

Optical Purity as a Programmable Variable for Controlling Polyolefin Tacticity in Living Coordinative Chain Transfer Polymerization: Application to the Stereomodulated LCCTP of α,ω -Nonconjugated Dienes

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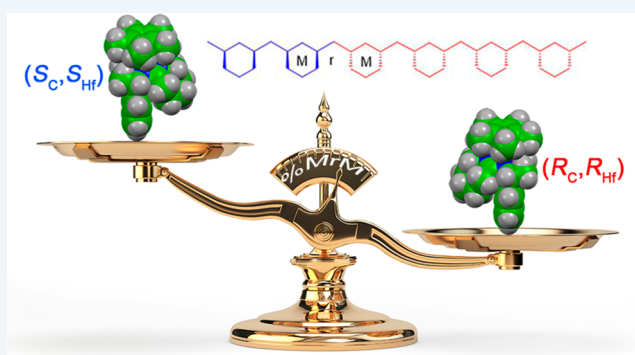
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ABSTRACT: Two-state, stereomodulated living coordinative chain transfer polymerization (LCCTP) of 1,6-heptadiene has been achieved to produce a series of *cis*-poly(methylene-1,3-cyclohexane) (*cis*-PMCH) with stereochemical microstructures that vary between two limiting forms as a function of the optical purity of the chiral C_1 -symmetric hafnium preinitiator **1** when activated by the borate co-initiator **B1** in the presence of a fixed excess amount of $ZnEt_2$. Optical purity as a programmable variable was demonstrated by premixing the pure homochiral (S_C, S_{Hf}) and (R_C, R_{Hf}) enantiomers of **1** in different ratios prior to activation. In contrast, the LCCTP of 1,5-hexadiene using a “racemic” mixture of **1** to produce *cis/trans*-poly(methylene-1,3-cyclopentane) (*cis/trans*-PMCP) was less successful due to the loss of stereocontrol for insertion under chain transfer conditions that arises with site epimerization at the transition metal center. A correlation is proposed between the diastereoselectivity and efficiency for the cyclization step in propagation and the magnitude of site epimerization due to reversible chain transfer. These results serve to validate the strategy of using the optical purity of an initiator as a programmable parameter for controlling polyolefin tacticity as well as to better establish the criteria that are required for achieving successful stereomodulated LCCTP for the production of next generation polyolefin materials.

KEYWORDS: tacticity, asymmetric, living, chain transfer, polymerization, polyolefin



One of the most remarkable features of polyolefins, which are manufactured on a colossal global scale each year through the transition-metal-mediated (coordinative) polymerization of ethene, propene, and higher-carbon-numbered linear and branched α -olefins, is that a wide variety of different “grades” can be produced that possess identical chemical compositions and molecular weight profiles but that differ greatly with respect to bulk physical properties.¹ For many of these materials, the unique structural feature that dictates the variation in properties can be traced back to differences in stereochemical microstructure, or tacticity.² For instance, while highly stereoregular *isotactic* polypropylene (PP) is a highly crystalline, high melting thermoplastic, *atactic* PP, in which the relative configurations of adjacent stereocenters are now completely randomized, is an amorphous, soft rubbery material.³ Importantly, in between these two limiting microstructures, there exists a continuum of PP materials that can display either subtle or dramatic changes in bulk physical properties as the level of incorporation of stereoerrors increases. Accordingly, after more than 60 years since the first introduction of the concept of polymer stereochemical

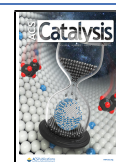
tacticity by Natta and co-workers,³ there still remains intense academic and industrial interest in the discovery and development of new types of transition-metal catalysts and polymerization processes that can provide controlled access to entirely new stereochemical grades of polyolefins.^{2,4–6} Herein, we now introduce the concept and experimental validation of “two-state” stereomodulated living coordinative chain transfer polymerization (LCCTP) that relies on the optical purity of a single configurationally stable, chiral transition-metal initiator as a programmable variable that can be used to rapidly access a continuum of stereochemical microstructures that exist between two limiting forms.^{6–8}

Scheme 1 provides a mechanistic comparison of our previously reported two-state stereomodulated living coor-

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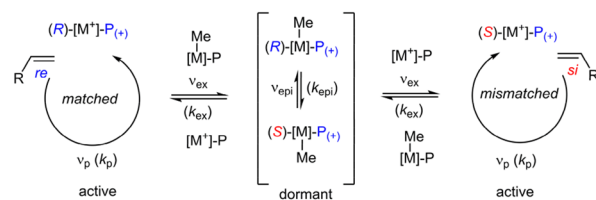
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Scheme 1. Mechanistic Comparison of Stereomodulated Two-State Living Coordinative Polymerization (LCP) vs Two-State Living Coordinative Chain Transfer Polymerization (LCCTP)^a

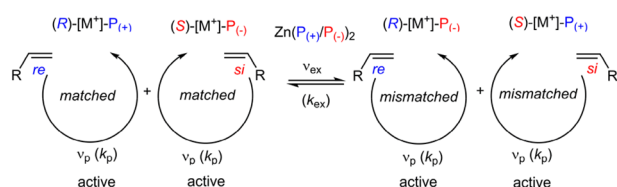
Two-State Stereomodulated LCP: $\nu_{\text{epi}}(k_{\text{epi}}) > \nu_{\text{ex}}(k_{\text{ex}}) \gg \nu_p(k_p)$



$$\% r \text{ stereoerror in } (m)_x m m m m (m)_y \propto [\text{dormant}] \propto (\% \text{ activation})^{-1}$$

external control

Two-State Stereomodulated LCCTP: $\nu_{\text{ex}}(k_{\text{ex}}) \gg \nu_p(k_p)$



$$\% r \text{ stereoerror in } (m)_x m m m m (m)_y \propto \frac{(R)-[M^*]-P(+)}{(S)-[M^*]-P(-)} \propto \text{optical purity (e.e.)}$$

external control

^a(R)- and (S)-labels denote absolute chirality of the transition-metal center, P(+) and P(-) denote the absolute chiral “handedness” of the isotactic polyolefin chain, and *re* and *si* denote the prochiral faces of an α -olefin.

inative polymerization (LCP) with the new strategy of two-state stereomodulated LCCTP for the “stereoengineering” of polyolefin microstructures.^{5,6c,d,7} As can be seen, both processes share the common feature of introducing *racemic* (*r*) dyad stereoerrors into an *isotactic* (*m*)_x *mmmm*(*m*)_y sequence of *meso* (*m*) dyads of a growing polyolefin chain with a specific “handedness” that is defined by a chiral C₁-symmetric propagator with a single coordination site that is “matched” for one of the enantiofaces (*re* or *si*) of the α -olefin.⁹ In a typical highly isoselective polymerization using chiral, but racemic, configurationally stable catalysts or initiators, cryptochirality¹⁰ that exists as the result of (pseudo) mirror plane symmetry for *isotactic* chains of sufficient length will effectively negate any impact that optical purity of the propagator has on the physical properties of the final polyolefin product.¹¹ However, for two-state stereomodulated LCP, the origin of *r* stereoerrors can be traced back to rapid and reversible *methyl group* exchange that occurs between a population of configurationally stable, cationic active propagators and a population of configurationally unstable, neutral dormant species that undergo metal-centered epimerization with a rate and rate constant, $\nu_{\text{epi}}(k_{\text{epi}})$, that is greater than those for group exchange, $\nu_{\text{ex}}(k_{\text{ex}})$, and with both of these being far greater in magnitude than the kinetic parameters for propagation, $\nu_p(k_p)$. In the absence of chain termination, this condition establishes the two-state system in which methyl group exchange involving a dormant state can regenerate an active propagator of either absolute configuration that is then matched or mismatched with respect to *isotactic* chain handedness with equal probability in the limit of no chain-

end control affecting diastereoselectivity. It is the subsequent insertion of the next α -olefin monomer with the “mismatched” active species that introduces the *r* stereoerror. Importantly, the probability of *r* stereoerror incorporation is proportional to the concentration of dormant states, which is, in turn, proportional to the concentration of transition-metal bonded methyl groups in the system at any given time. At the start of two-state stereomodulated LCP, this variable can be easily set by varying a substoichiometric amount of the “activating” borate co-initiator, [PhNHMe₂][B(C₆F₅)₄] (**B1**), that converts the chiral (but racemic), configurationally unstable C₁-symmetric cyclopentadienyl amidinate (CPAM) zirconium preinitiator, (η^5 -C₅Me₅)[N(Et)C(Me)N(^tBu)]ZrMe₂ (**I**), into the corresponding configurationally stable ion-pair initiator, {(η^5 -C₅Me₅)[N(Et)C(Me)N(^tBu)]Zr(Me)}[B(C₆F₅)₄] (**II**).^{6a,c,d,7} A unique twist to this correlation between the frequency of *r* stereoerror incorporation and percent activation is that temporal control over [Me] can also be used as a design tool for the production of unique stereochemical microstructures, such as well-defined *isotactic-atactic* stereoblock and stereogradient PP.^{6c,d}

For the proposed new two-state stereomodulated LCCTP process that is presented in Scheme 1, a *r* stereoerror now arises from a reversible *polymeryl* group (chain transfer) between the two configurationally stable enantiomeric forms of a chiral C₁-symmetric propagator. As shown, each of these are matched for a given enantioface of the α -olefin. Under rapid and reversible Zn-mediated chain transfer, the probability that a mismatched propagator will insert the α -olefin with the wrong handedness increases as the optical purity of the initiator decreases. When using optical purity as a controlling variable, it is most convenient if each enantiomer of a chiral configurationally stable preinitiator can be obtained in pure (homochiral) form, and then enantiomeric excess (ee) can be simply adjusted by premixing the two in desired ratios prior to activation.

Both two-state stereomodulated LCP and LCCTP can be described as degenerative transfer living polymerizations.¹² Accordingly, for $\nu_{\text{ex}}(k_{\text{ex}}) \gg \nu_p(k_p)$, fast reversible exchange occurs and all active and dormant states appear to propagate at the same rate to provide a tunable degree of polymerization (DP_n) and very narrow molecular weight distribution, as characterized by a polydispersity index, *D*, of ≤ 1.1 .¹³ Further, given the living character, each can provide well-defined polyolefin block copolymers through the sequential addition of monomers. In the case of stereomodulation, the absence of irreversible chain termination is critically important for providing a polyolefin product that is *stereochemically homogeneous* since all the growing chains are subject to the same probability of stereoerror incorporation at any moment of time. This connection between living character and homogeneity cannot be overemphasized enough, as it not only permits the successful design and production of unique stereochemical forms but also opens the door to new scientific and technological innovations, such as the electrospinning of thermoplastic elastomer fibers from nonfractionating solutions of *isotactic-atactic* stereoblock PP.¹⁴

The key advantage of LCCTP is that it provides a work-around solution to the “one-chain per active site” limitation of LCP by placing the practicality of scale up on the cost and availability of an inexpensive commodity metal alkyl, such as diethylzinc (ZnEt₂), triethylaluminum (AlEt₃), or a mixture of both.⁸ Thus, practical quantities (from grams to kilograms to

kilotons) of a wide variety of fundamentally new polyolefins can be obtained, and in this regard LCCTP is ideally suited for the large scale production of low to very low DP_n values. Further, reactive quenching of LCCTP by the addition of simple chemical reagents that cleave the transition-metal and main-group-metal–polymeryl bonds provides access to a wide variety of end-group-functionalized poly(α -olefin)s (x-PAOs).¹⁵ The ability to now design x-PAOs with a range of different occupied free volume profiles through judicious selection of the DP_n value in combination with the steric demands of a particular side chain is providing opportunities to explore the self-assembling behavior and nanostructures of new classes of polyolefin-based materials.¹⁶ Finally, as shown in Scheme 1, stereomodulated LCP requires partial activation and therefore the overall apparent rate of polymerization can decrease with low levels of activation due to a fewer number of active sites, and molecular weight distributions can broaden due to bimolecular association of active and dormant species through bridging methyl group interactions that reduce ν_{ex} relative to ν_p .^{12,13} For all of these reasons, the experimental validation of stereomodulated LCCTP as envisioned by Scheme 1 would be beneficial to the further advancement of polyolefin materials that realistically must all come from a very limited pool of industrially relevant olefin feedstocks.

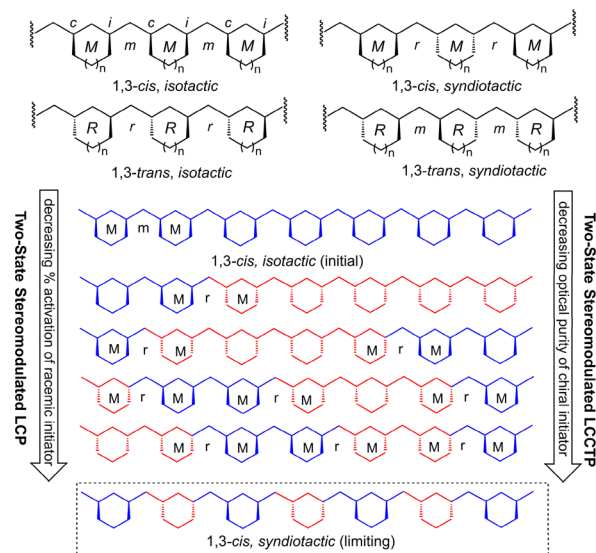
To the best of our knowledge, the only experimental support for the proposed mechanism of two-state stereomodulated LCCTP is a preliminary report by Busico and co-workers¹⁷ from 2007 in which it was shown by ¹³C NMR spectroscopy that an *isotactic* stereoblock microstructure for PP is produced from the *nonliving* coordinative chain transfer polymerization of propene when a racemic mixture of a C_1 -symmetric, chiral pyridyl-amide hafnium precatalyst (ee = 0%) is activated by excess equivalents of trimethylaluminum (AlMe₃)-modified methylaluminoxane (MAO) as a cocatalyst. When the same propene polymerization was conducted under identical chain transfer conditions using an enantiomerically pure (ee = 100%) sample of the same precatalyst, a similar ¹³C NMR analysis of the isolated *isotactic* PP now revealed that resonances for the $(m)_x(r)_y$ stereoerrors had been eliminated. However, no mention was made by these authors of using optical purity as a programmable factor for varying stereochemical tacticity between these two limits, and the stereochemical heterogeneity of the PP materials that are produced under the *nonliving* conditions of this system would have thwarted the effort. Given the C_1 -symmetry of the propagators involved in this system, it is notable that the study was also silent on the question of stereoselectivity for insertion being affected by either site epimerization of the transition-metal center,¹⁸ or reversible chain transfer, i.e. does it proceed with inversion or retention of stereochemistry? Finally, it is telling that in the more than 13 years since this publication appeared, and even longer since enantiopure, configurationally stable C_2 -symmetric *ansa*-bridged metallocenes were first documented as catalysts for stereoselective α -olefin polymerization,¹⁹ no follow up report has appeared to either suggest or probe the validity of the proposal for two-state stereomodulated LCCTP by the larger academic and industrial polyolefin communities.²⁰

In addition to having a robust and versatile homochiral transition-metal initiator for investigating stereomodulated LCCTP according to Scheme 1, there is also the very important question of which α -olefin monomer should one use. Propene polymerization has the advantage that a wealth of mechanism/microstructure correlations for PP have already

been established using ¹³C NMR analysis of the unique resonances arising from different stereochemical sequences that further benefit from reasonable chemical shift dispersion at the pentad, heptad, and higher levels.^{2,21} However, there are several advantages to working with a nongaseous olefin monomer under conditions in which temperature, pressure, and concentration of reactants can all be tightly and reproducibly controlled. This advantage is amplified for some stereoselective α -olefin polymerizations in which less than ideal regioselectivity for chain enchainment occurs and competing irreversible processes exist that introduce structural complexity that cannot be easily accounted for, such as in the case of propene polymerization where chain-walking and chain-end stereocenter epimerization have been shown to occur under low monomer concentration.^{22,23} Finally, the polyolefin product must be amenable to ¹³C NMR stereochemical microstructure analysis that can allow specific conclusions regarding mechanism to be reached based on literature precedent. Unfortunately, from the vast number of polyolefins derived from an α -olefin other than propene, the list of candidates meeting all these requirements is next to nil.

Poly(methylene-1,3-cycloalkane)s are obtained from the highly regioselective coordinative cyclopolymerization of α,ω -nonconjugated dienes.^{24–27} As Scheme 2 reveals, the stereo-

Scheme 2. Stereoengineering of PMCH Microstructure



chemical microstructures of these materials are more complex by virtue of two stereodefining steps that are involved in propagation. The first step is entioface complexation and migratory insertion (*i*) of the α -end of the diene that establishes the relative configuration of every other stereocenter in the microstructure or, formally, overall tacticity. The stereoselectivity of this step can be quantified by the parameter $\alpha = k_{si}/(k_{si} + k_{re})$, where k_{si} and k_{re} are the rate constants for insertion of the *si* and *re* faces of the α -olefin, respectively. The next step in propagation is cyclization (*c*) involving the ω -end of the diene and this proceeds with a *cis/trans* diastereoselectivity that can be quantified by a second parameter, $\sigma = k_{cis}/(k_{cis} + k_{trans})$, where k_{cis} and k_{trans} are the rate constants for *cis* and *trans* ring closure, respectively. The magnitudes of α and σ are governed by the nonbonded steric environment of the supporting ligand, at least in the well-studied case of the

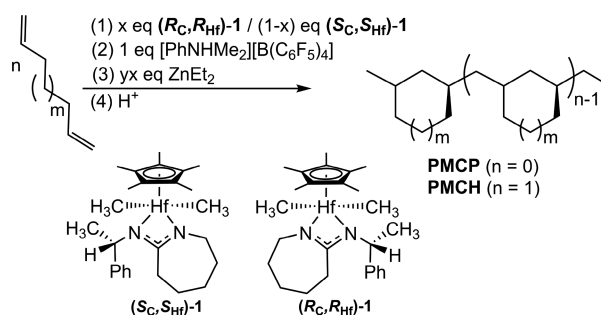
coordinative cyclopolymerization of 1,5-hexadiene to provide poly(methylene-1,3-cyclopentane) (PMCP). For a wide variety of transition-metal catalysts and initiators, high isoselectivity for insertion and relatively poor diastereoselectivity for cyclization is observed, and it is common to obtain 1,3-*cis/trans*, *isotactic* PMCP. Poor diastereoselectivity appears to go hand-in-hand with inefficient cyclization that can also provide 1–2% of pendant ω -butenyl side chains that arise through 1,2-entrainment of 1,5-hexadiene. In contrast, the few reports of the coordinative cyclopolymerization of 1,6-hexadiene that have appeared all present results showing a very high degree of isoselectivity for insertion and a high degree of *cis*-diastereoselectivity for cyclization to provide highly crystalline, 1,3-*cis*, *isotactic* poly(methylene-1,3-cyclohexane).^{24j,k,26b} Although it has not yet been computationally investigated, it is possible that the very high σ values in these cases are due to the longer α,ω -diene chain length that can more easily accommodate finding a single favored (lower energy) bicyclic transition state for cyclization vis-à-vis the more geometrically constrained transition state for 1,5-hexadiene coordinative cyclopolymerization in which small differences in multiple higher energy transition states exist. As a further consideration, Scheme 2 also presents the nomenclature that is useful for cataloging differences in stereochemical microstructures. To begin, it is convenient to use the *meso* (*m*) or *racemic* (*r*) labels to keep track of the relationship between adjacent stereocenters on two different cycloalkane rings, while *M* and *R* correspond to the respective *cis* and *trans* stereochemical relationships of adjacent stereocenters within each cycloalkane. The eight stereochemical tetrads arising from possible relative configurations of the four stereocenters of a sequence of two repeat units can then be uniquely classified as MmM (1,3-*cis*, *isotactic*), MrM (1,3-*cis*, *syndiotactic*), RrR (1,3-*trans*, *isotactic*), and RmR (1,3-*trans*, *syndiotactic*) for the limiting forms shown in Scheme 2. The remaining four possible tetrads that arise with *cis/trans* mixtures are then given as MmR, MrR, RmM, and RrM and are not shown. Most importantly, the stereochemical microstructures of PMCP and PMCH are both amenable to ¹³C NMR analysis, and in the case of PMCP this has included a quantitative determination of values for both α and σ at the tetrad level for different systems.^{25b,d,g} As a final consideration, the enantioselective coordinative polymerization of 1,5-hexadiene to yield optically active PMCP is well predated.^{25,27} According to Scheme 2, only the 1,3-*trans*, *isotactic* microstructure lacks mirror plane symmetry and is, therefore, chiral and can give rise to optical activity. In practice, however, as long as the *isotactic* criterion is met, a range of *cis/trans* ratios for PMCP have been shown to support optical activity due to the presence of an overall global noncentrosymmetry of each polymer chain.

The above discussion suggests that an investigation of the two-state stereomodulated LCCTP of α,ω -nonconjugated dienes has considerable merit. We also have a long-standing interest in using (stereomodulated) LCP that is based on our family of CPAM group 4 metal initiators to further the development of PMCP and PMCH materials. This includes the design and production of well-defined polyolefin block copolymers in which the conformational asymmetry provided by PMCP and PMCH domains drives microphase segregation in the condensed state to provide a variety of nanostructured morphologies, which, in the case of PMCH, are excellent high- T_g thermoplastic elastomers.^{26a,d} Both 1,5-hexadiene and 1,6-

heptadiene can also be obtained from abundant and inexpensive ethene through existing or proposed and validated industrially relevant processes, thereby ensuring long-term supply security. Finally, we have previously investigated the stereoengineering of the microstructure of *cis*-PMCH by our two-state stereomodulated LCP process employing **I** that is activated by varying substoichiometric equivalents of **B1**.^{26b} As shown in Scheme 2, it can be predicted that the outcome of this process is that the frequency of MrM tetrads will increase as percent level of activation decreases but that the limiting 1,3-*cis*, *syndiotactic* microstructure can never be reached. In practice, this is exactly what was verified. Most importantly highly crystalline, 1,3-*cis*, *isotactic* PMCH, which has a high melting temperature, T_m , of 208 °C but very slow crystallization kinetics as well as a high glass transition temperature, T_g , of 100 °C, can be converted by a low level of MrM stereoregulation into a much more tractable and processable amorphous material that retains the same technologically useful high T_g . However, all these intriguing new PMCP and PMCH materials can only be obtained in very limited quantities in the absence of stereomodulated LCCTP.

In a preliminary study, we demonstrated some time ago that the LCCTP of 1,5-hexadiene to provide PMCP was achievable using a C_2 -symmetric CPAM Hf initiator.^{8b} We have also just very recently reported the first example of *enantioselective* LCCTP using the readily available, optically pure (homochiral), and configurationally stable C_1 -symmetric caproamidinate hafnium preinitiators, (S_C,S_{Hf})- and (R_C,R_{Hf})-**1** that are shown in Scheme 3.^{27,28} Importantly, in the case of 1,5-

Scheme 3. Stereomodulated Living Coordinative Chain Transfer Cyclopolymerization of 1,5-Hexadiene and 1,6-Heptadiene



hexadiene, optically active *cis/trans*, *isotactic* PMCP materials were obtained of either handedness when the LCCTP of this monomer was conducted using either (S_C,S_{Hf})- or (R_C,R_{Hf})-**1** after activation by addition of 1.1 equiv of the borate co-initiator **B1** in the presence of a fixed stoichiometric excess of $ZnEt_2$. Further, when this LCCTP process is quenched by the addition of molecular iodine (I_2), practical quantities of optically active, iodo-terminated *cis/trans*, *isotactic* PMCP are produced. With these results in hand, we now have a system to test the validity of two-state stereomodulated LCCTP as conceived and as applied to the stereoengineering of both PMCP and PMCH. Fortunately, for the latter, we already have a library of materials by which to compare the expected outcome of stereochemical microstructure manipulation (see Scheme 2).

Homochiral and enantiopure (S_C,S_{Hf})-**1** and (R_C,R_{Hf})-**1** were prepared according to the previously published procedures,^{27,28} and different levels of optical purity (ee)

Table 1. LCP^a and LCCTP^b of 1,5-Hexadiene (HXD) and 1,6-Heptadiene (HPD) with Different Enantiomeric Excess (ee) Values for **1**

run	(<i>R_CR_{Hf}</i>)-/(<i>S_CS_{Hf}</i>)- 1	ee	diene (equiv)	ZnEt ₂ (equiv)	<i>t_p</i> (h)	yield (g)	<i>T_g</i> (°C) ^c	<i>T_m</i> (°C) ^c	<i>M_n</i> (kDa) ^d	<i>M_w</i> (kDa) ^d	<i>D</i> ^d	ref
1	0:100	100	HXD (100)	0	21	1.04	−5.52	97.5	16	17.6	1.09	27
2	0:100	100	HXD (486)	10	25	1.35	−48.0	64.1	3.8	4.3	1.12	27
3	50:50	0	HXD (912)	10	24	1.98	−24.8	84.8	7.5	9.2	1.22	
4	100:0	100	HPD (83)	0	20	0.30	96.1	166.3	8.6	11	1.29	
5	100:0	100	HPD (416)	10	24	1.20	62.3		2.1	2.5	1.19	
6	90:10	80	HPD (236)	5	24	0.69	64.4		2.0	2.4	1.20	
7	80:20	60	HPD (236)	5	24	0.80	70.3		2.2	2.7	1.22	
8	70:30	40	HPD (236)	5	24	0.79	66.1		2.0	2.4	1.21	
9	50:50	0	HPD (236)	5	24	0.81	61.3		2.1	2.4	1.22	

^aLCP performed using 44 μmol of **1** in 7 mL of PhCl at −5 °C. ^bLCCTP performed using 44 μmol of **1** in 7 mL of toluene at −5 °C. ^cDetermined by DSC. ^dDetermined by GPC.

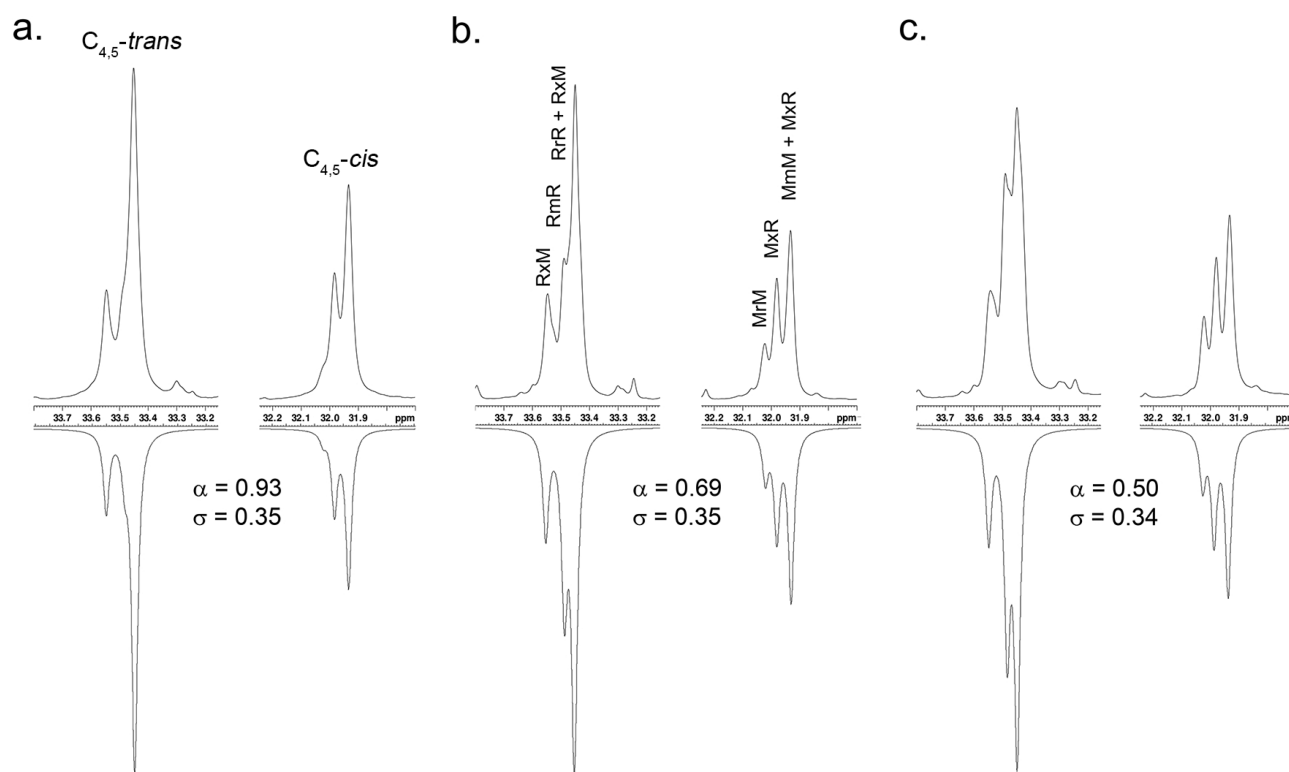


Figure 1. Selected portions of ¹³C{¹H} NMR (100 MHz, CDCl₃, 25 °C) spectra showing only the C_{4,5}-trans and C_{4,5}-cis resonances for PMCP obtained from (a) run 1, (b) run 2, and (c) run 3 of Table 1. In each section, the experimental data are provided on top while the mirrored data is the corresponding simulated spectra obtained from a tetrad analysis using the optimized α and σ parameters provided (line width set at 2.5 Hz).²² Tetrad labels provided in (b) are based on previous reported assignments.^{10b}

were established by mixing measured quantities of these two enantiomers together prior to performing the LCP and LCCTP of 1,5-hexadiene and 1,6-heptadiene according to the conditions presented in Table 1.²⁹ Also provided in this compilation are the relevant analytical and spectroscopic characterization data for the series of PMCP and PMCH materials that were obtained. Thus, to begin, the previously reported results for the LCP and LCCTP of 1,5-hexadiene using enantiomerically pure (*S_CS_{Hf}*)-**1** to produce optically active (+)-PMCP are reproduced in runs 1 and 2 of Table 1. These materials are included as benchmarks against which the microstructure of the PMCP that was now obtained from 1,5-hexadiene using a mixture of equal amounts of (*S_CS_{Hf}*)-**1** and (*R_CR_{Hf}*)-**1** (ee = 0%) under LCCTP conditions with 10 equiv of ZnEt₂ according to run 3 can be compared.

Figure 1 provides the results of quantitative ¹³C{¹H} NMR (100 MHz, CDCl₃, 25 °C) stereochemical analysis of the C_{4,5}-cis and C_{4,5}-trans resonances of these three materials at the tetrad level, along with the corresponding simulated spectra that were generated using the optimized α and σ parameters in each case.^{29,30} As can be seen, the diastereoselectivity for cyclization is poor in each case, with a σ value of about 0.35 that is typical for many reported catalysts. What is of significant interest is the high degree of isoselectivity (α = 0.93) that was achieved for the LCP of 1,5-hexadiene using enantiopure (*S_CS_{Hf}*)-**1** upon activation by **B1** in the absence of ZnEt₂ (see Figure 1a). Similarly high α values have been reported by us for the isoselective LCP of propene (α = 0.94), 1-butene (α = 0.98), and 1-hexene (α = 1.0) using the chiral (but racemic) C₁-symmetric CPAM initiator **II**. In sharp contrast, ¹³C NMR analysis of the PMCP material of run 2, which is still optically

active, clearly shows that a large erosion has occurred in stereoselectivity for insertion ($\alpha = 0.69$). Finally, the corresponding ^{13}C NMR spectra for the optically inactive PMCP obtained through stereomodulated LCCTP of 1,5-hexadiene using “racemic” **1** under otherwise identical conditions is, at first glance, very close in appearance (cf. Figure 1b and c), with a value for α of 0.50 providing the best fit. However, the slightly higher intensity for the RmR (1,3-*trans*, *syndiotactic*) tetrad of the PMCP from run 3 cannot be reproduced using the simple first-order statistical probability model alone. Accordingly, it is reasonable to conclude that this slight discrepancy is, in fact, due to Zn-mediated reversible exchange having occurred between the two enantiomeric propagating species derived from (S_C, S_{Hf})-**1** and (R_C, R_{Hf})-**1**.

Clearly, the results shown in Figure 1 for the three PMCP materials of runs 1–3 is not the level of validation required for establishing two-state stereomodulated LCCTP as a useful strategy for controlling stereochemical microstructure. However, these data do reveal important information regarding what other processes might be occurring that are competitive with the two-step mechanism of coordinative cyclopolymerization. Since the diastereoselectivity and efficiency for cyclization is not being affected between LCP and LCCTP, we can turn our attention to what might be happening at the first migratory insertion step. Here it can be noted that, for *isotactic* propagation to occur with C_1 -symmetric propagators, fast directional site epimerization, or back-skip, must occur after each migratory insertion event in order to establish a single coordination site at the transition metal center that has high enantioface selectivity for the α -olefin.¹⁸ Therefore, the most likely culprit for the reduction in stereocontrol is nondirectional site epimerization that occurs as the result of reversible chain transfer with the main group metal polymeryl species. On the other hand, the fact that α does not reduce to 0.5, which is expected for *atactic* propagation, is encouraging, and it suggests that more optimization of the steric environment of the capriamidinate ligand might lead to improvements in α to the level required for effective stereomodulated LCCTP. We have also considered the possibility that chain transfer under LCCTP conditions serves to produce two populations of diastereomeric active species through “ring-flipping” of the chiral capriamidinate ligand of **1**, and with each diastereomer now having a different degree of stereocontrol.³¹ It is also conceivable that the loss of stereocontrol under LCCTP is due to a Zn-mediated ligand modification that once again gives rise to multiple active species. However, in both of these scenarios, differences in the rates of propagation and exchange for different species would also be expected to produce much broader, and possibly, multimodal molecular weight distributions, neither of which are observed.³²

Looking back at our results for the stereoengineering of PMCH microstructure using two-state stereomodulated LCP, we noticed that no similar loss of stereocontrol was observed due to reversible methyl group exchange even at low levels of activation, that is, at high methyl group concentration. We conjecture here that the high degree of diastereoselectivity and efficiency for cyclization in this system might also be working in favor of supporting fast, directional site epimerization. If correct, then the two-state stereomodulated LCCTP of 1,6-heptadiene might also benefit.

Table 1 also summarizes the LCP and LCCTP of 1,6-heptadiene using (S_C, S_{Hf})-**1** and (R_C, R_{Hf})-**1**, along with the relevant analytical and spectroscopic characterization data for

the series of PMCH materials that were obtained.²⁹ To begin, the stereoselective LCP of 1,6-heptadiene (run 4) was first conducted using enantiopure (R_C, R_{Hf})-**1** that was activated by 1.1 equiv of **B1** to provide a highly crystalline PMCH material that was shown to be of very limited solubility in many common solvents. A ^1H NMR (800 MHz) spectrum recorded in 1,1,2,2-tetrachloroethane- d_2 (TCE- d_2) at 100 °C (see Figure S2) confirmed the lack of resonances for unsaturated end groups, which is expected for a LCP occurring in the absence of chain termination via β -hydrogen atom transfer processes and quantitative 1,3-cyclization of the diene monomer. Further, a high field $^{13}\text{C}\{^1\text{H}\}$ NMR (200 MHz, TCE- d_2 , 100 °C) spectrum that is reproduced in Figure 2 established that

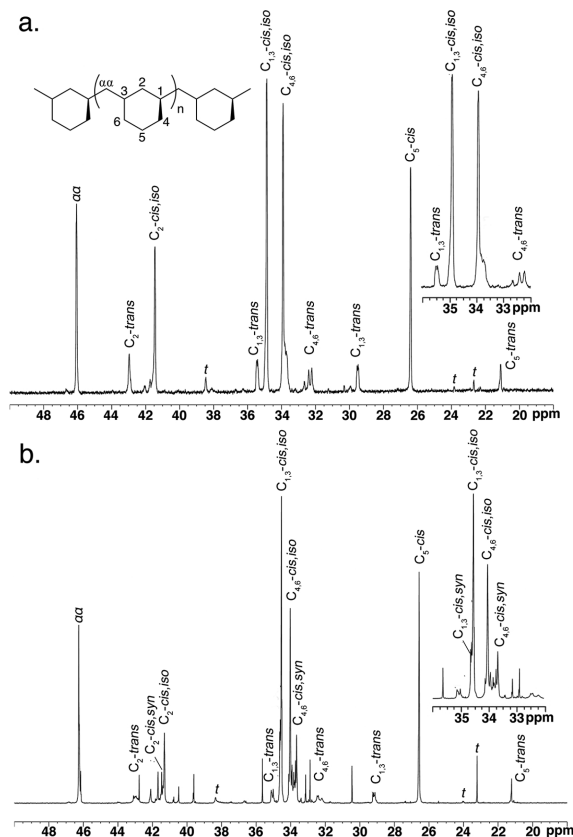


Figure 2. $^{13}\text{C}\{^1\text{H}\}$ NMR (200 MHz, TCE- d_2 , 100 °C) spectra of PMCH from (a) run 4 and (b) run 5 of Table 1. Resonance assignments are based on those previously reported for highly stereoregular 1,3-*cis*, *isotactic* PMCH^{24j} and for a series of PMCH materials prepared through two-state stereomodulated LCP.^{26b}

this PMCH material possesses a highly stereoregular 1,3-*cis*, *isotactic* stereochemical microstructure. However, the propagator derived from (R_C, R_{Hf})-**1** is less *cis*-stereoselective than the propagator derived from **II** as evidenced by the additional small set of ^{13}C resonances appearing in Figure 2a that are assigned to a small amount of 1,3-*trans* cyclization (see Scheme 3 and Figure S1). The presence of these 1,3-*trans* cyclohexane units within the polymer backbone further appear to be responsible for a reduction in crystallinity of the PMCH derived from (R_C, R_{Hf})-**1** relative to that from **II**, as assessed by wide-angle X-ray diffraction (WAXD) (see Figure S8). On the other hand, by the same criteria, **1** is more *cis*-stereoselective than a closely related Hf caproamidinate preinitiator that we have previously reported in which the chiral *N*-1-phenylethyl

group has been replaced by an achiral *N*-benzyl substituent.²⁸ Finally, unlike the case with optically active PMCP being obtained using (*S*_C,*S*_{Hf})-1 or (*R*_C,*R*_{Hf})-1, solution polarimetry of the PMCH material from run 4 failed to display any significant amount of optical rotation at the 589 nm sodium *D*-line. This result is in keeping with the higher degree of cryptochirality associated with a more stereoregular 1,3-*cis*, *isotactic* microstructure.

With a LCP baseline established, the LCCTP of 1,6-heptadiene was next performed using enantiopure (*R*_C,*R*_{Hf})-1 that was activated using 1.1 equiv of B1 in the presence of 10 equiv of ZnEt₂ according to run 5 of Table 1.²⁹ After the usual protic quench and workup, the isolated PMCH material now displayed physical properties that were very distinct from that of run 4. Most significantly, gel permeation chromatography (GPC) showed the expected decrease in molecular weight indices for a reversible chain transfer process, while the polydispersity remained very narrow (cf. *M*_n = 2.1 kDa, *M*_w = 2.5 kDa, *Đ* = 1.19). A further reduction in crystallinity along with slow crystallization kinetics is likely responsible for the absence of an observed *T*_m.^{26b} The depression in *T*_g on the other hand is reasonably a consequence of the lower degree of polymerization (see Table 1). Finally, a comparison of the ¹³C{¹H} NMR spectrum for this material with that of run 4, as provided in Figure 2, revealed two key findings regarding changes in stereochemical microstructure in going from LCP to LCCTP. First, as with PMCP, there is no dramatic change in the degree of diastereoselectivity and efficiency for cyclization obtained under the latter chain transfer conditions. On the other hand, the appearance of a few new resonances that can be assigned to the incorporation of MrM (1,3-*cis*, *syndiotactic*) tetrads indicates that a small degradation in stereoselectivity for insertion has once again occurred. Unfortunately, the complexity of the overlapping resonances within a small chemical shift window does not permit an attempt at a quantitative assessment of α and σ in this case. On the other hand, by inspection, it can be concluded that the extent of loss of stereocontrol in the LCCTP of 1,6-hexadiene by (*R*_C,*R*_{Hf})-1 to provide PMCH is qualitatively much less than that observed for the LCCTP of 1,5-hexadiene to provide PMCP under identical conditions. This observation tentatively provides further support for the hypothesis that, for highly isoselective *C*₁-symmetric propagators, the magnitude of α for the LCCTP of α,ω -nonconjugated dienes tracks with that for σ in the cyclization step. Additional studies are in progress to investigate this conjecture further.

Fortunately, the baseline for the LCCTP of 1,6-heptadiene using 1 provided by the data of Figure 2b established leaves room to experimentally determine if two-state stereomodulation is possible according to the Scheme 1. Accordingly, runs 6–9 of Table 1 were performed under LCCTP conditions that were identical to run 2, but with the optical purity of (*R*_C,*R*_{Hf})-1 artificially adjusted by mixing in known amounts of (*S*_C,*S*_{Hf})-1 prior to activation by 1.1 equiv of B1 relative to the total amount of 1. As can be seen from the results presented in Table 1, the series of PMCH materials that were obtained from these additional runs showed no variation in the GPC-determined *M*_n, *M*_w and *Đ* values, which were also all nearly identical to the molecular weight indices previously noted for the PMCH of run 2. Further, all the PMCH products from runs 6–9 were now qualitatively less crystalline than that of run 5, while *T*_g values remained essentially unchanged. This last observation is in keeping with our prior results for highly

crystalline *cis*, *isotactic* PMCH vs amorphous *cis*-PMCH.^{26b} Most importantly, the comparison of partial ¹³C NMR spectra for these materials that is provided in Figure 3 clearly

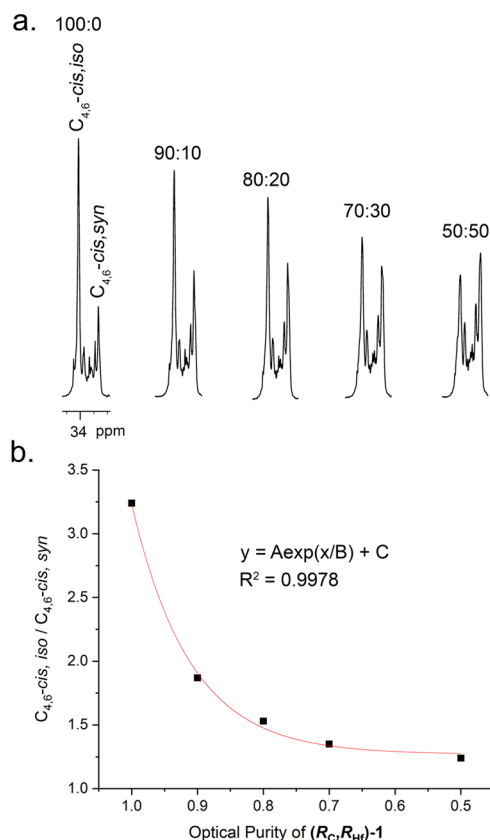


Figure 3. (a) Partial ¹³C{¹H} NMR (200 MHz, TCE-*d*₂, 100 °C) spectra for the C_{4,6} resonances of the series of PMCH products of Table 1 for runs (left to right) 6–9. (b) Quantitative analysis of the ratio of the MmM/MrM tetrads for C_{4,6} resonances of (a) as a function of optical purity of (*R*_C,*R*_{Hf})-1. The red line is an exponential fit of the data with the coefficient of determination (*R*²) shown. See the Supporting Information for variable numerical values.²⁹

substantiates the expectation from Scheme 3 that the level of incorporation of MrM tetrads increases as the optical purity (ee) of 1 steadily decreases in going from run 6 to run 9 according to Table 1. The quantitative fit of this data to an exponential decay (see red line in Figure 3) is in keeping with results obtained with two-state stereomodulated LCP of both propene and 1,6-heptadiene, and phenomenologically, it makes sense.

In summary, while further optimization is certainly required, two-state stereomodulated LCCTP using the optical purity of a single, chiral initiator as a programmable variable to obtain a family of different stereochemical grades of a polyolefin has now been validated. Importantly, this method has the significant advantage of providing access to practical quantities of a spectrum of unique polyolefin products that also include polyolefin block copolymers and end-group functionalized xPAOs.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acscatal.1c00633>.

Experimental details, including complete spectroscopic data (PDF)

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Notes

The authors declare the following competing financial interest(s): The corresponding author has a financial interest in the university spin-out company, Precision Polyolefins, LLC (PPL). This work did not involve any PPL personnel, funding, or other resources and all new intellectual property has been disclosed in accordance with state and federal requirements.

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