

(E)-Z Selectivity in 2-Butene Copolymerization by Group 4 Metallocenes. A Combined Density Functional Theory and Molecular Mechanics Study

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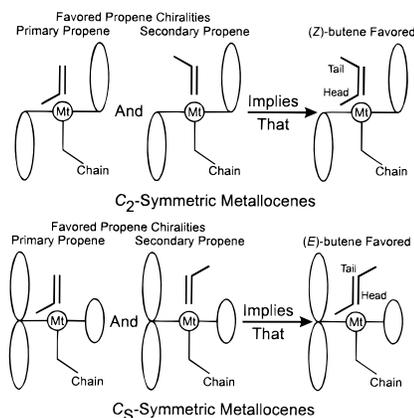
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During the past decade, experimental and theoretical studies¹ have shown that both primary (regioregular)^{2–6} and secondary (regioirregular)^{7–10} propene insertions are enantioselective with well-suited C_2 -symmetric (isospecific) and C_s -symmetric (syndiospecific) group 4 metallocenes. However, as sketched in Scheme 1, *opposite enantiofaces* are favored for primary and secondary propene insertion on C_2 -symmetric metallocenes, whereas *the same enantioface* is favored for primary and secondary insertion on C_s -symmetric metallocenes. In this framework, *if the same steric interactions which rule the enantioselectivity of primary and secondary propene insertions hold for 2-butene*, the insertion of (Z)-butene should be favored with C_2 -symmetric metallocenes, whereas insertion of (E)-butene should be favored with C_s -symmetric metallocenes.

To investigate this idea, which would confirm and summarize a large class of widely accepted mechanisms, we studied the insertion reactions of (Z)- and (E)-butene with catalytic systems based on the C_2 -symmetric $Me_2Si(1\text{-indenyl})_2$ ligand (bisInd) and on the C_s -symmetric $Me_2Si(\text{cyclopentadienyl-9-fluorenyl})$ ligand (CpFlu).¹¹ A double approach, based on combined quantum mechanics/molecular mechanics (QM/MM) techniques¹² and on

Scheme 1



selected ethene/2-butene copolymerization runs,²⁵ has been utilized.

The QM/MM transition states for (Z)- and (E)-butene insertion into the Zr–C(*n*-propyl) σ -bond of the C_2 -symmetric bisInd metallocene are reported in Figure 1A and B, respectively. According to the mechanism of the chiral orientation of the growing chain,^{29,30} the *n*-propyl group used to simulate a polyethylenic growing chain assumes a conformation which minimizes repulsive interactions with the C_2 -symmetric ligand, and the head-methyl group (see Scheme 1) is put on the opposite side relative to the growing chain to minimize steric interactions between the methyl group itself and the growing chain. This orientation of the head-methyl group implies that the (Z)-butene tail-methyl group (see Scheme 1) is located far from the aromatic rings of the bisInd ligand, whereas the (E)-butene tail-methyl group feels severe steric repulsion with one of the aromatic rings of the bisInd ligand. As a consequence, (Z)-butene insertion is favored relative to (E)-butene insertion.

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(12) The QM/MM calculations¹³ were carried out by using the density functional package ADF,¹⁴ modified^{15,16} to include the CHARMM molecular mechanics force field.¹⁷ The QM part of all the systems is always the cationic species $H_2SiCp_2Zr(n\text{-propyl})$, to which 2-butene or benzene is coordinated. When building the real QM/MM systems, only the H_2SiCp_2 ligand of the QM kernel has been modified, by transforming it into the bisInd and CpFlu ligands. All the reported structures represent stationary points on the combined QM/MM potential energy surface. More details on this approach can be found elsewhere.^{18,19} A triple- ζ STO basis set on Zr and a double- ζ STO basis set plus one polarization function for Si, C, and H were used.²⁰ The frozen-core approximation was applied up to the [Ar]3d¹⁰ configuration for Zr, the [Ne] core for Si, and the [He] core for C. All the calculations are at the gradient-corrected VWN²¹–BP86^{22–24} level of theory.

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(25) Copolymerizations were carried out in a 50-mL glass flask equipped with a magnetic stirrer. Sequentially, 7 mL of toluene, 5 mL of 2-butene, 565 mg of MAO dissolved in 9 mL of toluene, and 1×10^{-5} mol of metallocene dissolved in 1 mL of toluene were introduced. The flask was fed with a constant ethylene overpressure of 3 cm of paraffin oil. After 48 h, the copolymerizations were stopped by introducing a few milliliters of methanol. The obtained copolymer samples (50–100 mg) present number-average molecular weights in the range of 4000–40000 amu. ¹³C NMR spectra were recorded on an AM 250 Bruker spectrometer operating at 62.89 MHz at 393 K. Resonances were assigned on the basis of data reported in literature,²⁶ on DEPT ¹³C NMR experiment,²⁷ and on additivity Grant and Paul rules.²⁸

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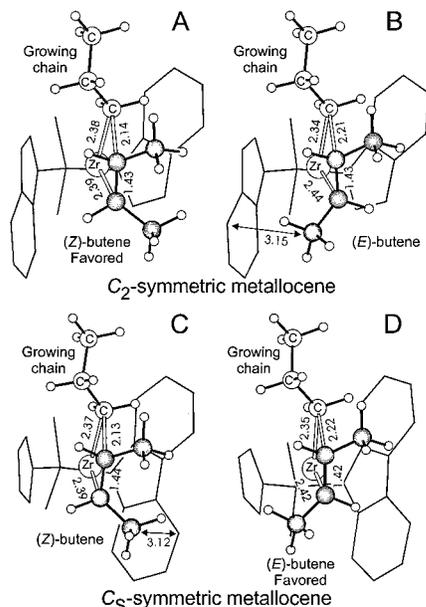


Figure 1. QM/MM transition states of 2-butene insertion reaction into the Zr–C σ -bond with the C_2 - and C_5 -symmetric metallocenes.

The QM/MM transition states for (*Z*)- and (*E*)-butene insertion into the Zr–C σ -bond of the C_5 -symmetric metallocene are reported in Figure 1C and D, respectively. Also in this case, the *n*-propyl group assumes a conformation to minimize repulsive interactions with the CpFlu ligand, and the head-methyl group is put on the opposite side relative to the growing chain. Now, the (*Z*)-butene tail-methyl group feels severe steric repulsion with the CpFlu ligand, whereas the (*E*)-butene tail-methyl group is located in an uncrowded region. As a consequence, (*E*)-butene insertion is favored relative to (*Z*)-butene insertion.

The energy diagrams corresponding to (*Z*)- and (*E*)-butene insertion reaction into the Zr–C σ -bond with the C_2 - and C_5 -symmetric metallocenes are reported in Figure 2. In the diagrams, reactants correspond to QM/MM minimum energy structures with a benzene molecule (to simulate the solvent) π -coordinated to the metal atom, and with the growing chain fully extended in an open sector. The first step along the reaction path corresponds to the solvent substitution reaction by the 2-butene molecule, which π -coordinates to the metal atom.³¹ The transition states correspond to structures A–D reported in Figure 1. In agreement with the previous geometrical analysis, (*Z*)-butene insertion on the C_2 -symmetric metallocene is favored relative to insertion of (*E*)-butene by 1.6 kcal·mol⁻¹, while (*E*)-butene insertion on the C_5 -symmetric metallocene is favored relative to insertion of (*Z*)-butene by 1.8 kcal·mol⁻¹. Finally, it is worth noting that (*Z*)-butene coordination is preferred both for C_2 - and C_5 -symmetric metallocenes. However, this energy preference is lower for the C_5 -symmetric metallocene, due to repulsive interactions between the coordinated (*Z*)-butene and the CpFlu ligand.

The results of selected ethene/2-butene copolymerization runs are reported in Table 1. In agreement with our theoretical analysis, C_2 - and C_5 -symmetric metallocenes scarcely insert (*E*)- and (*Z*)-butene, respectively, whereas C_2 - and C_5 -symmetric metallocenes insert relevant fractions of (*Z*)- and (*E*)-butene, respectively. Moreover, in agreement with our QM/MM analysis, when copolymerization experiments are run with a 40% (*Z*)-:60% (*E*)-2-butene mixture, the presence of the better coordinating (*Z*)-butene inhibits the reaction of (*E*)-butene with the C_5 -symmetric

(31) The coordination energy of benzene to the Me₂Si(1-indenyl)₂Zr(*n*-propyl) and Me₂Si(cyclopentadienyl-9-fluorenyl)Zr(*n*-propyl) cationic species amounts to -7.8 and -7.7 kcal·mol⁻¹, respectively.

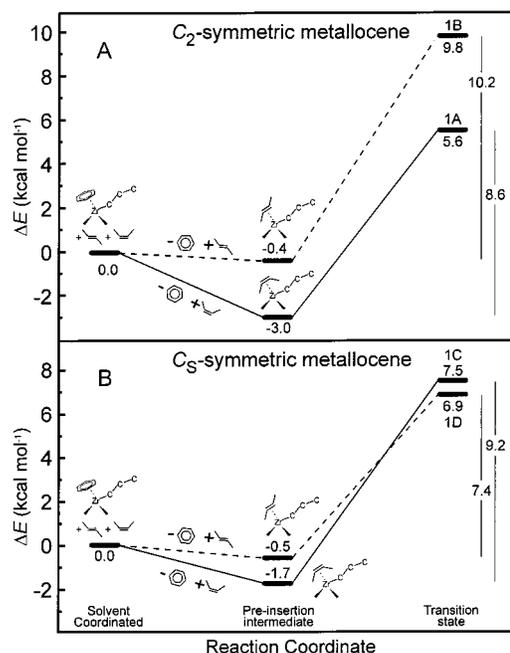


Figure 2. Energy diagrams corresponding to (*Z*)- and (*E*)-butene insertion reaction (continuous and dashed lines, respectively) into the Zr–C σ -bond with the C_2 - and C_5 -symmetric metallocenes.

Table 1. Molar Compositions of Ethene/2-Butene Copolymers

2-butene feed composition	C_2 -symmetric bisInd metallocene		C_5 -symmetric CpFlu metallocene	
	ethene (%)	butene (%)	ethene (%)	butene (%)
(<i>Z</i>)-butene	75	25 ^a	99	1 ^a
(<i>E</i>)-butene	99	1 ^b	86	14 ^b
mix (40% (<i>Z</i>): 60% (<i>E</i>))	93	7 ^a	98	2 ^b

^a Molar percent of inserted 2-butene units, mainly observed in ¹³C NMR spectra as isolated ethyl groups.³⁷ ^b Molar percent of inserted 2-butene units, mainly observed in ¹³C NMR spectra as isolated methyl groups.³⁷

metallocene, while the presence of the poorer coordinating (*E*)-butene is only able to reduce the amount of (*Z*)-butene insertions with the C_2 -symmetric metallocene.

In conclusions, the prediction that (*E*)-(Z) selectivity in the ethene/internal olefins copolymerization with group 4 metallocenes can be achieved by using ligands of suitable symmetry has been proved. In particular, it has been shown that C_2 - and C_5 -symmetric metallocenes are able to copolymerize ethene with (*Z*)- and (*E*)-butene, respectively.³²

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(32) This kind of selectivity for α,β -disubstituted olefins is expected for insertions into metal–alkyl bonds if the alkyl group is larger than methyl. Of course, this is related to the low enantioselectivity for primary α -olefins insertion into the Mt–H and Mt–CH₃ bonds.^{33–36}

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(37) The obtained copolymers incorporate (*E*)- and (*Z*)-butene units, generating isolated methyl and ethyl groups, respectively. Isolated methyl groups are reasonably produced by an isomerization reaction analogous to the well-known 3,1 isomerization reaction observed after secondary monomer insertions⁷ for propene polymerization by several metallocene-based catalytic systems. Isolated ethyl groups may be obtained through a different isomerization reaction of the 2-butene ending polymer chain.