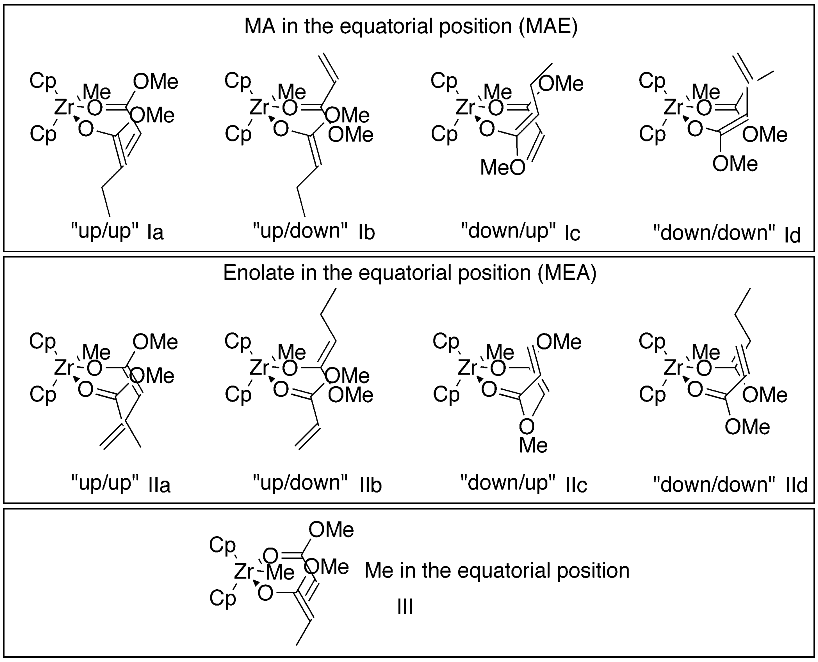


Table 2. Selected Interatomic Distances for Species Involved in GTP Catalized by a Neutral Monometallic Zirconocene[d]

complex	C=C(MA)	C−C	C=O	=O···Zr	−O−Zr	C−O	C=C(eno)	C···C
MAE “up/up”[b,c,d]	1.34	1.47	1.25	2.29	2.27	1.28	1.38	3.63
MAE “up/down”	1.34	1.47	1.24	2.33	2.24	1.29	1.38	3.85
MAE “down/down”	1.34	1.48	1.23	2.41	2.17	1.31	1.35	4.40
MAE “down/up”	1.34	1.48	1.23	2.42	2.19	1.30	1.35	6.03
MEA “up/up”[a,c,d]	1.34	1.48	1.22	5.35	2.06	1.319	1.35	7.43
MEA “up/down”	1.34	1.48	1.22	4.21	2.06	1.317	1.36	3.21
MEA “down/down”	1.33	1.48	1.22	4.66	2.05	1.322	1.35	3.85
transition state	**C=C(MA)**	**C−C**	**C=O**	**=O···Zr**	**−O−Zr**	**C−O**	**C=C(eno)**	**C···C**
MAE “up/up”	1.35	1.46	1.24	2.37	2.22	1.30	1.37	3.07
MAE “up/down”	1.36	1.45	1.24	2.31	2.27	1.29	1.38	2.93
MEA “up/down”	1.38	1.42	1.23	2.68	2.16	1.28	1.39	2.31
MEA “down/down”	1.39	1.42	1.26	2.50	2.20	1.28	1.40	2.14

[a] MAE = complex with MA in the equatorial position. [b] MEA = complex with enolate in the equatorial position. [c] Enolate double-bond configuration is *E* for complexes having MA in the equatorial position, *Z* for complexes with enolate in the equatorial position. [d] The GTP process for neutral zirconocenes is illustrated in Scheme 5.

Table 3. Relative Energies for Species Involved in GTP Catalyzed by a Neutral Monometallic Zirconocene[d]

complex	E_{rel}[a]	$E^{\ddagger}_{\mathrm{rel}}$[a]
MAE “up/up”[b,d]	−24.7	−17.3
MAE “up/down”	−22.6	−16.7
MAE “down/down”	−17.5	
MAE “down/up”	−19.9	
MEA “up/up”[c,d]	−36.4	
MEA “up/down”	−30.0	−22.4
MEA “down/down”	−37.5	−25.6

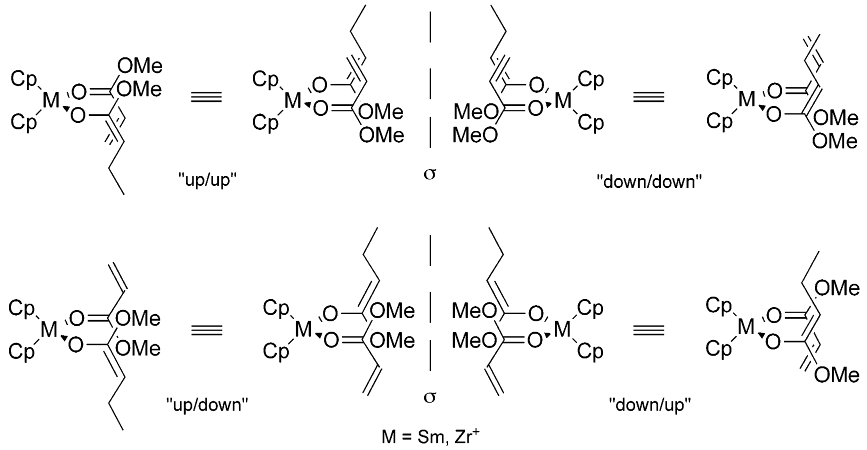
[a] Relative energies in kcal/mol. [b] MAE = structures with MA in the equatorial position. See Scheme 3. [c] MEA = structures with enolate in the equatorial position. See Scheme 3. [d] Enolate double-bond configuration is *E*. [e] The process is shown in Scheme 5.

conformations must be explored; see Scheme 4. As for the neutral zirconocene−MA−enolate complexes, the possible conformations are four, but the number of conformations that must be studied can be further reduced to two on the basis of symmetry. It can be seen from Scheme 4 that the “up/up”, “down/down” and “up/down”, “down/up” complexes are two pairs of mirror conformations. Since enantiomers have the same energies, only one complex from each of the two enantiomeric pairs was considered. Comparison of complexes having “up/down” and “down/up” revealed energy differences of less than 0.1 kcal/mol. As a result, only one pair was considered. Furthermore the same result was obtained for the corresponding metallacyclic products, which will be discussed in the next section.

Compared to the neutral zirconocene complexes, cationic zirconocene−enolate−MA complexes are understandably more stable for two reasons: first there is less crowding around the metal center, and second the metal is more positively charged, therefore interacting more strongly with the MA and enolate ligands. As a consequence, complexation energies range between −9.4 and −14.2 kcal/mol, as shown in Table 4. As expected, the distance from the enolate oxygen to Zr is shorter than that from the MA carbonyl oxygen (see Table 5), indicating that the former interaction is stronger (because the enolate is a stronger donor). Enolate−Zr distances range between 1.98 and 2.07 Å, while MA−Zr distances are on average 0.2 Å longer (2.15−2.26 Å).

The stereochemical outcome of the coupling reaction depends on the enantiotopic face of the enolate attacking MA. The “up/up” and “up/down” complexes will both form an *S* stereocenter because the enolate is facing MA with the same prochiral side, while for the same reason “down/down” and “down/up” geometries give rise to an *R* stereocenter. The orientation of

Scheme 4. Symmetry in the Conformations of Tetracoordinated Metallocene−Enolate−MA Complexes[a]



[a] M = Sm, Zr^+.

Table 4. Relative Energies for Species Involved in GTP[a] **Catalyzed by a Monometallic Cationic Zirconocene**

geometry	E_{rel} (complex)[b,c,d]	E_{rel} (metallacycle)[b,c,d]
"up/down"[e]	−25.2	−47.9
"down/down"	−30.1	−46.3

[a] The process is displayed in Scheme 6. [b] No transition states have been found on the potential energy surface. [c] Relative energies in kcal/mol. [d] The zero energy level of energy corresponds to the reactants (Cp_2ZrMe_2,$Cp_2ZrMeTHF^+$, MA, and THF). [e] See Scheme 4.

MA does not determine the configuration of the first stereocenter. However, the orientation of MA is important for the formation of the stereocenter in the following step, since after the coupling MA is transformed into an enolate. The implications that this has on stereoregularity will be discussed in the section on ring-opening reactions.

Neutral samarocene complexes are isoelectronic to cationic zirconocene complexes and also require that only two complex conformations be studied. Samarocene−enolate−MA complexes have many structural features in common with the corresponding cationic zirconocene complexes, like the pseudo-tetrahedral disposition of the ligands, which are however more distant from Sm because of its larger size and lower positive charge. O−Sm distances are roughly 0.2 A longer than the corresponding O−Zr ones, being 2.37−2.45 Å for MA. Complexation is exothermic by 10.1−10.7 kcal/mol, comparable to the analogous cationic zirconocene complexes.

Neutral Zirconocene-Catalyzed Polymerization. Transition state searches have been carried out for the two complexes of each family of the neutral zirconocene−enolate−MA complexes in which the interatomic C−C separation is shorter, namely, the "up/up" and "up/down" conformers with the MA in the equatorial position, and the "up/down" and "down/down" conformations with the enolate in the equatorial position. Neutral zirconocene complexes cannot exist unless Cp_2ZrMe_2 is added to the reaction medium, under which conditions it is demonstrated that Collin's bimetallic mechanism takes over for both the neutral and cationic mononuclear system.[8] We have nevertheless carried out an exploratory study of GTP catalyzed by a monometallic species for the sake of comparison with the samarium system. The mechanism for GTP by the neutral monometallic zirconocene is shown in Scheme 5. Geometrical changes are displayed in Table 2 and the energetics in Table 3 and Figure 1.

In the case when MA is already close to the metal center (i.e., when MA is in the equatorial position, see MAE of Scheme 3) simple rotation along selected torsion angles lead the π systems of the acrylate and of the enolate to a distance and a relative orientation suitable for the 1,4-conjugated nucleophilic addition to occur (see Scheme 5). The activation energy for the transition state (5.8−7.4 kcal/mol depending on the conformation, see Table 3) indicates a process with a low activation energy, leading rapidly to a very stable product. Consistently with the Hammond postulate,[21] the transition state maintains very much the characteristics of the reacting complex, as can be seen from the geometric data displayed in Table 2. At the transition state, the length of the incipient C−C bond is still longer than expected, around 3 Å, for both the transition states studied.

A much less ordered situation is encountered when MA occupies the axial position. In this case MA must come closer to Zr and the enolate before changes in bond lengths can be observed. Together with a more extensive motion, a higher energy barrier is observed for the second ligand configuration, and correspondingly the length of the incipient C−C bond is shorter (2.1−2.3 Å) in the transition state. Also the other bond lengths in MA and in the enolate change more.

Computations on the transition states of the second family (that of neutral zirconocene complexes having the enolate ligand in the equatorial position, see MEA of Scheme 3) indicate that the potential energy surface is quite flat as MA approaches the enolate; therefore even if substantial motion of MA is involved, the activation energy for the nucleophilic addition is at most only 6 kcal/mol higher than when MA occupies the equatorial position.

In the complexes, the C−O and C═C distances of the enolate, longer than normal C═O and C═C distances, reflect the fact that the electron pair is delocalized over these two bonds. As the interaction between the enolate oxygen and the Zr atoms weakens (longer Zr−O distance in the TS) and the terminal carbon of MA comes closer, electron density shifts toward the α-carbon to form the new C−C bond. Redistribution of the electron density is more advanced for the second type of transition states (i.e., those (MEA) with the enolate in the equatorial position); therefore the change of the bond orders is larger and the length of the incipient C−C bond is also much more typical, in the range 2.3−2.1 Å, as shown in Table 2. The complexes with the enolate in the middle (equatorial position) are more stable than those with MA in the middle by more than 5 kcal/mol, and also the transition states stemming

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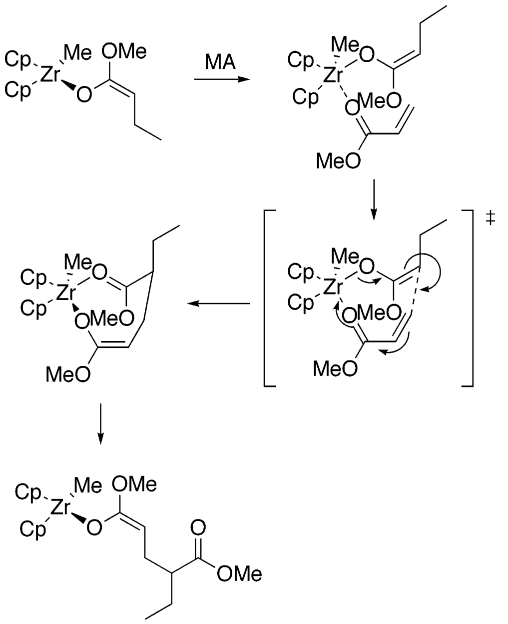
Table 5. Selected Interatomic Distances for Species Involved in GTP[a] Catalyzed by a Monometallic Cationic Zirconocene

complex[b,c]	C=C(MA)	C−C	C=O	=O···Zr	−O−Zr	C−O	C=C(eno)	C···C
"up/down"[d]	1.36	1.43	1.272	2.15	2.07	1.32	1.37	2.27
"down/down"	1.34	1.47	1.256	2.26	1.98	1.34	1.34	7.44

product	C=C(MA)	C−C	C=O	=O··Zr	-O−Zr	C−O	C=C(eno)	C··C
"up/down"	1.50	1.35	1.345	2.04	2.22	1.250	1.50	1.54
"down/down"	1.50	1.36	1.341	2.04	2.21	1.255	1.50	1.56

[a] The process is displayed in Scheme 6. [b] Distances in Å. [c] Bond labels have been retained for clarity, although bond orders in the products are different (refer to text). [d] See Scheme 4.

Scheme 5. Mechanism for GTP Catalyzed by a Monometallic Neutral Zirconocene



from them are comparably lower in energy, as can be seen from Table 3 and Figure 1; therefore the pathway with the enolate in the equatorial position (MEA) is the preferred one.

A further difference in the reaction mechanism of the two kinds of configurations is that no metallacyclic species was observed in the reaction path starting from the complexes with MA in the equatorial position (MAE), whereas a local minimum corresponding to this kind of structure was found when the enolate occupies the equatorial position. The energy of the eight-membered metallacycle is just a few kcal/mol below that of the reacting complex. The ring-opening TS (which presumably occurs without assistance from a MA molecule) has not been searched for extensively, and only approximate transition states have been obtained. The activation energy for this step seems to be very low, and the open product (a longer neutral zirconocene enolate with an added MA unit) is much lower in energy than the parent complex. It is likely that ring opening assisted by a MA molecule might have a lower activation energy or even proceed without a barrier. Differently from the cationic analogues described in the next section, the neutral zirconocene metallacyclic species should therefore be considered as relatively high-energy, unstable intermediates.

Cationic Zirconocene-Catalyzed Polymerization. The abstraction of a CH_3^- group from the neutral zirconocene leads to a cationic zirconocene with an increased positive charge and reduced steric bulk around the metal center. The mechanism for GTP by monometallic cationic zirconocene and neutral samarocene is shown in Scheme 6. While a distinct potential energy barrier has been found for all neutral zirconocene complexes (Figure 1), the first conjugated addition of the enolate α-carbon to the acrylate β-carbon in the cationic system is barrierless on the potential energy surface (Figure 2). This result has been confirmed with linear transit computations for both the forward (complex-to-product) and backward (product-to-complex) reaction coordinate. It can therefore be concluded that if a barrier actually exists, it is due to entropic factors not considered in our calculations and that it could only be detected studying the reaction on the free energy surface, which is presently computationally too expensive for the information it would afford. The product of the coupling reaction is a very stable eight-membered metallacyclic species, which lies 16.2−22.6 kcal/mol below the corresponding complex (Figure 2). The polymerization therefore is strongly exothermic, and the resting state is the metallacycle.

Samarocene-Catalyzed Polymerization. Neutral samarocene systems are structurally and electronically much closer to cationic zirconocenes than to neutral zirconocenes. As expected, the neutral samarocene system behaves as the previously studied cationic zirconocene, showing no activation barrier for the C−C coupling (Figure 3). Also in this case, this has been confirmed with linear transit computations for both the forward (complex-to-product) and backward (product-to-complex) reaction coordinate. The shape of the potential energy surface at the first addition step could be different from the following ones, in which the bulk of the growing polymer chain might contribute to a modest activation energy. Also in this case it has been found that the resting state is a metallacycle, which is 16.9−18.8 kcal/mol more stable than the parent reacting complex (see Table 6). The computed metallacycle bond lengths of the model neutral samarocene compare very well with the crystallographic measurements performed by Yasuda et al. on an analogous system containing pentamethylated Cp rings (see Table 7).[3]

Ring-Opening Reactions. Since neutral zirconocene systems seem to be much less efficient than cationic ones, the following discussion will be limited to cationic zirconocenes and the isoelectronic neutral samarocene systems.

While most symmetric systems afford non-stereoregular polymers, or syndiotactic polymers if the polymerizations are carried out at very low temperatures, isotactic polymers have been obtained with two Cp rings having different substituents.[22−25]

Stereocontrol has been attributed to enantiomorphic site control (isospecific) or chain-end control (syndiospecific), the latter meaning that the chirality of the previously formed stereocenter influences the stereochemistry of the following one. Since the systems studied in this work bear two identical Cp ligands, they are not expected to polymerize MA isospecifically.

Höcker et al. have shown that cationic zirconocenes similar to our model system, but containing a bridge between the Cp

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(23) Hölscher, M.; Keul, H.; Höcker, H. *Chem. Eur. J.* **2001**, *7*, 5419.

(24) Hölscher, M.; Keul, H.; Höcker, H. *Macromol. Rapid Commun.* **2000**, *21*, 1093.

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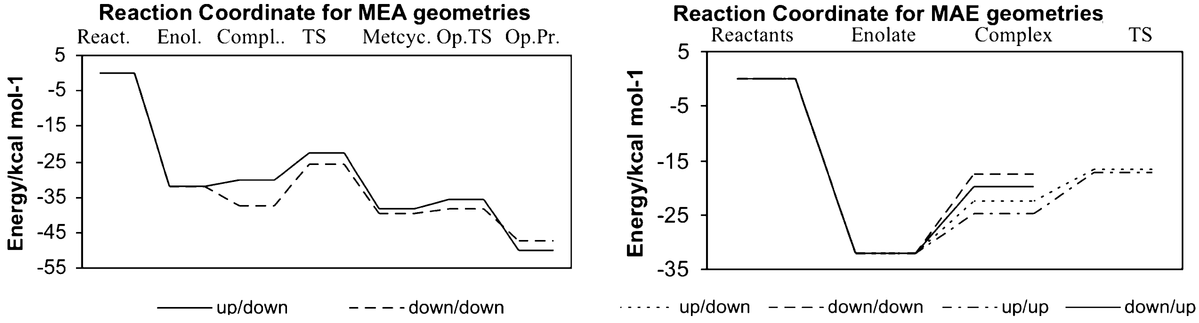


Figure 1. Energy profile for GTP involving a monometallic neutral zirconocene. The different species are shown in Scheme 5. Geometrical parameters are shown in Table 2 and energies in Table 3.

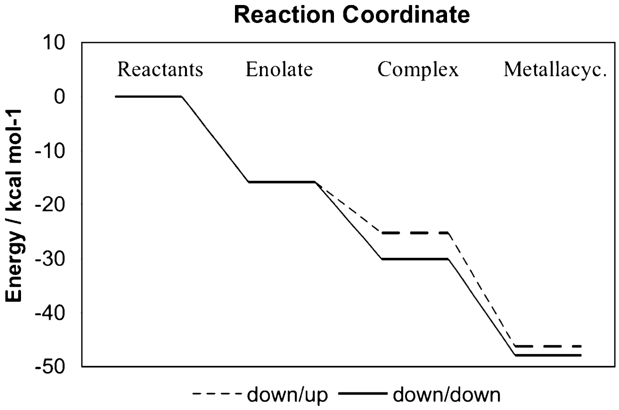


Figure 2. Energy profile for GTP catalyzed by a monometallic cationic zirconocene. The process is illustrated in Scheme 6. Geometrical parameters are shown in Table 5 and energies in Table 4.

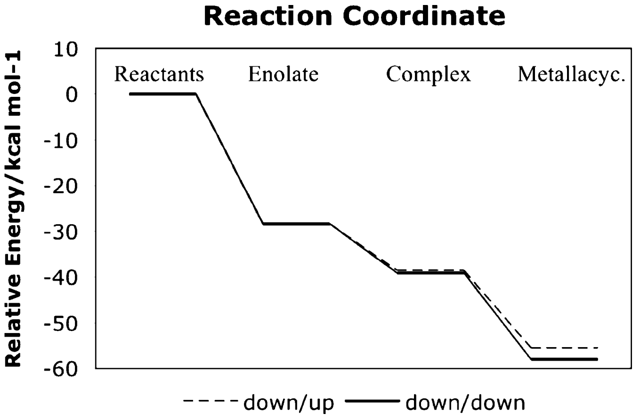


Figure 3. Energy profile for GTP catalyzed by a monometallic neutral samarocene. The process is illustrated in Scheme 6. Geometrical parameters are shown in Table 7 and energies in Table 6.

Scheme 6. Mechanism for GTP Catalyzed by a Monometallic Cationic Zirconocene or a Monometallic Neutral Samarocene

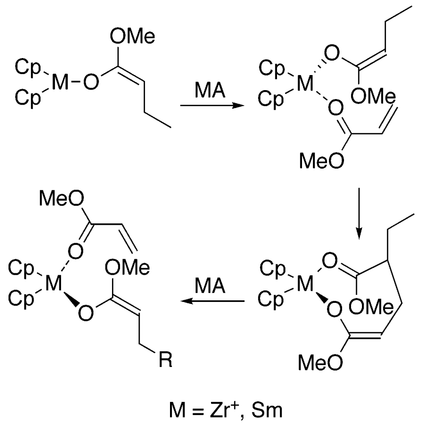


Table 6. Relative Energies for Species Involved in GTP[a] Catalyzed by a Monometallic Cationic Zirconocene

geometry	E_{rel} (complex)[b,c,d]	E_{rel} (metallacycle)[b,c,d]
"down/up"[e]	−38.5	−55.5
"down/down"	−39.1	−57.9

[a] The process is displayed in Scheme 6. [b] No transition states have been found on the potential energy surface. [c] Relative energies in kcal/mol. [d] The zero energy level of energy corresponds to the reactants ($Cp_2SmMeTHF$, MA, and THF). [e] See Scheme 4.

rings, are good catalysts for the production of syndio PMMA at low temperatures and that similar unsymmetrical systems in which a Cp ring has been substituted with an indenyl ring are isospecific at somewhat higher temperatures.[22]

In order for the second kind of stereocontrol to be effective, the weak influence exerted by the chiral center must not be overcome by thermal fluctuations, and therefore syndio-enriched polymers are usually obtained only when the polymerization process is performed at very low temperatures.

Also, it is reasonable to assume that the closer the last formed stereocenter is to the active site, the greater will be its influence on the formation of syndio products. The metallacycle is the resting state in GTP catalysis by both cationic zirconocene and neutral samarocene. In this restrained conformation the stereocenter is in the metallacycle where it is better able to exert its influence than in the corresponding species in which the metallacycle has been opened. Therefore, the ring-opening step, assisted by an incoming MA molecule, is likely to be the one responsible for stereoregularity (or lack thereof) in the polymer.

To open the ring, an incoming MA molecule must substitute the ester ligand generated from the enolate after the coupling reaction. This can occur in two ways: axially from the same side of the ester group ("frontside attack") of from the opposite axial position ("backside attack"). The direction from which the MA molecule comes, and the "up" or "down" orientation of the enolate group formed from the MA ester group in the coupling, determines the stereochemistry of the stereocenter formed in the following coupling reaction.

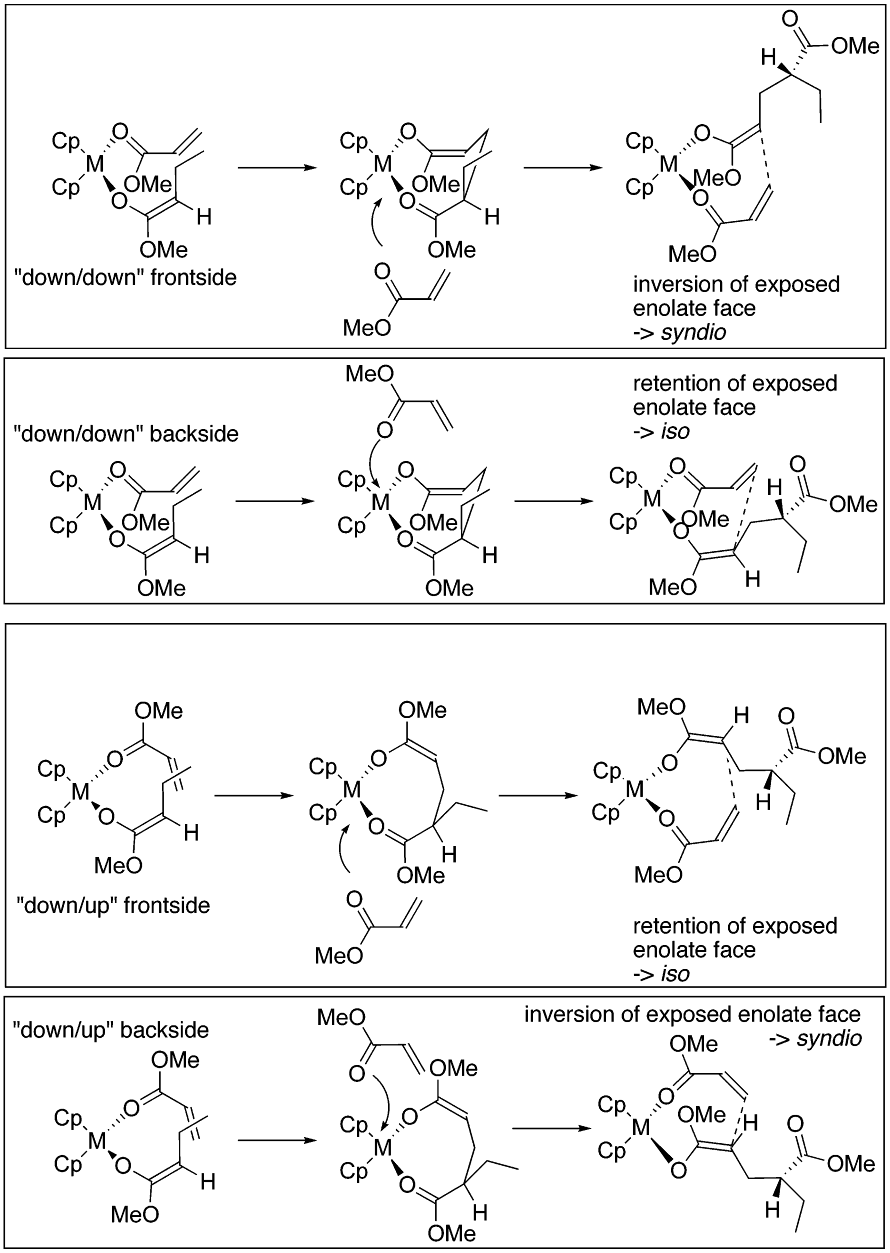
It can be seen from Scheme 7 that when the ring opening occurs through a backside attack, the enolate coordination site is maintained, whereas with a frontside attack the enolate coordination site is inverted at each propagation step. In addition, in the case of the metallacycle obtained from the "up/up" type of complex, after the backside attack the enolate is again in the "up" position, which means that the stereocenter formed in the next coupling reaction will have the same absolute configuration as the previous one, thereby leading to an isotactic polymer.

Table 7. Selected Interatomic Distances for Species Involved in GTPa Catalyzed by a Monometallic Neutral Samarocene

complex[b,c]	C=C(MA)	C−C	C=O	=O···Sm	−O−Sm	C−O	C=C(eno)	C···C
"down/down"[d]	1.39	1.45	1.24	2.37	2.23	1.30	1.37	3.20
"down/up"	1.34	1.46	1.24	2.45	2.20	1.30	1.36	5.36
product	C=C(MA)	C−C	C=O	=O···Sm	−O−Sm	C−O	C=C(eno)	C···C
"down/down"	1.50	1.37	1.30	2.19	2.46	1.24	1.51	1.57
"down/up"	1.49	1.37	1.30	2.22	2.43	1.24	1.50	1.61
exptl[e]	1.52	1.39	1.31	2.19	2.39	1.23	1.53	1.61

[a] The process is displayed in Scheme 6. [b] Distances in Å. [c] Bond labels have been retained for clarity, although bond orders in the products are different (refer to text). [d] See Scheme 4. [e] Reference 26.

Scheme 7. Stereoregularity Control in Neutral Sm- and Cationic Zr-Catalyzed Processes



The opposite result is achieved by the frontside attack: the enolate is in the "up" position but the coordination site has changed; therefore the other enantiotopic face is involved in the following propagation step, leading to the production of a syndiotactic polymer. The metallacycle obtained from the "down/up" (or "up/down") complex follows the same rule: the enolate coordination site is maintained with the backside attack and inverted with the frontside attack. However, the MeO group of the enolate is now facing the opposite direction compared to the previous step. Therefore the backside attack in this case leads to the syndio product, whereas the frontside attack leads to the iso product, as shown in Scheme 7.

In all cases, a reaction path presenting two transition states separated by an intermediate is observed for all systems and all types of attack. Figure 4 shows the energy profiles of the frontside and backside attacks for Sm- and Zr-based systems of the chosen conformations. The reaction coordinate corresponds to the incoming MA-to-metal minus the leaving ester-

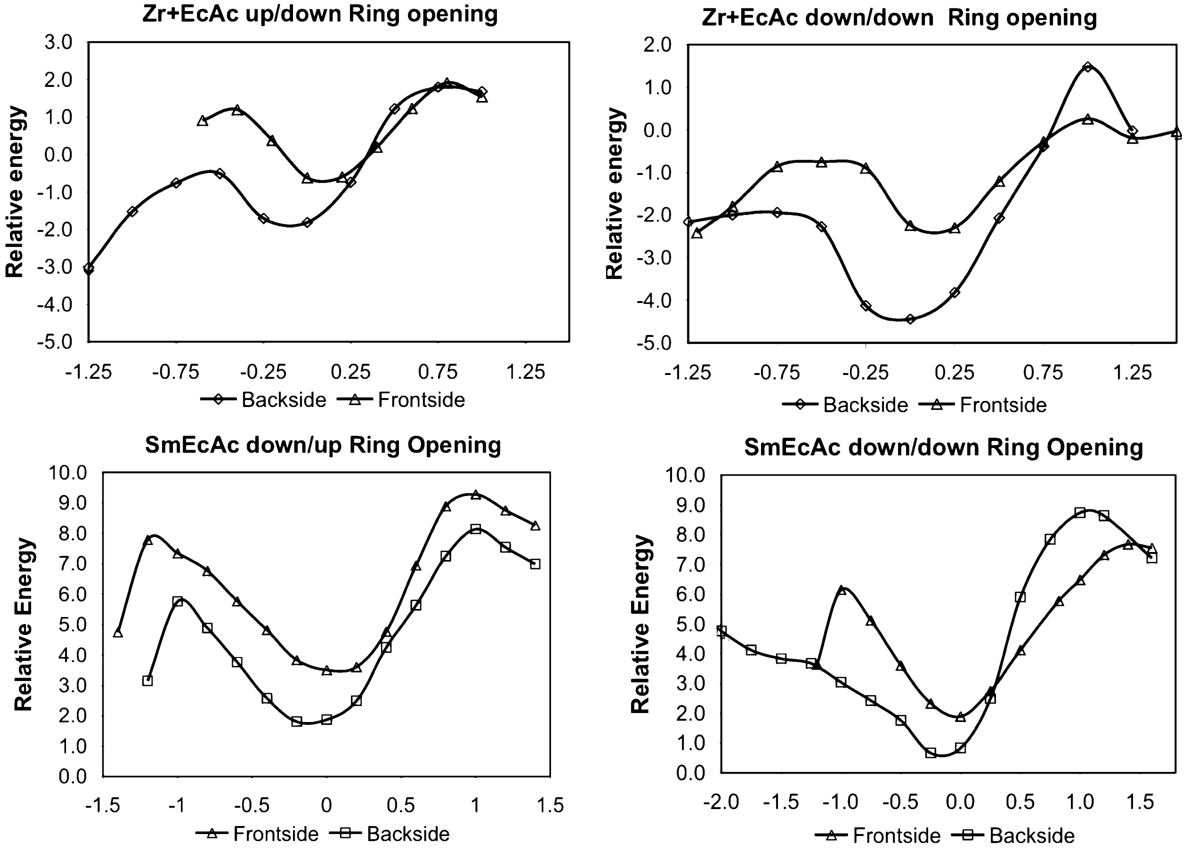


Figure 4. Energy profiles for ring-opening reactions involving a monometallic cationic zirconocene or a monometallic neutral samarocene. The process is illustrated in Schemes 7 and 8. Energies correspond to the constrained geometry optimizations along the reaction coordinate. Geometrical parameters and energies for the fully optimized stationary points are shown in Tables 8 and 9.

to-metal distance. As MA approaches the metallacycle, the energy of the system increases because of added steric crowding around the metal center. The geometric rearrangement forces a smaller O−metal−O angle in the metallacycle, causing more ring strain, as shown in Table 8. This fact also provides a qualitative criterion for establishing the relative stability of competing transition states: the transition states in which the O−metal−O angle is tighter are higher in energy. The energy reaches a maximum when the reaction coordinate ranges approximately from 1.4 to 0.75 Å. Stabilizing electronic interactions between MA and the metal center start to play a more important role thereafter, driving the energy of the system to a local minimum around 0 Å (see Table 8) on the reaction coordinate. Taking the energy of the parent metallacycle plus MA as reference, cationic zirconocene ring-opening transition states are more stable than the corresponding neutral samarocene species by 5.3−8.3 kcal/mol, while the difference for the intermediates is 0.9−6.6 kcal/mol (see Table 9). However, Zr-based and Sm-based systems show the same trends. The energy profiles for all ring-opening reactions are reported in Figure 4. It can be seen that in most of the cases the approximate transition states leading to the syndio product are around 1 kcal/mol lower than those leading to the iso product. A possible reason is that the metallacycle is more strained in the transition states leading to the iso product. This is particularly evident for the ring opening of the "down/up" neutral Sm metallacycle, in which the energy difference between the syndio channel and the iso channel is greatest. In that case the most stable transition state has an O−M−O angle that is wider than that of the competing transition state by 4°.

Table 8. Selected Interatomic Distances (in Å) for Metallacycles and the Corresponding First Ring-Opening Transition States

metallacycle	MA···M[b,c]	=O···M[d]	−O−M[e]	O−M−O[f]
Zr^+ dd[g]		2.21	2.04	90.0
Zr^+ ud[h]		2.22	2.04	99.5
Sm dd[i]		2.46	2.19	83.0
Sm du		2.43	2.22	82.0
transition state	**MA···M**	**=O···M**	**−O−M**	**O−M−O**
Zr^+ dd backside	3.25	2.25	2.04	81.9
Zr^+ dd frontside	3.29	2.24	2.05	83.4
Zr^+ ud backside	2.97	2.28	2.01	84.1
Zr^+ ud frontside	2.99	2.25	2.05	81.9
Sm dd backside	3.46	2.50	2.21	79.5
Sm dd frontside	3.46	2.49	2.21	78.4
Sm du backside	3.38	2.38	2.27	82.0
Sm du frontside	3.55	2.44	2.21	78.1
intermediate	**MA···M**	**=O···M**	**−O−M**	**O−M−O**
Zr^+ dd backside	2.39	2.36	2.05	74.2
Zr^+ dd frontside	2.48	2.30	2.08	75.7
Zr^+ ud backside	2.41	2.39	2.04	75.9
Zr^+ ud frontside	2.44	2.32	2.07	76.8
Sm dd backside	2.43	2.56	2.25	75.1
Sm dd frontside	2.53	2.55	2.23	74.4
Sm du backside	2.43	2.51	2.25	76.9
Sm du frontside	2.55	2.54	2.26	73.2

[a] The process is displayed in Scheme 6. [b] M = Sm or Zr (as appropriate). [c] MA···M = distance of the methyl acrylate incoming group to the central metal. [d] =O···M = distance of the ester leaving group to the central metal. [e] −O−M = distance of the enolate to the central metal. [f] O−M−O = angle formed by the oxygen ligands in the metallacycle (in deg). [g] dd = "down/down". [h] ud = "up/down". [i] du = "down/up".

As the reaction coordinate goes from positive values to 0 Å, MA moves toward the metal while the ester group moves away very little. After reaching the ring-opening intermediate and going to negative values of the reaction coordinate, the ester

Table 9. Relative Energies of the Species Involved in the Ring Opening Reactions[a]

	E_{rel}[b,c]		
	1st TS	intermediate	2nd TS
Zr^+ dd backside[d]	−0.4	−5.0	−3.2
Zr^+ dd frontside	−0.6	−3.0	−0.3
Zr^+ ud backside[e]	0.9	−2.4	−0.8
Zr^+ ud frontside	1.0	−1.7	0.6
Sm dd backside	7.7	−0.8	2.4
Sm dd frontside	6.6	1.6	2.4
Sm du backside[f]	6.3	0.0	4.5
Sm du frontside	8.1	2.8	6.2

[a] The process is displayed in Scheme 6. [b] Relative energies are in kcal/mol. [c] The reference energy corresponds to the metallacycle + MA at infinite distance. [d] dd = "down/down". [e] ud = "up/down". [f] du = "down/up".

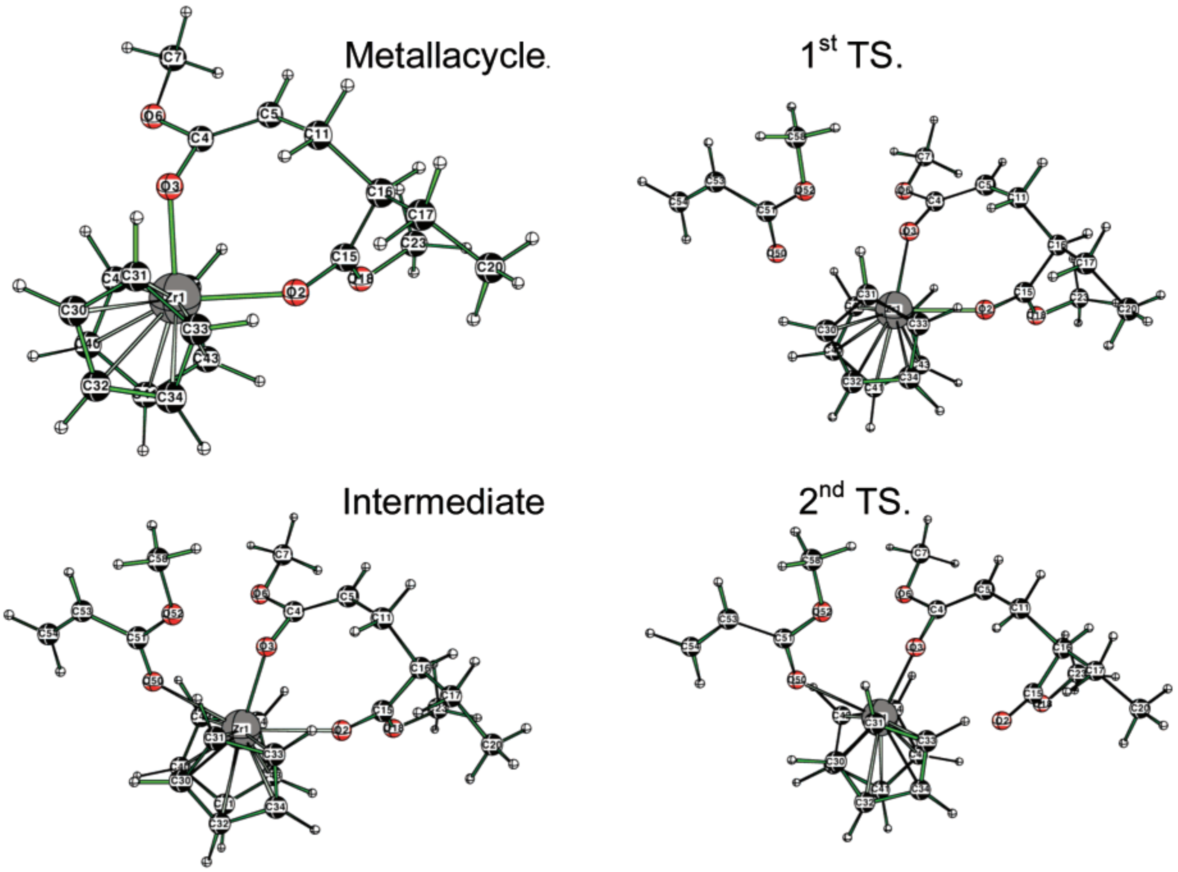
group leaves the coordination site on the metal while the MA-to-metal distance barely changes. The energy rises again, due to the weakening of the ester−metal interaction and to the strain created in the metallacycle being opened. When the ester group is sufficiently far from the metal, the metallacycle is completely open and the geometry can relax, recovering the strain energy and generating the metallocene−enolate−MA complex for the next coupling reaction.

Representative structures for the ring-opening process, relative to the backside ring opening of the "down/down" cationic zirconocene metallacycle, are shown in Figure 5.

Kinetic Scheme for the Prediction of Stereoregularity. Scheme 8 depicts the metallacycle-opening reaction pathways that lead to the formation of a new complex. The metallacycle (A or A′, depending on the conformation) can undergo backside or frontside ring opening, generating a new complex (D, D′, E, or E′), which does not necessarily have the conformation of the previous cycle. The process consists of two elementary steps and has two distinct transition states. An intermediate (B, B′, C, or C′) is formed after the first transition state. Once the second transition state is passed, the metallacycle is fully open and a new enolate−acrylate complex is formed. A rotational movement is necessary to bring together the partners in the coupling, as in the first propagation step, for which no barrier was found on the potential energy surface. Fast interconversion between complexes could result in loss of stereoselectivity. However, the coupling is likely to be faster because the rotation involved in the conformational change is hindered in two ways. First, it results in steric repulsion between the ligands. Second, it requires changing the oxygen lone pair involved in the σ-donation, which proceeds through a transition state in which there is no overlap between the orbitals of oxygen and the metal. Formation of a new C−C bond is rapid and irreversible, and the system returns almost immediately to its metallacycle resting state. Since the coupling reaction is a barrierless process on the potential energy surface, the ring opening is the rate-determining step, and particularly important is the first transition state, which is higher in energy than the second one.

At each cycle a dyad is formed, which can be **m** (*meso*, indicating isotactic product) or **r** (*racemic*, indicating syndiotactic product). For each metallacycle conformation there is an iso and a syndio channel, and at each cycle the growing polymer chain can rest in either state A or A′ because crossovers are made possible during the ring-opening step. Both the branch starting from A and the one starting from A′ contribute to the overall stereoregularity, proportionately to how fast they lead to the next metallacycle.

Knowing the free energy of activation, rate constants can be computed using the transition state theory. Since we ultimately


Metallacycle.

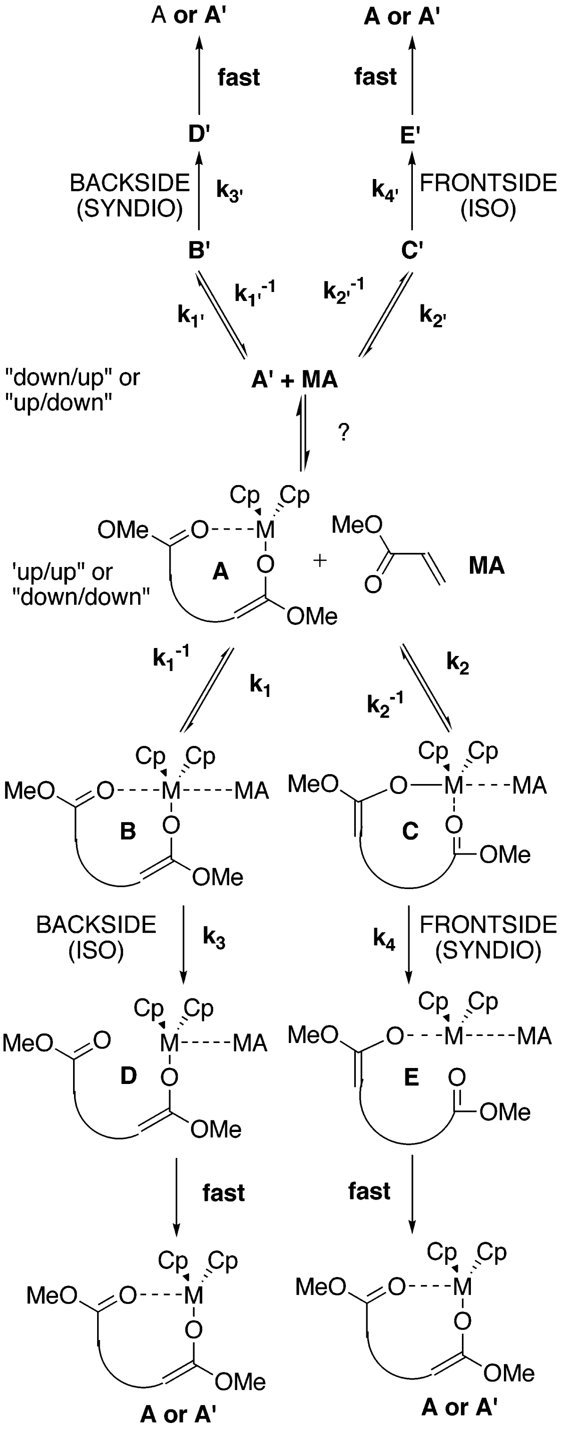
1st TS.

Intermediate

2nd TS.

Figure 5. Computed structures for the species involved in the backside ring opening of the "down/down" cationic zirconocene metallacycle.

Scheme 8. Kinetic Scheme for the Prediction of Stereoregularity



are interested in relative rates between iso and syndio channels, entropic effects can be neglected, as they will be nearly the same in either case. We assume that the reaction is carried out at −95 °C, as in the methyl methacrylate GTP experiments performed by Yasuda et al. with neutral samarocenes, which afforded more than 95% syndiotactic PMMA experimentally.[4]

A detailed derivation of the kinetic equations is included in the Supporting Information for the sake of brevity, which leads to the approximate expression for the syndio/iso dyad composition ratio in the polymer, χ.

$$\chi = \frac{(k_1 + k_2)\frac{k_2}{k_1} + (k_{1'} + k_{2'})\frac{k_{2'}}{k_{1'}}}{k_1 + k_2 + k_{1'} + k_{2'}} \qquad (1)$$

The equation has a normalization term that approximates the global polymerization rate, and the sum in the numerator corresponds to the sum of the stereoregularities of each branch times the contribution of that branch to the overall rate (i.e., the weight factor).

The syndiotactic character in the polymer is predicted as follows:

$$\text{SYNDIO\%} = \frac{\chi}{\chi + 1}100 \qquad (2)$$

PMA obtained from the neutral samarocene is predicted to have 99% syndiotactic character at −95 °C; syndiotacticity decreases to 92% at 50 °C, as reported in Table 10. In the same temperature range, the syndiotactic character in the PMA obtained from the cationic zirconocene is much lower, ranging from 64 to 58% between −95 and 50 °C. It is worth mentioning that in both systems one of the two conformations of the metallacycle is opened more easily than the other, thus giving a dominant contribution to the overall rate and selectivity.

The low selectivity shown by the cationic zirconocene is not unexpected, for the fact that it bears two unsubstituted, unbridged cyclopentadienyl ligands. It is expected that selectivity can be tuned through the design of appropriately substituted ansa bis-cyclopentadienyl systems.

Although these are approximate results, they are qualitatively in agreement with the results from two experimental groups. Höcker et al. report 89% syndiotacticity for PMMA produced at −45 °C using an unsymmetrical cationic *ansa*-zirconocene,[22] while they have not attempted acrylate polymerizations. The experiments conducted by Yasuda et al. using a neutral samarocene led to 95% syndiotacticity in the polymerization of methyl methacrylate at −95 °C (75% at 25 °C)[4] and a maximum syndiotacticity of 60% for the polymerization of MA at −78 °C.[26]

Conclusions

Through this DFT study, we have explored the mechanism of the group transfer polymerization of methyl acrylate, catalyzed by cationic or neutral d-block or f-block monometallic metallocenes. From our calculations the process catalyzed by a neutral monometallic zirconocene appears to be slower than that catalyzed by a cationic monometallic zirconocene. The GTP catalyzed by a neutral samarocene shows a close similarity to that catalyzed by the cationic zirconocene because the two systems are isoelectronic. No energy barrier has been encountered on the potential energy surface in the C−C coupling reaction catalyzed by these two systems, whereas when a neutral zirconocene is involved, a moderate activation energy is found. Also the products of the reaction are different, since in the GTP catalyzed by a cationic zirconocene or by a neutral samarocene a very stable metallacycle is formed, which is the resting state in the whole polymerization, while in the GTP catalyzed by the neutral zirconocene the metallacycle is only a high-energy intermediate.

The factors driving polymer stereoregularity have been studied for the processes catalyzed by the neutral samarocene

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[26] Ihara, E.; Morimoto, M.; Yasuda, H. M*acromolecules* **1995**, *28*, 7886.

Table 10. Predicted Percent Syndiotacticities for the GTP of Methyl Acrylate, Catalyzed by a Neutral Zirconocene or a Neutral Samarocene

T (°C)	Cp_2Zr^+	Cp_2Sm
−95	64	99
−50	62	98
−25	61	96
0	60	95
25	59	94
50	58	92

and the cationic zirconocene. A relationship between stereoregularity and relative disposition of the acrylate and enolate ligands, as well as the direction of the incoming acrylate molecule, has been found. The first transition state in the opening of the metallacycle resting state, assisted by an incoming acrylate molecule, is the most important elementary step. On the basis of these discoveries a kinetic model for the prediction of stereoregularity has been developed, which has shown to be qualitatively in agreement with the experimental data available for similar systems.

Acknowledgment. This work has been supported by BASF. T.Z. thanks the Canadian government for a Canada Research Chair in theoretical inorganic chemistry.

Supporting Information Available: Derivation of the equation for the prediction of stereoselectivity. This material is available free of charge via the Internet at http://pubs.acs.org.

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