Stereoerror Formation in the Polymerization of Propylene Catalyzed by a Titanium Bis(benzamidinate) Dichloride Complex Activated by MAO

Victoria Volkis, Michal Rodensky, Anatolii Lisovskii, Yael Balazs, and Moris S. Eisen*

Department of Chemistry and Institute of Catalysis Science and Technology, Technion—Israel Institute of Technology, Haifa 32000, Israel

Summary: A new mechanism for the formation of stereoerrors during the polymerization of propylene, promoted by the C_2-symmetric benzamidinate titanium complex 1, has been observed at low and high pressure using unlabeled and 2-d-labeled propylene. The use of deuterated propylene induces higher tacticities and molecular weights of the resulting polymers. At high pressure, the polymerization of the deuterated propylene induces faster insertion and termination processes. The new epimerization mechanism, which may be accompanied by a CH_2/$CD(Me)$ exchange, is presented.
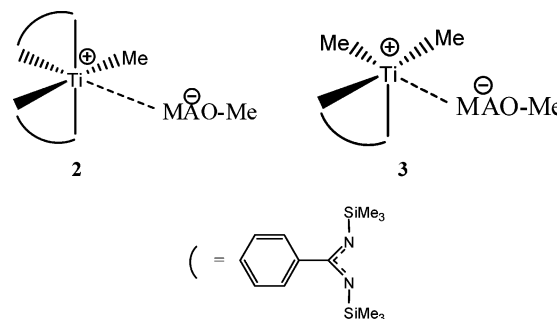
The stereoselectivity in the polymerization of propylene catalyzed by cationic C_2-symmetric metallocenes is usually considered to be a result of two competing reactions: (a) stereoregular polymerization inducing isotacticity[1] and (b) intramolecular epimerization of the growing polymer chain inducing stereoerrors.[2] For the latter process two epimerization mechanisms have been proposed: the first one, proposed by Busico et al.,[3] leads to the formation of single errors in the polymer chain;[4] the second mechanism, proposed by Resconi, includes in addition the formation of internal double bonds and singular chain ends.[3,5]

For metallocenes, experiments with labeled propylene were performed which indicate that the formation of single stereoerrors is the main operative epimerization mechanism.[4b,6,7]

We have shown that C_2-symmetric, octahedral titanium bis(benzamidinate) complexes (**1**),[8] activated by MAO, act as active catalysts for the polymerization of propylene, producing elastomeric polymers. We have disclosed that the tacticity of the

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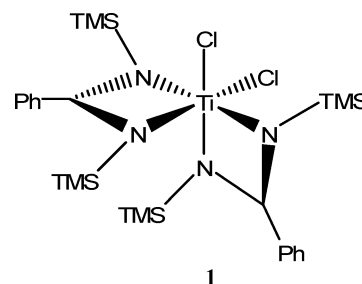
resulting polymer may be modulated by pressure.[9] Fractionalization of the obtained elastomers resulted in two fractions: a minor solid, hexane-insoluble fraction with high molecular weight and isotacticity and a major hexane-soluble, low to medium molecular weight elastomeric fraction. The formation of the different polymer fractions was recently elucidated to be a result of a disproportionation of complex **1** with MAO toward only two active species, complexes **2** and **3**.[10] In the polymer-

2   **3**

ization of propylene, complex **2** was found to be responsible for the isotactic fraction of the polymer and complex **3** for the elastomeric polymer.

We have explained the formation of the elastomers via the chain epimerization mechanism,[4,5] which was also corroborated by the isomerization of alkenes.[11] Recently, we have found that in the polymerization of propylene, in addition to the pressure, the solvent also has a huge influence on the properties of the resulting elastomers.[12] Due to the large difference observed in the polymerization of propylene between metallocenes and octahedral heteroallylic complexes (*mmmm* did not change as

* To whom correspondence should be addressed. E-mail: chmoris@tx.technion.ac.il.

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Table 1. Results of the Polymerization of Deuterated and Non-Deuterated Propylene Catalyzed by Complex 1[a]

run	P (atm)	substrate	T, h	$10^{-3}A^b$	hexane-soluble fraction				hexane-insoluble fraction			
					amt, %	M_w	MWD[c]	$mmmm^d$ %	amt, %	M_w	MWD[c]	$mmmm^d$ %
1	9.2	$H_2C=CDCH_3$	3	0.58	38	82 000	2.05	11	62	183000	2.33	88
2	9.2	$H_2C=CHCH_3$	3	0.26	92	17 000	2.22	14	8	25000	2.9	73
3	1.5	$H_2C=CDCH_3$	22	0.54	100	99 000	1.77	12.5	0			
4	1.5	$H_2C=CHCH_3$	22	0.48	100	88 000	2.26	9.4	0			

[a] Ti:Al = 1:800, 3 mL toluene, 5 mg of catalyst. [b] A = activity, in units of g of PP (mol of Ti)$^{-1}$ h^{-1}. [c] M_w/M_n. [d] Isotactic pentad content.
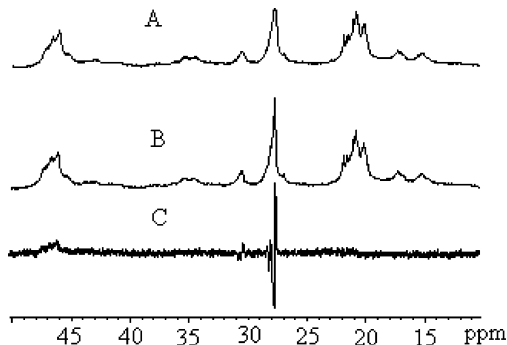

Figure 1. ^{13}C NMR decoupled and difference spectra of deuterated polypropylene, produced at high pressure by complex **1**: (A) ^{13}C-{^{1}H}{^{2}H}; (B) ^{13}C{^{1}H}; (C) difference spectrum (A − B).

a function of temperature, unlike the amount of the misinsertions; the large effect of the solvents), the chain epimerization mechanism cannot account for the observed trends. In this publication, we present the experimental discrimination between possible error formation pathways by comparing the polymerization of propylene and its β-deuterated analogue at low (1.5 atm) and high (9 atm) pressure promoted by complex **1**, activated by MAO.

2-*d*-Propylene was synthesized in situ[3,13] by reacting the corresponding Grignard reagent with D$_2$O and drying the gas via triisobutylaluminum before its polymerization.

The polymerization results are presented in Table 1. Polymers obtained at high pressure were fractionalized in refluxing hexane, whereas polymers formed at low pressure were found to be soluble in hexane regardless of the monomer used. From Table 1, two general trends were observed: a higher activity and a higher molecular weight were obtained for the deuterated polypropylene, as compared to the case for its nondeuterated analogues. These trends were retained in both soluble and insoluble fractions and at high or low pressure. At high pressure, the insoluble fraction for the deuterated polymer (62%) was found to be much higher than that of the nondeuterated polymer (8%). With regard to the tacticity, only for the hexane-insoluble fraction of the deuterated polymer was a higher *mmmm* (88%) obtained, whereas the soluble fractions exhibit similar tacticities.

Since the amount of the active species (complexes **2** and **3**) is independent of the amount of propylene,[10] the distribution of the polymeric fractions obtained in the deuterated polymer indicates that a faster polymerization rate is operative for complex **2**, inducing larger amounts of the isotactic fraction as compared to that of the nondeuterated polymer. The elastomeric fraction that is obtained from complex **3** shows similar rates of insertion for both deuterated and nondeuterated monomers (ri$_H$/ri$_D$ = 1.16), and since β-H elimination was found to be the main termination pathway for this polymeric fraction, a larger ratio among rates of termination is observed (rt$_H$/ri$_D$ = 5.5).[3,14] For the isotactic polymer that is obtained via complex **2**, the rates of insertion and termination for the deuterated monomer
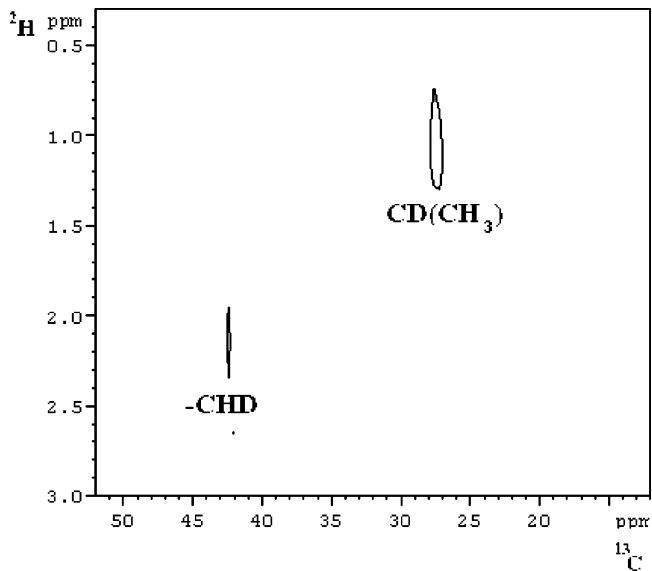

Figure 2. ^{13}C{^{2}H} HETCOR NMR of the hexane-soluble fraction of polypropylene produced by complex **1** at high pressure.

are much higher than those for the regular propylene (ri$_D$/ri$_H$ = 17 and rt$_D$/rt$_H$ = 13).[3]

The faster rate of insertions and terminations for the deuterated monomer can be rationalized by the fact that deuterium is an electron-releasing atom, as compared to hydrogen.[15] Hence, its additional interaction (in addition to the strong metal−carbon double-bond interaction) with the metal in the more confined complex **2** induces the monomer geometrical disposition for a more effective process, as proposed in species **4** and **5** for the
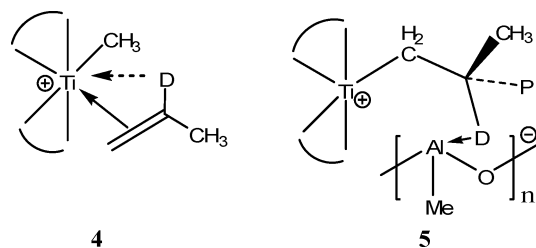
insertion and termination processes. In addition, a larger deuterium interaction (as compared to hydrogen) has been observed for the intramolecular olefin insertion to titanocene complexes activated by MAO.[16] Interestingly, recently we have

(14) From the presented data, no kinetic isotope effects can be estimated, since the calculated rates are based on molecular weights, which are a function of both insertion and termination rates (these are not single elementary steps).

(15) For a theoretical discussion on better deuterium electron-donating properties when attached to sp^2 carbons and their interaction with metals, inducing partial rehybridization from sp^2 to sp^3, see: (a) Halevi, E. A. *Prog. Phys. Org. Chem.* **1963**, *1*, 109. (b) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985; p 38. (c) Streitwieser, A., Jr.; Klein, H. S. *J. Am. Chem. Soc.* **1963**, *85*, 2759.

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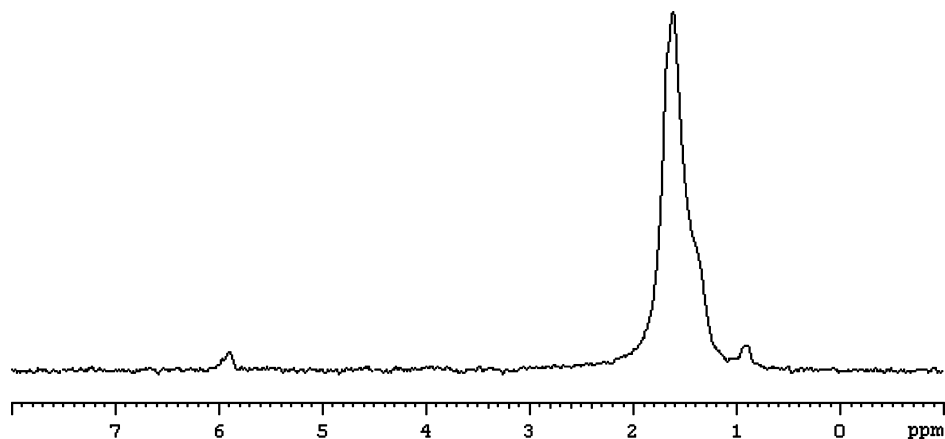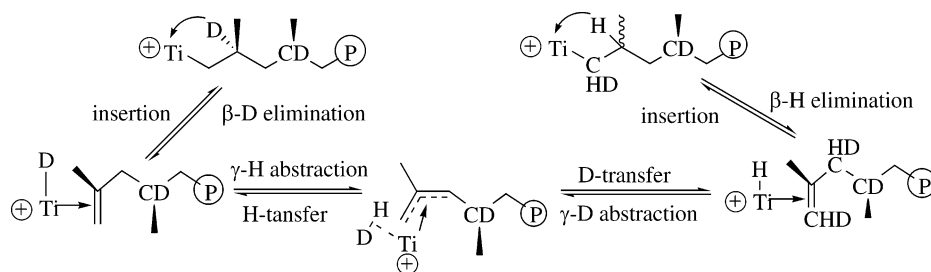
Figure 3. ^{2}H NMR spectrum of deuterated polypropylene, obtained with benzamidinate catalyst.

Scheme 1.   Proposed Mechanism for the Formation of −CH− and −CHD Groups in the Deuterated Polymers

shown that the termination process of the stereoregular polymeric fraction obtained through the active species **2** is predominantly via an aluminum transfer pathway.[10]

To clarify the pathways for the possible formation of stereoerrors, we performed two NMR experiments. In the first experiment we acquired the ^{13}C{^{1}H} spectrum of the deuterated polymer and then, under the same conditions, the corresponding ^{13}C{^{2}H}{^{1}H} spectrum. The difference between the spectra shows the chemical shifts corresponding to deuterated sites in the polymer, even when the spectra were obtained at low concentrations (Figure 1).[17] The second experiment was a two-dimensional ^{13}C−^{2}H HETCOR NMR (Figure 2),[18] employed to corroborate our findings of the first experiment. In addition, ^{2}H NMR, DEPT-45, and^{1}H{^{13}C}-HMQC spectra of all polymers were also acquired and analyzed.

If stereoerrors from Busico's epimerization type would have been operative, we should have expected to observe a signal corresponding to deuterated carbon atoms at 19.8 ppm corresponding to the *mrrm* methyl pentad.[3,14]

Figure 1 shows the ^{13}C{^{2}H}, ^{13}C{^{2}H}{^{1}H}, and difference spectra for the deuterated polypropylene produced by the benzamidinate complex **1** at high pressure, indicating that *Busico's and Resconi's epimerization mechanisms are not operative*. Similar results were obtained for the low-pressure experiments as well. It is important to point out that no epimerization is observed for the hexane-insoluble fraction. The small signal observed at 30.8 ppm is a result of two consecutive 2,1-misinsertions, resulting in only one symmetrical deuterated signal.[3]

These NMR results were corroborated by ^{13}C{^{2}H} HETCOR experiments (Figure 2), also showing no deuterium in the methyl region but, surprisingly, deuterium atoms in the methylene region (CHD), in addition to those expected for the CD(CH$_3$)

moieties. Interestingly, this C−H/C−D exchange was found only for the hexane-soluble polymeric fractions obtained by the active species **3**.

Corroborating these results, ^{2}H NMR of the deuterated polymers (Figure 3) shows a broad signal with two maxima at δ 1.25 and 1.55 ppm, which correspond to the CH*D*CD(CH$_3$)
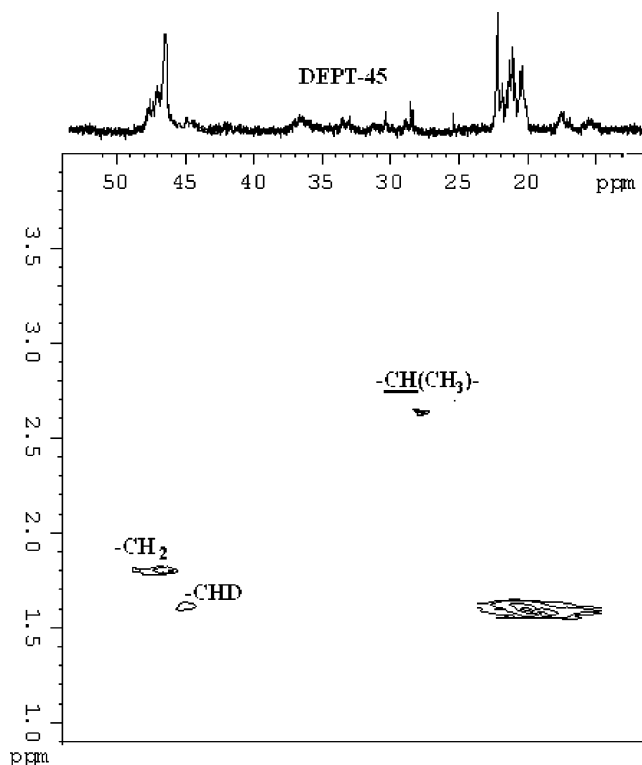

Figure 4. ^{13}C{^{2}H}-HMQC and ^{13}C DEPT-45 spectra of the hexane-soluble fraction of deuterated polypropylene produced by complex **1** at high pressure.

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(17) The scope of the method is presented in the Supporting Information for various deuterated and nondeuterated compounds.

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and C*D*(CH₃) moieties, respectively. In addition, the signals at 0.9 and 5.9 ppm correspond to the saturated and unsaturated chain ends.

Furthermore, the two-dimensional ^{1}H{^{13}C} correlation spectrum (HMQC) (Figure 4) of the hexane-soluble fraction shows two cross-peaks correlated with the same type of carbon signals at the methylene region (C*H*₂ and C*H*D groups) and a nondeuterated methyne group (C*H*(CH₃)), in addition to the methyl correlation.

A plausible CH₂/CHD exchange and a new epimerization mechanism are presented in Scheme 1. The process involves a β-deuterium elimination followed by a rapid γ-hydrogen abstraction (from the methylene group and not from the methyl group, as in Resconi's mechanism[5]), forming the allenic intermediate **6**. This abstraction must be lower in energy as compared to the same γ-H abstraction from the terminal methyl group, presumably due to the formation of the more stable substituted double bond. Deuterium transfer followed by hydrogen transfer leads to the observed exchange and an epimerization of the methyl group. On the basis of the results, we can conclude that the exchange process is much faster by far than the monomer insertion.

In summary, we have presented a new exchange and epimerization pathway responsible for the stereoerror formation in the polymerization of α-olefins promoted by an octahedral benzamidinate complex. Similar deuterium experiments for other octahedral complexes are underway.

Supporting Information Available: Text, tables, and figures giving general procedures, details on the synthesis of deuterated propylene, epimerization mechanisms, equations for the calculation of the rates, and misinsertion scheme. This material is available free of charge via the Internet at http://pubs.acs.org.

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