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Dinuclear Bis-Propagators for the Stereoselective Living Coordinative Chain Transfer Polymerization of Propene

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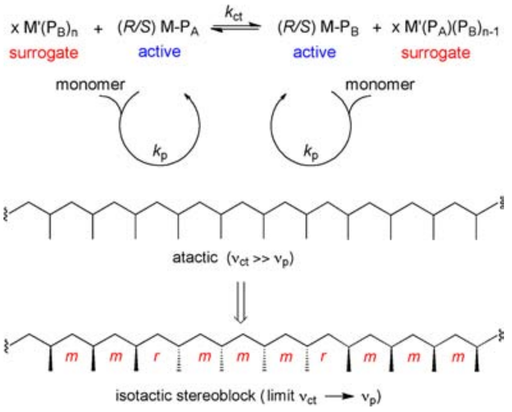
Supporting Information

ABSTRACT: Modulation of steric interactions remote from the active sites within a series of dinuclear bis-propagators derived from racemic **2**–**4** was used to attenuate the rate of reversible chain transfer between active transition-metal centers and excess equivalents of inactive main-group-metal alkyl species relative to chain growth propagation, as a strategy for achieving the stereoselective living coordinative chain transfer polymerization of propene to provide isotactic stereoblock polypropene. Under identical conditions, the corresponding mononuclear propagator derived from racemic **1** produced only atactic polypropene.

Living coordinative chain transfer polymerization (LCCTP) of olefins provides the opportunity to design, produce, and investigate the physical properties of a broad range of new classes of "precision" polyolefins while at the same time establishing a viable workaround solution to the "one-chain-per-active-site" limitation on the yield imposed by a traditional living polymerization.[1−5] LCCTP is based on the rapid and reversible polymeryl group (chain) transfer between active transition-metal propagating centers and excess equivalents of inactive main-group-metal alkyl species serving as "surrogate" chain growth sites (Scheme 1).[4] Under conditions where the rate and rate constant for reversible chain transfer are far greater in magnitude than those for chain growth propagation [i.e., ν_{ct} (k_{ct}) $\gg$ ν_p (k_p)], the populations of the active and surrogate sites appear to propagate at the same rate, and the final yield of the precision polyolefin is a function of the total amount of the relatively inexpensive main-group-metal surrogate rather than that of an expensive transition-metal initiator.[6,7] The mechanism shown in Scheme 1 provides many other desirable features of a living polymerization,[5] but to date, stereoselective LCCTP of α-olefins, and in particular of commercially relevant propene, remains unrealized. The primary challenge here is that when $\nu_{ct} \gg \nu_p$, the high frequency of reversible chain transfers between a surrogate and equal populations of the two enantiomeric forms (i.e., *R* and *S*) in a racemic (*R*/*S*) mixture of a chiral active transition-metal propagator generates a random (atactic) arrangement of the relative configurations of stereocenters along the polymer backbone of the final polyolefin product, even if each chain growth insertion of the α-olefin monomer proceeds at the active site with a high degree of enantioface stereoselectivity or even with stereospecificity (i.e., 100% stereoselectivity). Although the simple solution to this conundrum would be to employ an enantiomerically pure transition-metal initiator in order to ensure that each reversible chain transfer event occurs between active species with the same absolute configuration,[8] in practice, this strategy is easier said than done because of the notoriously low configurational stability of transition-metal complexes when chirality resides at the metal center as well as challenges associated with the optical resolution of such complexes in the first place. Herein we report the design and execution of a seemingly counterintuitive new strategy for achieving the stereoselective LCCTP of propene (to give *isotactic* polypropene) that employs a diastereomeric mixture of a racemic dinuclear bis-propagator under conditions where the corresponding racemic mononuclear propagator provides only *atactic* polypropene.[9] These results establish the importance of "regional" steric interactions, which are remote from the "local" immediate coordination environment of the active site, as a new design tool for exerting control over polyolefin microstructure that is unique to dinuclear bis-propagators vis-à-vis their mononuclear counterparts.[10,11]

Scheme 1



The lower half of Scheme 1 presents the basis for an alternative strategy for obtaining stereoselectivity during LCCTP when a racemic mixture of a chiral (isoselective) transition-metal propagator is employed. Specifically, when ν_{ct} is attenuated relative to ν_p, a longer run of an isotactic sequence within the growing polymer chain can be established prior to a chain transfer event involving a surrogate species. Thus, upon chain back-transfer, there is an equal probability for the polymer chain to return to an active propagator with either the same absolute configuration (i.e., handedness), which would serve to extend the

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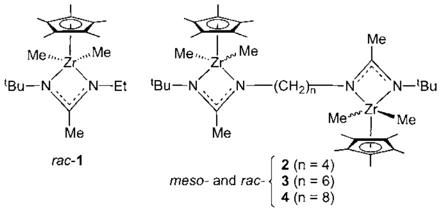
isotactic sequence in the propagating chain even further, or with the opposite handedness, which would serve to generate an *isotactic stereoblock* microstructure that is distinguished by the presence of $(m)_x mr(m)_y$ (e.g., *mmrm* pentad and *mmmrmm* heptad) stereosequences, as depicted in Scheme 1.[9,12] In this scenario, since the isotactic block length is a function of the frequency of reversible chain transfer, the ability to exert external control over ν_{ct} and ν_p in programmed fashion could be used to generate a family of different grades of isotactic stereoblock polypropene materials of varying average block length. While the polymerization would remain strictly living in character, one important consequence of pursuing this strategy would be that the molecular weight distribution, as characterized by the polydispersity index D ($=M_w/M_n$, where M_w and M_n are the weight- and number-average molecular weights, respectively), of the isotactic stereoblock polypropene material should increase as k_{ct} approaches k_p, since $D \approx 1 + (k_p/k_{ct})$ for a "two-state" living polymerization such as that depicted in Scheme 1.[5,13]

In practice, a significant obstacle to overcome is how best to target a reduction in the rate of reversible chain transfer between active and surrogate species while keeping all of the other kinetic parameters for processes occurring at the active center the same or nearly the same. Mononuclear propagators are severely handicapped in this respect because of the short length scale over which changes in nonbonded steric interactions are efficiently transmitted about the transition metal center. Thus, increasing the magnitude of these local steric interactions to inhibit intermolecular chain transfer can have a simultaneous negative impact on the rate of propagation and enantioface selectivity because of steric crowding of the monomer coordination site. On the other hand, dinuclear bis-propagators for the coordination polymerization of olefins, in which two active sites are held in close proximity to one another via either a rigid or flexible molecular tether, are characterized by an intrinsically much more complex steric environment that also includes steric interactions between the two growing polymeryl chains as well as with two large counteranions (vide infra). Since these steric interactions occur at a distance from the immediate coordination environment of the transition metal, an increase in their magnitude may not have as significant an impact on the active sites.

We previously reported that cationic, monocyclopentadienyl, monoamidinate group 4 metal methyl complexes having the general formula $\{(\eta^5\text{-}C_5R_5)M[N(R^1)C(R^2)N(R^3)\text{-}\kappa^2\text{-}N,N'](Me)\}^+[B(C_6F_5)_4]^-$ (**I**) (M = Zr, Hf), which are derived from the corresponding neutral dimethyl precursors and a stoichiometric equivalent of $[PhNHMe_2][B(C_6F_5)_4]$ (**II**), can serve as structurally well-defined initiators for LCCTP of ethene, propene, longer-chain α-olefins, cycloalkenes, and nonconjugated α,ω-dienes in toluene solution using excess equivalents of dialkylzinc (ZnR_2) or trialkylaluminum (AlR_3) reagents as chain growth surrogates.[4,5] We also showed that the cationic initiator derived from a racemic mixture of the chiral C_1-symmetric derivative *rac*-**1** shown in Scheme 2 can effect the living isotactic polymerization of α-olefins, which is highly stereoselective in the case of propene [*mmmm* pentad = 0.70, enantioface selectivity (σ) = 0.92] and stereospecific in the case of 1-hexene (*mmmm*, σ > 0.98).[14] However, when **1** was employed for the LCCTP of propene using 20 equiv of $ZnEt_2$ under the standard conditions of Table 1, the polypropene product had narrow polydispersity but was amorphous in nature because of a very low degree of microstructural stereoregularity (i.e., atactic, *mmmm* = 0.253), as confirmed by ^{13}C NMR stereochemical microstructure analysis (Table 1, run 1).[15,16] Unfortunately, as with all related dimethyl derivatives, **1** is configurationally unstable in solution due to a low energy barrier (e.g., $\Delta G^{\ddagger}$ < 10.5 kcal mol^{-1}) for metal-centered racemization, which proceeds via facile "amidinate ring flipping".[14,17] In addition, all efforts to obtain diastereomerically and enantiomerically pure analogues of **1** through incorporation of stereogenic centers on the amidinate fragment failed due to resultant inactivity for polymerization that is attributed to an olefin coordination site that is highly sensitive to steric crowding.[18]

Scheme 2



During the course of investigations involving fast and reversible *methyl* group exchange between active (configurationally stable), cationic, polymeryl species and inactive (configurationally unstable) neutral, methyl, polymeryl dormant states derived from **I**,[4,14b−d] we had reason to prepare and characterize a series of closely related tethered dinuclear bis-propagators derived from the corresponding precursors **2**−**4** (Scheme 2) that exist in solution as a mixture of meso and racemic diastereomers.[19] That study determined that the cationic active sites in the dinuclear bis-propagators are also configurationally stable in solution and display nearly the same degree of enantioface selectivity and activity for propene polymerization as can be achieved using mononuclear **1** (cf. **2**, σ = 0.89; **3**, 0.91; **4**, 0.92). On the other hand, and most significantly, much higher barriers for metal-centered epimerization were observed for neutral methyl, polymeryl dormant states in these dinuclear systems, with the barrier height increasing further as the magnitude of nonbonded steric interactions between the two transition-metal centers increased with shortening of the molecular tether (i.e., proceeding from **4** to **3** to **2**). Importantly, these results provided the first evidence that an increase in remote regional steric interactions within a dinuclear bis-propagator can favorably modulate the rate of a process that is competitive with chain growth propagation without having a detrimental effect on the latter.[19b]

In the present work, a preliminary screen revealed that the dinuclear bis-propagators derived from **2**−**4** were effective for the LCCTP of propene starting with 20 equiv of $ZnEt_2$ (Table 1, runs 2−4), and ^1H NMR spectra (600 MHz, 1,1,2,2-$C_2Cl_4D_2$, 90 °C) of the polypropene products confirmed the living character of the polymerizations, as there was no evidence of vinyl end-group resonances that might arise from chain termination via irreversible β-hydrogen transfer processes. Gratifyingly, as Table 1 shows, both M_n and D were observed to decrease with increasing molecular tether length, as expected for an increase in ν_{ct} (k_{ct}) relative to ν_p (k_p) due to greater steric accessibility for bimolecular chain transfer as the two cationic active sites are moved increasingly farther apart within the series [cf. **2** (M_n = 4.71 kDa, D = 1.71) > **3** (3.54, 1.62) > **4** (2.91, 1.24)]. The ^{13}C NMR stereochemical microstructural analysis data presented in Table 1 provide additional support for this conclusion. To begin, it is important first to deconvolute the *mmmm* pentad values of column 12 in order to account separately for the degrees of polypropene stereoirregularity arising from monomer enantio-

Table 1. LCCTP of Propene Using Mononuclear and Dinuclear Initiators Derived from **1** and **2**−**4**, Respectively[a]

run	I[b]	equiv of $ZnEt_2$[c]	t_p (h)	yield (g)	M_w (kDa)[d]	M_n (kDa)[d]	$Đ$	T_m (°C)[e]	T_g (°C)[e]	%cryst[f]	*mmmm*[g]	*mmmmrr* + *mmmrrm* + *mmrrmm*[g]	*mmmmmr* + *rmmmmr* + *mmmmrm* + *mrmmrm* + *mmmrmm*[g]
1	**1**	20	15	1.39	3.25	2.85	1.14	–	−26.4	–	0.253	0.106	0.383
2	**2**	20	23	1.48	8.07	4.71	1.71	86.3	−22.5	9.6	0.467	0.282	0.094
3	**3**	20	23	1.37	5.72	3.54	1.62	100.9	−27.4	16.3	0.555	0.169	0.159
4	**4**	20	23	1.10	3.59	2.91	1.24	83.9	−27.3	1.5	0.362	0.134	0.281
5	**1**	0	3	0.36	30.4	24.6	1.23	111.9	−10.6	23.6	0.694	0.184	–
6	**1**	5	10	0.80	6.10	4.97	1.23	93.4	−18.9	10.7	0.557	0.160	0.184
7	**1**	10	20	1.81	5.81	4.92	1.18	76.1	−17.7	5.2	0.490	0.149	0.256
8	**1**	20	30	2.06	4.40	3.93	1.12	–	−22.5	–	0.318	0.134	0.365
9	**3**	0	3	0.32	31.9	24.9	1.28	114.8	−8.5	23.7	0.697	0.187	–
10	**3**	5	10	0.72	8.98	4.09	2.20	106.6	−22.2	18.7	0.630	0.184	0.093
11	**3**	10	20	1.48	8.96	3.57	2.51	107.6	−20.4	21.9	0.652	0.176	0.094
12	**3**	20	30	1.80	4.27	2.50	1.71	95.3	−27.1	12.3	0.565	0.174	0.166

[a] Conditions: $[I]_0$ = 1.25 mM for **1** and 0.625 mM for **2**−**4** in toluene (runs 1−4) or chlorobenzene (runs 5−12), propene (5 psi), −10 °C. [b] Initiator precusor. [c] Relative to each transition-metal center in I. [d] Determined by gel-permeation chromatography (tetrahydrofuran, 40 °C, polystyrene standards). [e] Determined by differential scanning calorimetry (DSC). [f] Determined by DSC. [g] Determined by $^{13}C\{^1H\}$ NMR spectroscopy (150 MHz, 1,1,2,2-$C_2Cl_4D_2$, 90 °C).[15]

face selectivity (given by the sum of the *mmmmrr*, *mmmrrm*, and *mmrrmm* heptads of column 13) and reversible chain transfer (given by the sum of the *mmmmmr*, *rmmmmr*, *mmmmrm*, *mrmmrm*, and *mmmrmm* heptads of column 14). After this deconvolution, the latter values clearly show that ν_{ct} (k_{ct}) does in fact increase for the dinuclear bis-propagators in the order **2** < **3** < **4**. Furthermore, the lower crystallinity of isotactic stereoblock polypropene obtained from **2** (9.6%) relative to that from **3** (16.3%) (Table 1) can be attributed to the longer but less stereoregular stereoblocks in the former material arising from the lower enantioface selectivity for the dinuclear bis-propagator with the shorter tether.

On the basis of the above results, further detailed comparisons using **1** and **3** under different LCCTP conditions were next pursued (Table 1). For **1**, increasing the concentration of the surrogate relative to the propagator had the anticipated effect of decreasing the isotactic block length (*mmmm*), melting temperature (T_m), and percent crystallinity (%cryst) of the isotactic stereoblock polypropene until an amorphous, atactic material was obtained starting with 20 equiv of $ZnEt_2$ as the surrogate (runs 5−8). In contrast, LCCTP of propene using **3** under identical conditions provided a set of highly crystalline isotactic stereoblock polypropene samples for which the *mmmm*, T_m, and %cryst remained fairly constant as the amount of surrogate increased, with these values only beginning to erode at 20 equiv of $ZnEt_2$ (runs 9−12). Figure 1 presents partial ^{13}C NMR spectra of the methyl region for the isotactic stereoblock polypropenes in this collection, in which the dramatic differences in stereoregularity of the materials obtained from LCCTP using mononuclear **1** (Figure 1a−d) and dinuclear **3** (Figure 1e−h) can be qualitatively assessed.

Wide-angle X-ray diffraction (WAXD) studies further revealed sharp differences in the solid-state structures of the polypropene materials obtained from **1** and **3** under LCCTP (Figure 2). As a frame of reference, isotactic polypropene obtained from **1** and **3** under non-LCCTP conditions predominantly adopts the α crystalline form with diffraction peaks occurring at 2θ = 14.2, 17.1, 18.6, and 21.1° for $(110)_\alpha$, $(040)_\alpha$, $(130)_\alpha$, and $(111)_\alpha$, respectively (Figure 2a,e).[20] However, when 10 equiv of $ZnEt_2$ was employed for LCCTP using **1**, the polypropene displayed an α/γ disordered modification intermediate between the α and γ forms with a characteristic diffraction peak at 2θ = 20.1° for $(117)_\gamma$ (Figure 2c).[20] On the other hand, under identical LCCTP conditions, dinuclear **3** provided crystalline polypropene with high isotacticity that largely maintained the α form (Figure 2g). Finally, with 20 equiv of $ZnEt_2$, mononuclear **1** yielded amorphous polypropene characterized by the absence of crystalline diffraction peaks (Figure 2d), while the polypropene obtained from dinuclear **3** was still crystalline but just beginning to exhibit evidence of structural disorder in the solid state (Figure 2h).

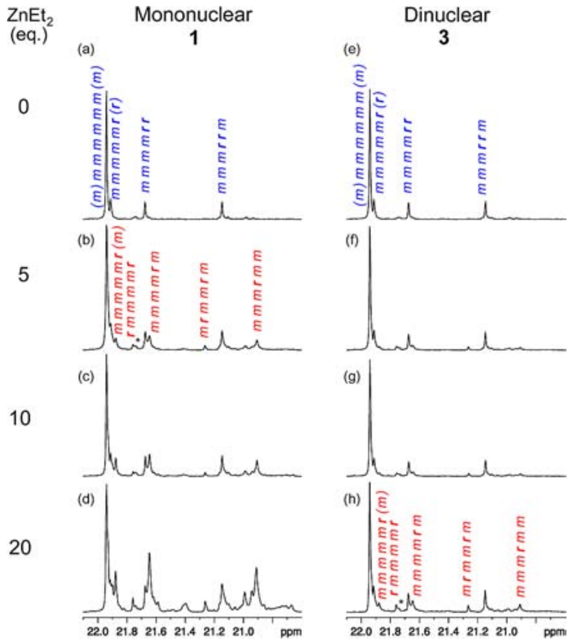


Figure 1. Partial ^{13}C NMR spectra (150 MHz, 1,1,2,2,-$C_2Cl_4D_2$, 90 °C) of the methyl region for the polypropene materials from (a−d) runs 5−8 and (e−h) runs 9−12 in Table 1. Assignments for heptad stereosequences arising from enantiomorphic site control and isotactic stereoblock microstructure are presented in blue and red, respectively. Resonances marked with an asterisk (*) are for end groups.[16]

In conclusion, programmed manipulation of the more complex steric environment of dinuclear bis-propagators, comprising both regional and local effects, can be used as a tool for modulating the rate of a dynamic bimolecular process

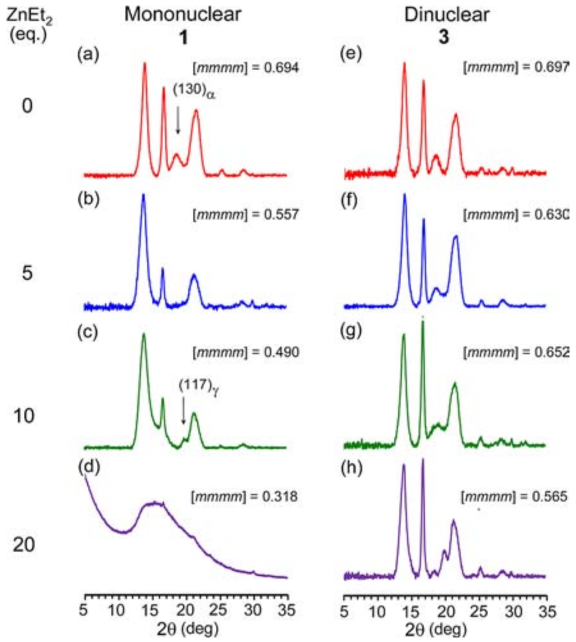


Figure 2. WAXD profiles of unannealed polypropene materials from (a–d) runs 5–8 and (e–h) runs 9–12 in Table 1.

that is competitive with pseudo-first-order chain growth. When coupled with the ability to control directly the concentrations of active and surrogate species in LCCTP, the present results serve as an important extension of the "one catalyst, many materials" paradigm that a living "two-state" coordination polymerization can provide.[5]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, including complete spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(6) The initiator and propagator are the molecularly discrete transition-metal species that exist in solution before and after coordinative insertion of the monomer, respectively. A surrogate is a catalytically inactive main-group-metal species that appears to engage in chain growth through rapid, reversible polymeryl group transfer.

(7) For LCCTP, the final yield of the polyolefin is a function of the degree of polymerization, $X_n = \{[\text{monomer}]_0 - [\text{monomer}]_t\}/\{[\text{initiator}]_0 + mn[\text{surrogate}]_0\}$, where m is the number of molar equivalents of surrogate employed and n is the number of equivalent alkyl groups on the surrogate engaged in reversible chain transfer (e.g., $n = 2$ for ZnR$_2$). In more direct practical terms, the yield depends on the amount of surrogate used in excess of the initiator, the value of n, and the polymerization time (t_p) when the monomer is available in excess.

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