Elucidation of Substituent Effects in the Polymerization of Propylene Promoted by Titanium Amidinates

Sinai Aharonovich, Mark Botoshansky, Yael S. Balazs, and Moris S. Eisen*

Schulich Faculty of Chemistry and Institute of Catalysis Science and Technology, Technion-Israel Institute of Technology, Kyriat Hata-Noechion, Haifa 32000, Israel

Supporting Information

ABSTRACT: In polymerization reactions, the molecular weight of the polymer depends on the rates of monomer insertion, chain termination, and chain transfer. Here we do present studies indicating why chelating octahedral benzamidinate group IV complexes, which promote the polymerization of propylene with MAO, exhibit a linear free energy relationship with the steric Taft parameter. We correlate that this relationship is encountered with the para substituent of the aromatic ring, far away from the active catalytic site. A number of known events are put together to shed light on the effect of the ancillary ligands in the catalytic polymerization, and a new plausible mechanism for the process is presented.

Polypropylene is among the most commercially important polymers, with a global annual production of ca. $4 \times 10^7$ tons, about 6 kg per capita in 2006, with an additional 17% growth expected until 2020.1 The quest for new polyolefins with valuable physical and mechanical properties has advanced significantly in the last two decades with the development of homogeneous group IV catalysts with, or without, the cyclopentadienyl ligands.1−3 Group IV complexes containing the amidinate ligands (NR1CR2NR3)−, which are well-known for their rich coordination chemistry and the facile tailoring of their electronic and steric properties,4 have been unique as olefin polymerization catalysts.5,6 We have found that in comparison to its phenyl analogue, the bis(p-tolylamidinate)-titanium dichloride produces polypropylene with a higher molecular weight, but with reduced catalytic activity.6 This substituent effect is intriguing because of the remoteness of the para substituent from the active metal center in the κ2-bonded amidinate, which excludes significant steric, inductive, field, or resonative effects (vide infra).

To elucidate the underlying mechanism of the substituent effect, we have prepared a series of seven additional substituted bis(arylamidinate)titanium dichlorides by salt metathesis reactions between TiCl4 and the corresponding lithium amidinates (eq 1).7

In the solid state of complexes 1−9 the titanium center adopts a distorted cis C2 octahedral environment in which two arylamidinate ligands create two nearly orthogonal Ti−N−C−N rings. Further, the near-orthogonality of the aryl ring and the amidinate NCN plane excludes significant resonance effects in the solid state (see Figure 1 for the structure of complex 2, and the Supporting Information for detailed crystallographic data of complexes 4−9).8

After activation with MAO (methylalumoxane) the catalytic systems obtained from complexes 1−9 polymerized propylene into two polymeric fractions (Table 1), separable by ether extraction (the extraction in hexane gives the same results). The ether fraction is obtained as an elastomeric polymer, whereas the ether-insoluble polymer is a solid material with large isotactic domains, as observed in Table 1.

We have shown that the highly stereo- and regioregular solid fraction (ca. 10% of the polymer mass) is produced by a cationic, pseudo-C2-symmetric, bis(κ2-amidinate) alkyl cationic
species, whereas the less stereo- and regioregular elastomeric fraction is produced by the corresponding cationic monoamidinate dialkyl species, which result from in situ ligand metathesis between the bis(amidinate) titanium and MAO aluminum centers. In addition we have shown that if we perform a polymerization with the corresponding cationic monoamidinate dialkyl metal complex, the same results are obtained, indicating the formation of the corresponding cationic bis(amidinate)mono alkyl complex.

If for a certain process with a rate $r$ an isolated substituent (X) effect is operative in the rate-determining step (RDS) itself, or in a pre-RDS step(s) in fast equilibrium with the RDS, log($r(X)/r(H)$) should correlate linearly with the appropriate substituent parameters. Therefore, we calculated for each polymeric fraction (isotactic and elastomeric) the rates for insertion and termination for each complex, $r_i(X)$ and $r_t(X)$, respectively, and normalize them with respect to the same rate obtained for the unsubstituted complex (X = H). These normalized rates, $R_i(X)$ and $R_t(X)$, respectively, were calculated according to eq 2.

$$R_i(X) = \frac{m_{pp}(X) M_n(H)}{m_{pp}(H) M_n(X)} = \frac{R_i(X)}{M_n(X)}$$

Attempts to find a linear free energy relationship (LFER) between various electronic substituent parameters such as $\sigma_P$, $\sigma_{P+}$, $\sigma^*$, $\sigma_P^0$, and others and log $R_i(X)$ or log $R_t(X)$ for both fractions failed. However, unexpectedly, an LFER was found only between log $R_t(X)$ for the elastomeric fraction and the Taft steric parameter $E'_s$ for complexes 1−7 (Figure 2), whereas no correlations were found for the stereoregular fraction. This LFER outstandingly and strongly indicates that the steric bulk of the para substituent hinders the RDS of the termination process for the elastomeric fraction. It is important to point out that the correlation was normalized when different amounts of the active species, for the different complexes, were obtained.

Monitoring the catalytic mixture of complex 2 using $^1$H−$^{13}$C NMR and COSY and characterization of the elastomeric polymer indicates that $\beta$-H elimination is the major operative chain transfer process. Since in the transition state (TS) of this process the minimal distance between the para substituent and the $\alpha$-methylene of the alkyl chain is ca. 6.7 Å in a $\kappa^2$-amidinate (Figure 3), we envisioned that the observed steric...
effect is only possible in a κ₁-syn-bonded amidinate (complex I). This MAO-induced amidinate lability is supported both by its transfer to Al (metathesis; vide supra), and by the polymerization results of the ortho-substituted complexes 8 and 9 (Table 1).\(^8\)

The different activities and polymer properties obtained by the o-OMe benzamidinate complex 8, in comparison to the similar catalytic behavior of the complex p-OMe (2), and the corresponding Et-substituted complexes 9 and 4 can be rationalized by the coordination of the pendant OMe group to the titanium center, which is possible only in complex 8, after the amidinate chelate is opened. Interestingly, a similar opening and tautomerization has been reported for the 2-pyridyl amidinate ligand 15 in its lithium\(^1\) and thorium\(^1\) complexes.

Further support for the opening of the amidinate chelate comes from NOE studies of the catalytic mixture of complex 2.\(^7\) When each of the methoxy, TMS, or MAO methyl signals is selectively irradiated (Figure 4ii−iv, respectively), an NOE is observed for the other two signals.

This NOE agrees with a κ₁-E-syn species in which the OMe···Me-M (M = Si, Ti, Al) distance is less than 5 Å.\(^1\) Further, a lack of direct Al−OMe coordination is also supported by the observed small shielding of the OMe signal in the catalytic mixture vs its complex alone (compare parts i and v of Figure 4). This result is also corroborated by its contrast with the etherate of AlMe3 in C\(_7\)D\(_8\), where the ether methyl signal is deshielded by 0.4 ppm.\(^1\) It is important to point out that in the precatalyst complex no NOE is observed if no MAO is added.\(^2\)

As a plausible mechanism, we suggest that the activation process occurs first by the methylation of the dichlorides 1−7 by MAO and the concomitant amidinate transfer to Al, to produce the monoamidinate titanium trimethyl complex, as shown already (A, Scheme 1).\(^9\) We have already shown that, in the dialkyl or dichloride complexes 1−7, the ligands are dynamic in solution, interconverting between κ₁ and κ₂ conformations; however, no stable isolable η-arene complexes were formed.\(^3\)

Complex A further reacts with MAO and propylene in several steps to produce the cationic κ₁-E-anti monoamidinate species B, which can isomerizes via a C−N bond rotation to the E-syn tautomer C, which can, probably, gain additional stability by the rapid coordination of the titanium center to the aromatic ring. It is important to indicate that if we start from the monoamidinate complex, the exact same results are obtained as we have already indicated for similar systems due to their dynamic behavior.\(^9\)

In these "constrained geometry"-like species, the spatial proximity of the aryl substituent to the cationic titanium center will hinder the polymeric chain from adopting the necessary conformation for the β-H elimination step, or preceding steps, such as β-agostic interactions, to occur (D). The susceptibility of the β-H elimination RDS to relatively small interferences is demonstrated by the living propylene polymerization of the well-known fluorinated FI catalysts, in which the weak F−H−C interactions (27 kJ/mol) are enough to suppress the elimination.\(^3\)

In conclusion, we exploited LFER studies to extract valuable structural clues about the monoamidinate cationic species. The dependence of the β-H elimination rate in these species solely on the steric bulk of the benzamidinate para substituent is corroborated by an opening of the chelating amidinate ligand and, consequently, steric obstruction by the substituent to fast...
pre-RDS stages. The opening of the chelating amidinate is also
supported by the existence of NOEs between the para
substituent, the TMS methyl group, and MAO and by the
unique polymerization behavior of the o-OMe benzamidine
complex.

ASSOCIATED CONTENT

Supporting Information
Text, figures, tables, and CIF files giving experimental
procedures for the preparation of complexes 1−9 and details
on their use as polymerization catalysts at high pressure or
under NMR monitoring conditions, crystallographic data for
complexes 2 and 4−9, and the development of mathematical
expressions for normalized rates. This material is available free
of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author
*E-mail: chmoris@tx.technion.ac.il.

Notes
The authors declare no competing financial interest.

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