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Response to comments by V. Busico and R. Cipullo[1] on the paper titled “Error formation in *ansa*-zirconocene-catalyzed isotactic propylene polymerization”[2]

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Isotactic polypropylene (PP) produced with heterogeneous $TiCl_3$-type catalyst, hereinafter referred to as *het-i*-PP, is one of the largest volume thermoplastics. The material is characterized by a set of valuable application properties. Two simple-to-measure indicators of the macroscopic properties for *het-i*-PP are the melting transition temperature ($T_m = 160–165°C$) and solvent resistance (hot heptane insoluble yield, IY, 99%), which are closely related to the stereoregularity of PP’s microstructure.

The seminal works of Ewen [3] and of Kaminsky and Brintzinger [4] discovered that stereoselective polymerization of propylene and other α-olefins can be catalyzed using stereorigid C_2-symmetric *ansa*-metallocene compounds. However, the metallocene isotactic polypropylene (*met-i*-PP) obtained with the most frequently investigated precursors: *rac*-ethylenebis(1-η^5-indenyl)dichlorozirconium or *rac*-ethylenebis(1-η^5-4,5,6,7-tetrahydroindenyl)dichlorozirconium activated with methylaluminoxane (MAO), exhibit very inferior indicators [4–6] ($T_m \approx 125°C$, IY ≈ 0). Röll et al. ([6]c) Mise et al. [7], and Spaleck et al. [8] investigated the stereo- and regio-selectivity of chiral alkyl-substituted dimethylsilylene bridged zirconocene catalyst and found that the T_m and %*m m m m* pentads of *met-i*-PP are strongly dependent on the number of the alkyl substituents and their location. These observations led to the development of metallocene structures that can produce commercially acceptable *met-i*-PP.

Various research groups have sought to elucidate the mechanism of formation of stereo- and regio-errors in *ansa*-metallocene-catalyzed isospecific propylene polymerizations to promote further catalyst development. Leclerc and Brintzinger [9] reported signals of deuterium-labeled *m r r m* pentads in polymers made from (*E*)- or (*Z*)-[1D] propene with MAO-activated *ansa*-zirconocene catalyst, showing that stereoerrors arise mainly from an isomerization of the Zr-bound chain-end. There are several reports that isotacticities and chain lengths of *met-i*-PP increase with increasing propylene pressure [10–13]. The mechanism most frequently considered for an isomerization of metal–alkyl units is β-H elimination to a metal-hydride–olefin complex, rotation of the olefin ligand around the metal–olefin bond, and reinsertion to form the rearranged metal–alkyl unit [14,15]. Busico and coworkers [10] proposed that such a reaction sequence could cause epimerization of the stereochemical configuration of the last inserted monomer.

One focus of our research is to consider and experimentally investigate other sources of stereoerror formation, in addition to those discussed above. Our MM-2 calculation results [16] indicate that only a relatively low fraction of ‘intrinsic’ stereoerrors are caused by faulty enantiofacial olefin insertion, because the transition state steric energy for reverse-face addition is ca. 3 kcal mol^{-1} higher than the normal-face addition. In nearly all reported isospecific propylene polymerizations, the chiral precursors used are their racemic mixtures. Stereoerror could result when the propagating chain of the prevailing methine configuration bound to a metal center of one chirality interchanges with the opposite antipode’s chain. The possibility of this chain transfer event (chain–site interchange) were investi-

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[1] See [1].

[2] Song et al., 1996 [2].

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gated by comparing propylene polymerizations [2] in the presence of the cation bis(O-acetyl-(*R*)mandelate of (*S*)ethylenebis(4,5,6,7-tetrahydro-1-η^5-indenyl)zirconium ($\mathbf{1}^+(S)$) and of a mixture of diastereomers ($\mathbf{1}^+(R/S)$). In order to minimize ion-pair interactions, the cocatalyst employed was triphenylcarbenium-tetrakis(pentafluorophenyl) borate (**2**) and tri-*i*-butylaluminum (TIBA) [17] instead of MAO.

The stereoregularities of the PPs produced by $\mathbf{1}^+(S)$ and by $\mathbf{1}^+(R/S)$ are quite different. The former gives PP of high T_m and [*m m m m*], which are insensitive to [Zr], T_p, or immobilization on silica. In contrast, the latter gives PP having much lower T_m and [*m m m m*], which became worse with the increase of [Zr] and T_p. On the other hand, more stereoregular PP was obtained when $\mathbf{1}^+(R/S)$ is supported on silica. These results may be explained by the interchange of PP chains bound to the $\mathbf{1}^+(R)$ site with those bound to the $\mathbf{1}^+(S)$ sites, which results in a steric inversion. Similar interchanges in the catalysis by the enantiomer $\mathbf{1}^+(S)$ do not cause stereoerror formation. Siedle et al. [18] had demonstrated the occurence of exchange of methyl groups between zirconocene or with zirconocenium species by ^{13}C-NMR. Monomer–dimer equilibria in homo- and hetero-dinuclear cationic zirconium complexes have been reported [19]. An X-ray molecular structure had been determined for the catalytically active dimeric $[Cp''_2ZrMe(\mu\text{-}Me)MeZrCp''_2]^+[MePBB]^-$, where $Cp'' = \eta^5\text{-}1,2\text{-}Me_2C_5H_3$ and $MePBB = MeB(2C_6F_4\text{–}C_6F_5)_3$ [20]. The formation and dissociation of monomer–dimer complexes would promote interchange of alkyl groups.

An increase of [TIBA] in the catalysis was found to cause a decrement of stereoregularity of PP produced by the $\mathbf{1}^+(R/S)$ system. This suggests possible participation of aluminum centers in the chain–site interchanges. ^{13}C-NMR [18] and kinetic [19] evidences for heterodinuclear complexes of cationic alkyl zirconium and alkyl aluminum complexes have been reported.

Recently, Busico and Cipullo wrote a critique [1] of our work [2], to which we make responses here to points raised by them in the order of appearance by the paragraph number because the manuscript is not paginated.

In the first paragraph, Busico and Cipullo [1] attributed the decrease of stereospecificity of C_2-symmetric metallocene catalysts with decreasing propylene pressure to be the manifestation of an epimerization mechanism because the propagation has first-order rate-dependence with respect to the monomer ($[M]^n$, $n = 1$), while $n = 0$ for epimerization. Actually, both $n = 1$ and $n > 1$ dependences, depending upon the propylene pressure, have been reported for syndiospecific, hemiisospecific, as well as isospecific metallocene catalysts ([10]e, [20–22]). In all these instances, the co-ordination of two propylene molecules with the zirconocenium ion should have profound electronic and steric effects on α-agostic interactions [24,25], β-H elimination [10], chain-end isomerization [9] and accessibility of metal center to chain–site interchange [2]. These effects are all likely to lower the occurrence of the stereoerror formation processes, while increasing the rate of monomer insertion.

In the next three paragraphs, Busico and Cipullo [1] restated their proposal that stereoerrors are formed by intramolecular reaction of epimerization of the growing polypropylene chain involving the racemization of the original stereoregular last-inserted monomeric units, without intermediate detachment of the growing polymer chain from the Zr atom, ([10]a). They cited the D-label redistribution and isotope effect in the polymerization of propene-1-*d* [9] to support the epimerization hypothesis. However, the isomerization scheme 1 ([9]a) and schemes 1–3 ([9]b) of Leclerc and Brintzinger contain neither the formation of Zr–H, nor of co-ordinated disubstituted olefins. They were doubtful that the mechanism proposed by Busico and Cipullo could explain all their results ([9]b).

Busico and Cipullo ([10]a) ruled out the possibility of active site isomerization or transfer events of polymer chains between active sites of opposite chirality because the microstructure of PP indicates the occurrence of (*m m m m r r m m m* . . . .) rather than of (. . . . . *m m m m r m m m* . . . .) stereodefects; for instance at very high propylene concentration. This is true when the polymerization is highly stereoselective. However, under conditions conducive to stereodefect formation [2], the ^{13}C-NMR of PP can have significant [*m r m m*] intensity, and the [*m m m r*]:[*m m r r*]:[*m r r m*] deviate appreciably from the ratio 2:2:1 required for a strong enantiomorphic-site controlling model. In these cases, one cannot be overly reliant on symmetry arguments and model fitting of ^{13}C-NMR steric distributions. Instead, one should test the hypothesis directly, such as the direct comparison of racemic and enantiomeric catalysts, when addressing the possibility of transfer of PP chains between active sites of opposite chirality.

Paragraph eight [1] showed that Busico and Cipullo missed the point of our experiments. Sample 1 prepared with $\mathbf{1}^+(R/S)$ has low stereoregularity and low T_m (116.6°C), probably due to chain–site interchanges. On the other hand, sample 11 prepared with $\mathbf{1}^+(S)$ is high in stereoregularity and T_m (151.9°C) because interchanges of chains of the same methine configuration bound to metal centers of the same chirality cannot lead to a stereodefect. Earlier, Rieger et al. ([5]b) had established that the T_m of *met-i*-PP scales with [*m m m m*]; the low [*m m m m*] value of 71% for sample 1 as compared with high [*m m m m*] values of 99.9% for sample 11, are consistent with their different T_ms. Sample 1 also contains regio-irregularities. The enchainment of a stereoerror can slow down the subsequent monomer insertion, which can allow abnormal processes to compete.

Paragraph nine stated that no reports of differences in polymer structure by racemic and enantiomerically pure C_2-symmetric metallocene have appeared to date. This may just mean that experimental conditions that tend to favor chain–site interchange, i.e. high [Zr], [Al], T_p and low [propylene], have not been employed. Busico and Cipullo cited a personal communication with Brintzinger and Reinmuth (reference 10) that racemic and enantiomerically pure forms of dimethylsilylenebis(2 - methyl - 4 - *t* - butyl - cyclopentadienyl)$ZrCl_2$ gave polypropylene of virtually identical stereo-and regio-regularities. We are not knowledgeable of these results, but are not surprised by them. This compound has strategically placed methyl and *t*-butyl substituents at 2 and 4 positions, which makes one of the α-agostic interactions highly favored ([9]b). Such geometrical constraint could render stereoerror formation processes, including chain–site interchange, ineffectual.

In paragraphs 10-13, Busico and Cipullo shifted our reported NMR peak positions to make them coincide with ethylene–propylene copolymer sequences. The assignment of peak at 21.6, 20.9 and 20.1 ppm to *m m m r*, *m m r m* and *m r r m* pentads of polypropylene follow those given by Zambelli et al. [26]. Ethylene and propylene polymerizations and copolymerizations were carried out on different vacuum lines in our laboratories. It is physically impossible to have samples 1 and 8 contaminated by ethylene and not samples 5 and 11. The fact that Figure 1 of C_2C_3 copolymer [1] resembled that of sample 1 is irrelevant since we did not copolymerize ethylene and propylene in this work [2]. In any case, our research's concern with ^{13}C-NMR spectra is chiefly in regard to the homosteric pentad abundance.

We have applied the experimental conditions of high [Zr] and T_p, which tend to promote chain–site interchanges in isospecific polymerization, to syndiospecific polymerization by C_s-symmetric diphenylmethylidene(1-η^5-cyclopentadienyl)(9-η^5-fluorenyl)dichlorozirconium. No appreciable effect of [Zr] and T_p were observed on the *syndio*tacticity of the polypropylenes formed [27]. This is expected because chain–site interchange in this polymerization would not result in stereoerror formation. On the other hand, both the chain-end isomerization and the β-H epimerization should cause the formation of stereoerrors in *syndio*tactic polypropylene.

In order to test the possible occurence of chain–site interchange, we have carried out propylene polymerization in the presence of a mixture of a C_2-symmetric zirconocene (*rac*-ethylenebis[1-η^5-indenyl]dichlozirconium) or *rac*-dimethylsilylenebis[1-η^5-indenyl]dichlorozirconium and a C_{2v} symmetric zirconocene (ethylenebis[9-η^5-fluorenyl]dichlorozirconium) activated with **2** and TIBA [28]. Fractionation of the product showed the presence of an isotactic–atactic block PP along with the expected i-PP and atactic-PP. The stereoblock copolymer is most probably formed by chain–site interchanges. This mixture exhibits excellent thermoplastic elastomer properties.

In conclusion, we have demonstrated that interchange of growing polymer chains can occur under certain experimental conditions. In the case of isospecific catalysis by racemic metallocenes, the consequence can be the introduction of stereodefects. No effect on polymer microstructure resulted in the case of catalysis by the enantomer. Nor does chain–site interchange modify the structure of *syndio*tactic PP in catalysis by C_s-symmetric zirconocene. When there are both isospecific and aspecific metallocenes present, chain–site interchange produces stereoblock copolymers. Our work is concerned only with stereoerror formation caused by intermolecular processes, which are separate from and in addition to the intramolecular processes, such as those described by Busico and coworkers [10] and by Leclerc and Brintzinger [9].

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