Living Polymerization

DOI: 10.1002/ange.200601616

Bimolecular Control over Polypropene Stereochemical Microstructure in a Well-Defined Two-State System and a New Fundamental Form: Stereogradient Polypropene**

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The recent development of transition-metal complexes that can function as catalysts for the stereoselective Ziegler–Natta polymerization of propene has provided a wealth of new polypropene-based materials through extensive manipulations of the ligand environment about the metal center.[1] The currently practiced "one catalyst–one material" strategy, however, has significant disadvantages and practical limitations for fine-tuning physical properties of the polypropene material through minor adjustments about a given microstructure, or for accessing a completely different microstructure altogether. Thus, not only is it a labor-intensive synthetic undertaking to prepare a large variety of catalyst structural variants that may, or may not, yield a desired microstructure but even after several decades of effort the "rational design" of new catalysts that can produce a specific polypropene microstructure is still out of reach; and even more so for non-metallocene-based systems.[2]

Dynamic unimolecular processes that are competitive with propagation, such as site isomerization in structurally constrained C_1-symmetric *ansa*-bridged metallocenes,[3] conformational flexibility in unconstrained "oscillating" metallocenes,[4] and "chain-end epimerization"[5] or ligand-sphere rearrangements in non-metallocenes,[6] can give rise to polypropene materials that display promising technologically desirable properties as the result of varying degrees and patterns of stereoerror incorporation, such as in the case of elastomeric polypropene.[3–6] Owing to the intrinsically low energy barriers associated with these unimolecular processes, however, to date, the only means available by which to exert some level of external control in order to access, to a significant degree, a wider range of microstructures for a given catalyst has been to capitalize on the bimolecular nature of propagation (olefin complexation) by varying propene pressure, and hence the rate of propagation (v_p) versus that of

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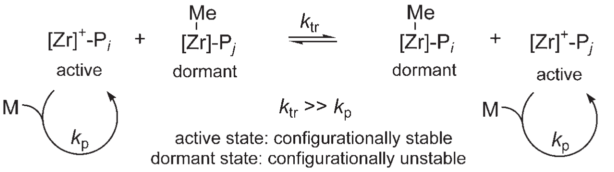
[**] Funding for this work was provided by the NSF (CHE-0092493). We thank the ACS Division of Organic Chemistry for a graduate fellowship (to M.B.H.) sponsored by the Proctor and Gamble Company.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

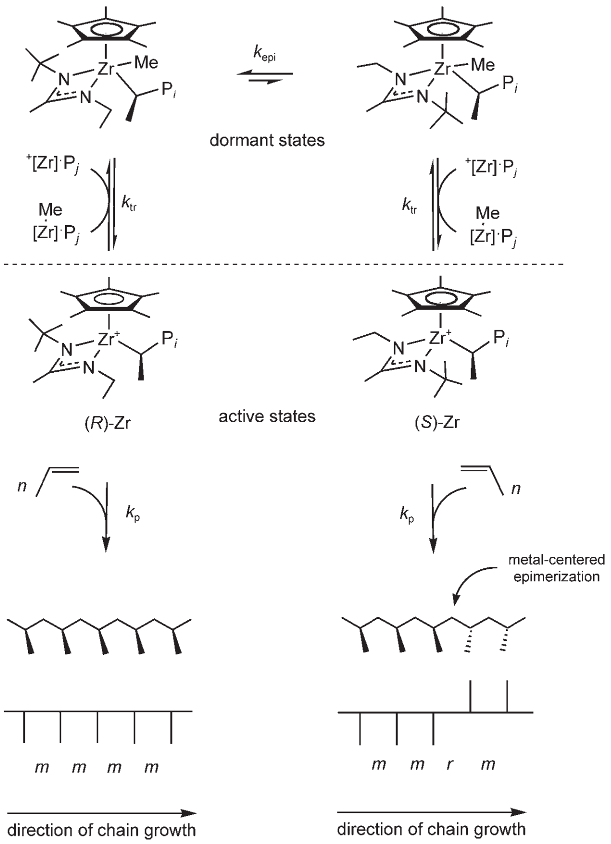
the unimolecular process.[3g] Herein, we now provide a different strategy by which to break the “one catalyst–one material” strategy by documenting control over a dynamic bimolecular process within a well-defined two-state system composed of active (configurationally stable) and dormant (configurationally unstable) centers that interconvert through methyl group exchange. Importantly, as the evolution of microstructure in this system is a function of the frequency with which the growing polymer chain resides in the dormant state, we demonstrate that it is possible to exert an unprecedented level of control in accessing virtually an unlimited number of discrete polypropene microstructures that range from being highly isotactic to atactic as the result of predictable degrees of incorporation of stereoerrors of a known type. By taking advantage of the living nature of propene polymerization in this system, we further demonstrate the ability to overlay both temporal and bimolecular control as a means by which to prepare a fundamental new form, stereogradient polypropene, for which unequivocal proof of stereochemical microstructural homogeneity is presented.

We previously documented that upon full “activation” of the preinitiator, (η^5-C_5Me_5)$ZrMe_2$[N(Et)C(Me)N(*t*Bu)] (**1**), through methyl group protonolysis using a stoichiometric amount of the borate, [$PhNHMe_2$][$B(C_6F_5)_4$] (**2**), the living Ziegler–Natta polymerization of propene and higher α-olefins, such as 1-hexene, is highly isotactic ($mmmm = 0.71$, $\sigma = 0.94$) for the former and isospecific ($\sigma = 1.0$) for the latter.[7,8] At substoichiometric levels of activation (i.e. $[\mathbf{1}]_0/[\mathbf{2}]_0 > 1.0$), propagation still occurs in living fashion, but it now proceeds through the degenerative methyl group transfer process shown in Scheme 1 in which all metal centers, both active and dormant, appear to propagate simultaneously due to the rate of methyl group transfer being much faster than that of propagation, $v_{tr} \gg v_p$.[9,10] These relative rates also ensure that the number-average degree of polymerization (X_n) is a function of only the initial concentration of the preinitiator, not the amount of borate activator employed (i.e. $X_n \approx [M]_0/[\mathbf{1}]_0$), and that the polypropene materials display narrow polydispersities ($D = M_w/M_n$) as $D \approx 1 + (k_p/k_{tr})$ and $k_{tr} \gg k_p$.[11] However, as a result of a dormant state that is configurationally unstable with respect to metal-centered epimerization, which proceeds with a rate that must be faster than both methyl group transfer and propagation (i.e. $v_{epi} > v_{tr} \gg v_p$), an atactic microstructure is produced at 50% activation (i.e. $[\mathbf{1}]_0/[\mathbf{2}]_0 = 2.0$).[8,9,12]



Scheme 1. Living degenerative-transfer Ziegler–Natta polymerization of α-olefins. P_i and P_j refer to growing polymer chains.

A more detailed analysis of stereoerror incorporation that occurs during propagation at substoichiometric levels of activation of **1** by **2** is presented in Scheme 2. Here it can be seen that because monomer enchainment is highly stereoselective for the cationic active sites, the occurrence of an isolated *mmrm* pentad stereoerror[13] is directly traceable to the growing polymer chain having resided in the dormant state, where metal-centered epimerization occurs to provide one of two different diastereomeric propagating centers with equal probability upon exiting back to the active state (see the processes occurring above the dashed line in Scheme 2). Accordingly, by directly manipulating the bimolecular rate of group transfer (v_{tr}) relative to the rate of propagation (v_p), which is pseudo-first order in the presence of a large excess of monomer, and by simply changing either the absolute concentration of all the metal-containing species in solution or the concentration of transferable methyl groups using different levels of substoichiometric activation, it should be possible to influence the frequency of attaining the dormant state, and thereby, the stereochemical microstructure of the growing polymer chain. Gratifyingly, in practice, this proved



Scheme 2. Mechanism of stereoerror incorporation that occurs under living degenerative-transfer conditions. P_i and P_j refer to growing polymer chains, and *m* and *r* denote *meso* and racemic (*rac*) stereochemical relationships, respectively, between adjacent stereocenters of the polymer backbone.[13] Depicted relative and absolute configurational relationships for the metal centers and the polymer chains are for illustrative purposes only.

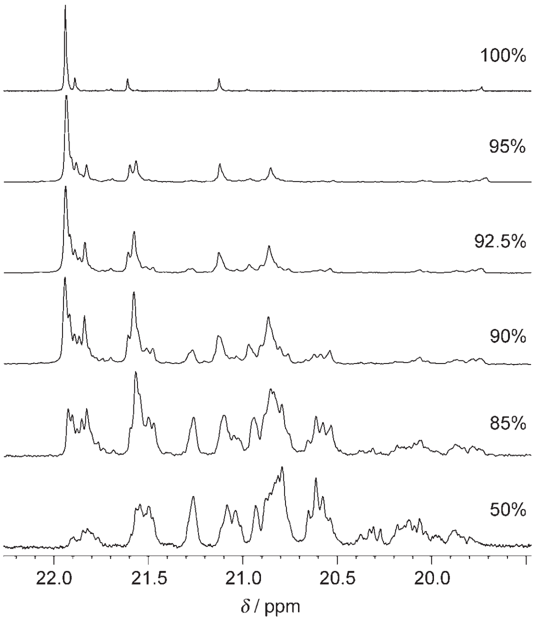


Figure 1. $^{13}C\{^1H\}$ NMR (125 MHz, 1,1,2,2-$C_2D_4Cl_2$, 70 °C) spectra of the methyl region of polypropene obtained as a function of % activation of **1** by **2**. Note that the spectra are shown with increasing arbitrary *y* scaling (top to bottom) for the sake of clarity (polymerization conditions: 34.5 kPa propene, −10 °C, C_6H_5Cl, $[\mathbf{1}]_0=2.5$ mM).

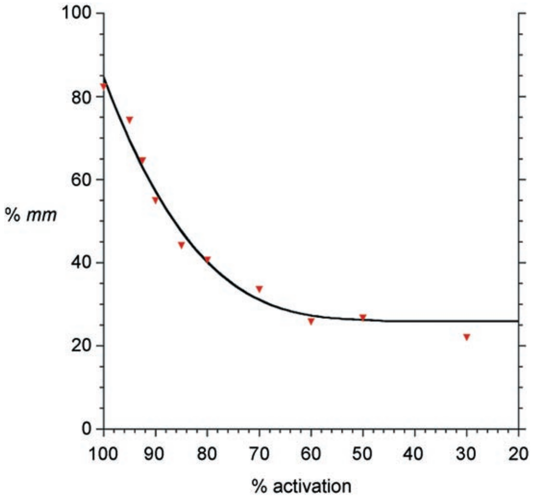


Figure 2. % *mm* (at the triad level of ^{13}C NMR stereoerror analysis) of the ^{13}C NMR spectra of Figure 1 and other polypropene materials obtained as a function of % activation under the same polymerization conditions.

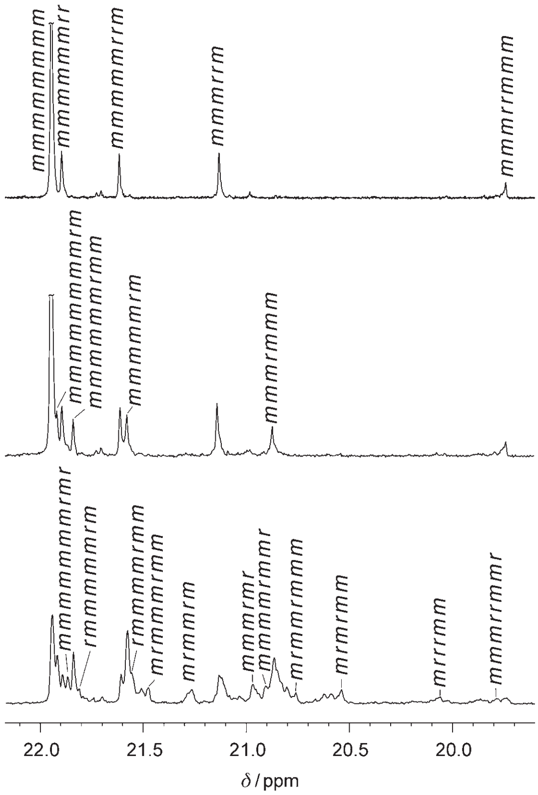


Figure 3. ^{13}C NMR spectra from Figure 1 showing partial heptad and higher level stereoerror assignments for the methyl region of polypropene obtained as a function of % activation of **1** (top to bottom: 100, 95, and 90%). Note that at 100% activation the nature of the stereoerrors are consistent with exclusive enantiomorphic site control of propagation.[1b]

to be the case as observed by the series of ^{13}C NMR spectra for the methyl region of the polypropene materials shown in Figure 1 in which the highly isotactic microstructure obtained at 100 % activation is transformed to an atactic one by simply decreasing the level of activation. In Figure 2, the % *mm* stereochemical triad content is plotted as a function of % activation and better illustrates the rate and nonlinear fashion in which this transformation occurs. Furthermore, a preliminary stereochemical analysis of these spectra at the heptad and higher level of analysis (Figure 3) is consistent with the expected decrease in isotactic sequence length with a decrease in % activation due to an increasing incorporation of isolated *mr* triad stereoerrors that arise as the result of epimerization of the propagating center according to Scheme 2. Confirmation of this mechanism of stereoerror incorporation is of significant importance in that, until now, it has only been possible to introduce varying amounts of *rr* triad stereoerrors as a means of controlling polypropene isotacticity by manipulating the degree of stereoselectivity for propene enantioface complexation and subsequent insertion.[1d] While propagation by a "chain-end control" mechanism that is dictated by the growing polymer chain can give rise to the type of isolated *mr* pentad stereoerror observed here,[1b] no clear means exist by which one could conceivably manipulate, over a wide range, the degree of chain-end control through modification of the ligand sphere of the catalyst. Accordingly, our demonstrated approach to introduce varying levels of *mr* triad stereoerrors in simple fashion by using only a single catalyst is not only unique but the range of new polypropene materials that are now obtainable by this process may exhibit technologically desirable physical properties. Finally, although not presented here, in preliminary investigations we have been able to demonstrate that for a given level of % activation, another level of bimolecular control (i.e. "fine-tuning") about a particular microstructure can be achieved by simply varying solvent volume, and hence, the absolute concentrations of the active and dormant species. As expected, isotacticity increases as the concentrations of these species decrease.

In addition to providing an unprecedented level of control over *mr* stereoerror incorporation, the present bimolecular control of stereochemical microstructure can be used to prepare a new fundamental form, stereogradient polypropene, by simply varying the concentration of the dormant species as a function of time. Importantly, this stereogradient polypropene can only be produced by using a living system, as chain-transfer that occurs in nonliving systems would produce stereochemical heterogeneity within the final isolated material. As a proof of concept, after an initial 30 min period of atactic chain growth at 60% activation, a programmable syringe pump was used to steadily increase the level of activation to a final 100% by introducing an additional 0.5 equiv of the borate **2** as a function of time (see Figure 4A). To unequivocally establish both the stereogradient nature and the stereochemical homogeneity of the final material, pre-initiator **1**, with ^{13}C(99%)-labeled methyl groups, was used to place a ^{13}C-labeled methyl end group at the beginning of polymer chain growth. Aliquots were then taken as a function of time, and ^{13}C NMR spectra were obtained for the isolated materials, a selection of which are shown in Figure 4B. By using the ^{13}C-labeled methyl end group resonances that appear between $\delta = 22.5$–23.0 ppm (not shown) as an internal reference, difference ^{13}C NMR spectra were produced (Figure 4C) which confirmed that chain growth steadily changes from being completely atactic to being highly isotactic as a function of time. Importantly, with additional aliquots and difference spectra it was possible to demonstrate that the % *mmmm* content of the material closely tracks the ramp profile for addition of **2** (see red shading in Figure 4A). Thus, by programming different ramp profiles, together with reversing the direction of the ramp through addition of a recently reported reagent that can be used to selectively methylate cationic propagating centers so as to increase the concentration of dormant states (i.e. to essentially "lower" the level of activation),[8] an infinite variety of new stereogradient polypropene materials can be envisioned and prepared.

In summary, by taking advantage of the bimolecular nature of degenerative-transfer living Ziegler–Natta polymerization, we have demonstrated that an intrinsic configurational instability of the dormant state can be harnessed to produce an unlimited variety of new polypropene materials from a single catalyst. The strategy presented here should also be readily transferable to other catalyst systems (e.g. those that are syndioselective at 100% activation), thereby expanding even further the range, and possibly the future, of polypropene-based commercial products.

Received: April 24, 2006

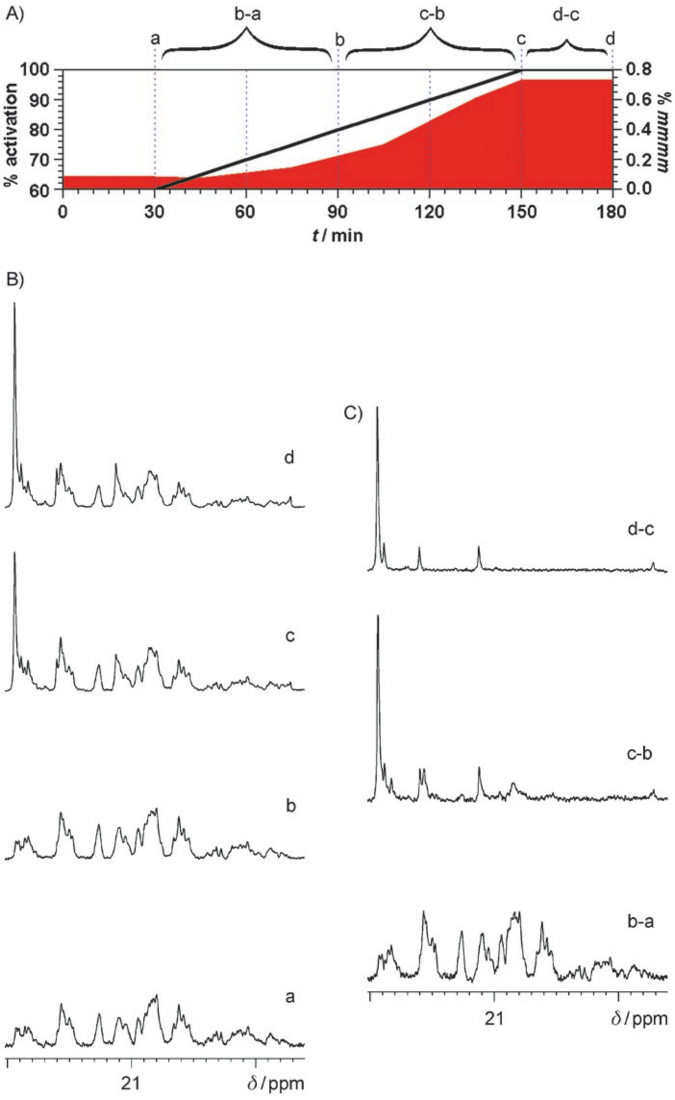


Figure 4. A) Ramp profile (black line) for addition of 0.5 equiv of **2** to change the level of activation from 60% to 100% and % *mmmm* content as a function of time (red shading) as determined from: B) ^{13}C NMR (125 MHz, 1,1,2,2-$C_2D_4Cl_2$, 70 °C) spectra (for the methyl region of polypropene) of aliquots taken as a function of time, and C) their difference spectra using the resonances (not shown) of a ^{13}C(99%)-labeled methyl end group as an internal reference.

Keywords: block copolymers · polymerization · polypropene · thermoplastic elastomers · Ziegler–Natta polymerization

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