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Enantioselective Living Coordinative Chain Transfer Polymerization: Production of Optically Active End-Group-Functionalized (+)- or (–)-Poly(methylene-1,3-cyclopentane) via a Homochiral C_1 -Symmetric Caproamidinate Hafnium Initiator

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phenylethyl-caproamidinate hafnium preinitiators ($S_{C_r}S_{Hf}$)-1 and ($R_{C_r}R_{Hf}$)-1, respectively, can be used in combination with the borate coinitiator [PhNHMe₂][B(C_6F_5)₄] (**B**) and excess equivalents of ZnEt₂ for the enantioselective living coordinative chain transfer polymerization (LCCTP) of 1,5-hexadiene to provide (+)- and (-)-poly(methylene-1,3-cyclopentane) (PMCP) of tunable molecular weight and very narrow polydispersity. Use of excess I₂ to quench LCCTP provides the corresponding (+)- and (-)-iodoterminated PMCP products. This enantioselective LCCTP process serves to establish access to readily available, practical, and scalable quantities of optically active liquid crystalline end-group-functionalized xPMCP building blocks for material science and technology discovery.



KEYWORDS: enantioselective, living, chain transfer, polymerization, polyolefin

he design and validation of new polymerization processes that can deliver practical quantities of "next generation" polyolefins with unprecedented structures and properties from the limited pool of commercially available olefin monomers is of substantial academic and industrial interest.¹ Toward this goal, we have been engaged for some time in the development of living coordinative chain transfer polymerization (LCCTP) of ethene, propene, longer-chain α -olefins, and $\alpha_{i}\omega$ -nonconjugated dienes as a means by which to provide access to a broad range of new fundamental forms of polyolefins that includes all the benefits provided by a living system but with the "one-chain-per-active-site" limitation on scalability removed.² As shown in Scheme 1, at the heart of LCCTP is rapid and reversible polymeryl group (chain) transfer that occurs between a small population of active transition-metal propagating species and a much larger population of inactive main-group-metal "surrogate" chain growth centers. In the absence of irreversible chain termination, and under the conditions where the rate and rate constant for reversible chain transfer, $\nu_{\rm ct}$ and $k_{\rm ct\prime}$ are much greater in magnitude than those for propagation, $u_{\rm p}$ and $k_{\rm p}$, all desired features of a living polymerization can be achieved, including a tunable numberaverage degree of polymerization (DP_n) and very narrow molecular weight distribution, with a polydispersity index, D

 $(=M_w/M_p)$ of ≤ 1.1 , where M_p and M_w are the number-average and weight-average molecular weight indices, respectively. Furthermore, the ability to obtain practical quantities-from grams to kilograms to kilotons-is now largely dictated by the cost and availability of the commodity main-group-metal alkyl used to generate the surrogate centers, such as diethyl zinc $(ZnEt_2)$ or triethylaluminum (AlEt₃), rather than that of the much more synthetically involved and expensive transitionmetal initiator, which also has the added disadvantage of possessing a high molar mass vis-à-vis the olefin monomer. Finally, through post-polymerization reactions that can be conducted with the initial main-group-metal polymeryl product that is obtained from LCCTP with a variety of chemical reagents, a larger portfolio of different end-groupfunctionalized poly(α -olefinates) (xPAOs) of diverse structure can be rapidly generated.^{2d,5} Indeed, as currently practiced, LCCTP is ideally suited for the production of low to ultra-low

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Scheme 1



molecular weight xPAOs of extremely narrow polydispersity. Importantly, xPAOs represent a category of polyolefins that has not been previously accessible for routine study, nor as a source for new technological innovation.⁵ Herein, we now report the first demonstration of enantioselective LCCTP and apply this new process to the production of (+)- and (-)-iodoterminated poly(methylene-1,3-cyclopentane) (I-PMCP) of tunable molecular weight and very narrow polydispersity using 1,5-hexadiene (HD) as the monomer and excess equivalents of ZnEt₂ as the source of surrogate centers. We further reveal that this enantioselective LCCTP process is uniquely performed using a newly developed homochiral and configurationally stable C_1 -symmetric cyclopentadienyl, caproamidinate hafnium pre-initiator (1) that is easily obtained in either $(S_{C}S_{Hf})$ or $(R_{C}R_{Hf})$ enantioform through a short synthetic route that does not require optical resolution of a racemic intermediate or product.

Beginning with the pioneering work of Coates and Waymouth,⁶ optically active PMCP has been previously reported in the literature.⁷ Naga and co-workers⁸ have also documented the unique cholesteric liquid crystalline properties of low molecular weight samples. However, all these prior studies involved non-living polymerizations using configurationally constrained, C_2 -symmetric transition-metal catalysts that yielded PMCP materials of substantially large DP_n and *D* values. Furthermore, to the best of our knowledge, there has never been a report of optically active, end-group-functionalized PMCP.

With regard to the present work, the chief difficulty in achieving stereo- and enantioselective LCCTP using the known family of group 4 metal cyclopentadienyl amidinate pre-initiators of general formula, $(\eta^5-C_5R_5)[(\kappa^2-(N,N)-N(R^1)-C(R^2)N(R^3))]M(CH_3)_2$ (M = Zr and Hf) (I), is that C_1 -symmetric derivatives, where $R^1 \neq R^3$, are known to engage in very facile metal-centered racemization that formally proceeds through a low-energy barrier amidinate "ring-flipping" process according to Scheme 2.

Indeed, in the 20 years since our first report of the stereospecific living coordination polymerization (LCP) of 1-hexene that provides isotactic poly(1-hexene) (iPH) using C_1 -





symmetric Ia (M = Zr, R = R² = CH₃, R¹ = ^tBu, R³ = Et), all attempts to design and secure a configurationally stable derivative of I through manipulation of non-bonded steric interactions within the ligand sphere have failed in both the cases of M = Zr and Hf.^{9,10} For stereo- and enantioselective LCCTP, the need for configurational stability of C_1 -symmetric I is to ensure that such derivatives can be obtained and retained in an enantiomerically pure (homochiral) form as a single stereoisomer. More to the point, as Scheme 3 reveals,

Scheme 3



rapid reversible chain transfer that occurs between a racemic mixture of active transition-metal propagators through the intermediacy of the main-group-metal surrogate centers will give rise to an *atactic* polyolefin stereochemical microstructure, even if each chain growth insertion of a monomer has proceeded in a stereospecific fashion. On the other hand, assuming that reversible chain transfer proceeds with retention of stereoconfiguration of the transition-metal center, then a population of a single enantioform of the active species should provide an isotactic microstructure.¹¹ Fortunately, as shown in Scheme 2 and previously confirmed for Ia, "activation" by addition of one equivalent of the borate co-initiator, $[PhNHMe_2][B(C_6F_5)_4]$ (B), serves to generate the corresponding ion-pair initiator, $[(\eta^5-C_5R_5)](\kappa^2-(N,N)-N(R^1)C (R^2)N(R^3))]M(CH_3)][B(C_6F_5)_4]$ (II), which is now configurationally stable for the lifetime of polymerization due to a contraction of the metal-nitrogen bonds with the amidinate fragment that then substantially raises the barrier for racemization.9a,b,e

Seeking to avoid lengthy synthetic schemes and the need for optical resolution of a racemic product, we first explored different strategies for obtaining homochiral variants of I in which chirality is positioned within the \mathbb{R}^1 , \mathbb{R}^2 , and \mathbb{R}^3 amidinate substituents.¹² Unfortunately, these early studies were discouraging in that either: (1) metal-centered epimerization still occurred to provide a mixture of diastereomeric preinitiators, (2) derivatives of II were now too sterically encumbered to be active as initiators for either LCP or LCCTP, or (3) living character for polymerization could not be substantiated. Recently, a significant breakthrough of the impasse to configurationally stable, homochiral C_1 -symmetric derivatives of I was made possible with our introduction of N-substituted iminocaprolactams as the basis for a structurally versatile new line of "caproamidinate" derivatives of I and II.¹³ As shown in Scheme 4, a large variety of N-substituted iminocaprolactams

Scheme 4



(III) can first be easily prepared on a large scale and in high yield from ε -caprolactam through a two-step process involving *O*-methylcaprolactim as an intermediate that is simply condensed with a range of primary amines.^{14,15} For the present report, we chose to prepare and investigate the homochiral *N*-(1-phenylethyl) derivatives, (*R*)-IIIa and (*S*)-IIIa, with a specific optical rotation $\alpha_D^{26} = -73.7$ and $+75.9^{\circ}$ (c = 2, CH₃Cl), respectively, as both of the required (*R*)- and (*S*)-1-phenylethylamines are relatively inexpensive and can be reliably obtained in enantiopure large quantities.¹⁶ Finally, the desired new homochiral caproamidinate hafnium derivatives ($S_{C_1}S_{H_f}$)-1 and ($R_{C_1}R_{H_f}$)-1 were obtained in high yield, with $\alpha_D^{26} = +31.8$ and -31.2° (c = 1, toluene), respectively, by condensing the respective (*S*)- or (*R*)-IIIa with Cp*HfMe₃¹⁷ (Cp* = η^5 -C₅Me₅) according to Scheme 4.¹⁸

Analytical and spectroscopic characterization of (S_{C}, S_{Hf}) -1 provided data that is fully consistent with the structure depicted in Scheme 4. Molecular structures of (S_{C}, S_{Hf}) -1 and $(R_{C}R_{Hf})$ -1 that were obtained by single-crystal X-ray analyses further confirmed this assignment, and as reproduced in Figure 1 for the former, this structural information was then also used to assign the absolute stereochemical configuration of the Hf center relative to that of the known chirality of the N-1phenylethyl substituent.^{18,19} Importantly, variable temperature proton nuclear magnetic resonance (¹H NMR, 400 and 500 MHz, toluene- d_8) studies conducted of (S_C, S_{Hf}) -1 over the temperature range of 203-368 K (see Figures S12 and S13) provided the surprising fact that metal-centered epimerization of 1 is exceedingly slow on the NMR time frame at 298 K, and in fact, for all practical purposes, the single (S_{C}, S_{Hf}) diastereomer is the only one that appears to exist in solution at this temperature. Cooling the NMR sample to lower temperature revealed the existence of ring-conformational dynamics involving ¹H resonances of the two protons on C16 of (S_{C}, S_{Hf}) -1 (see Figure 1a). However, these spectra showed no indication of dynamic exchange involving the ¹H resonances for the two diastereotopic methyl groups that are bonded to the Hf center.¹⁸ On the other hand, clear evidence for this latter process did appear upon heating the NMR sample well above ambient temperature.¹⁸ Based on the



Figure 1. (a) Molecular structure (30% thermal ellipsoids) of $(S_{Cr}S_{Hf})$ -1. Hydrogen atoms have been removed for the sake of clarity except for H1 which is represented by a sphere of arbitrary size. (b) Space filling representation of structure in (a), which includes all hydrogen atoms (white), that highlights steric packing interactions between the Cp* ligand (green), the *N*-(*S*)-1-phenylethyl substituent (red), caproamidinate ligand (orange), and nitrogen atoms (blue).¹⁸

coalescence temperature, T_c , of 368 K, a first-order approximation of the free energy of activation for metalcentered epimerization for $(S_{Cr}S_{Hf})$ -1 at this temperature is $\Delta G_c^{\ddagger} = 19.8$ kcal mol⁻¹.²⁰ In contrast, the corresponding ΔG_c^{\ddagger} value for racemization of Ia is less than 11 kcal mol⁻¹ at the T_c of 225 K.^{9b} A space-filling representation of the molecular structure of (S_C, S_{Hf}) -1 that is shown in Figure 1b strongly suggests that the origin of configurational stability is due to the magnitude of non-bonded steric interactions between substituents. However, it is also important to recognize that the bicyclic nature of the caproamidinate group is also very likely contributing to configurational stability by enforcing a κ^2 - N_rN bidentate bonding interaction with the metal center that raises the energy barrier for metal-centered epimerization via a Ndissociative pathway.^{21,22}

To date, no example of the stereoselective LCP of α -olefins using a homochiral transition-metal initiator of C_1 -symmetry has been reported. With this in mind, a preliminary investigation of the LCP of 1-hexene was first conducted at 268 K in chlorobenzene using a combination of $(S_{Cr}S_{Hf})$ -1 and B according to previously published procedures.^{9,18} After the usual workup and purification, the isolated polymeric material was determined by ¹H and ¹³C{¹H} NMR spectroscopy to be highly stereo- and regioregular isotactic poly(1-hexene) with no evidence of chain-termination through β -hydrogen transfer processes being observed (see Figure S11). Collectively, these data are critical for establishing that the initiator derived from 1 is both active for α -olefin polymerization and that propagation proceeds with a high degree of stereocontrol over monomer enantioface selectivity and migratory insertion into the growing polymer chain. Not surprisingly, however, polarimetry revealed the absence of any optical activity for this material, which is undoubtedly a consequence of *cryptochirality* that occurs for an isotactic polyolefin microstructure, which at a sufficiently high DP_n value can be envisioned as having mirror planes orientated at right angles to the linear chain axis (see Scheme 3).^{23,24}

The limiting stereochemical microstructures for PMCP that are shown in Scheme 5 are more complex than those of linear acyclic polyolefins. As indicated for the cis, isotactic microstructure, the relative configuration of the initial chiral center,





and every other chiral center along the polymer backbone, is first established through enantiomorphic site control by the metal that is enforced during α -olefin insertion (i) of HD. The configuration of the next adjacent chiral center, and hence, the cis or trans stereoisomeric relationship of each of the 1,3cyclopentane rings is then subsequently determined by the stereoselectivity of ring-closing (c) that involves migratory insertion of the remaining ω -olefin moiety. As the trans, isotactic microstructure of PMCP lacks any mirror plane symmetry, it is formally the only limiting microstructure that is chiral both globally and at the individual repeating unit level. Achieving the necessary degree of stereocontrol over both *i* and c during propagation to obtain highly stereoregular trans, isotactic PMCP, however, is an exceedingly challenging task.⁶, On the other hand, PMCP with a cis/trans ratio of other than 1/0 guarantees that the overall polymer microstructure will be asymmetric, and accordingly, the material will be intrinsically chiral and possess optical activity if it can be produced in an enantioselective manner. This conclusion is supported by the previous reports of optical activity for cis/trans, isotactic $PMCP^{6-8}$ and by the results presented in Table 1 for the LCP and LCCTP of HD using (S_C, S_{Hf}) -1 and (R_C, R_{Hf}) -1.

To begin, the LCP of HD using (S_{C}, S_{Hf}) -1 under standard conditions at 268 K provided highly isotactic PMCP with a cis/trans ratio of 38.5/61.5 for 1,3-cyclopolymerization as determined by the ¹H and ¹³C NMR spectra that are reproduced in Figures 2a and 3a.¹⁸ This analysis also confirmed a living character for the polymerization by the absence of vinylidene resonances that might have arisen from chain termination. The resonances that do appear in the region for unsaturation can be traced to a very small amount (ca. 1.4%) of random 1,2- or 2,1-chain insertion of HD into the growing chain that is commonly observed with the level of α only insertion being dependent upon the nature of the transition-metal propagator. In this regard, at first glance, the LCP of HD using (S_{C}, S_{Hf}) -1 appears to produce cis/trans, isotactic PMCP that is indistinguishable from the material that we previously reported by employing C_1 -symmetric Ia under



Figure 2. Partial $^1\mathrm{H}$ NMR (400 MHz, CDCl₃, 298 K) spectra of PMCP and I-PMCP from (a) run 1 and (b) run 6 of Table 1, respectively.

similar conditions.^{2b,10a} However, in the present case, the PMCP from run 1 of Table 1 is now optically active with α_D^{26} = +11.2° (*c* = 2, CHCl₃), and this value is similar to that reported for other optically active PMCP possessing a cis/trans, isotactic microstructure.^{6–8}

Finally, by dropping the temperature to 243 K, LCP of HD now provided isotactic PMCP with slightly higher % cis and % 1,3 content of 42.7 and 98.8, respectively (see run 2, Table 1). In keeping with an increase in pseudo-mirror symmetry, this PMCP product exhibited a reduced specific optical rotation of $\alpha_{\rm D}^{26} = +7.5^{\circ}$.

End-group-functionalized xPAOs that can be obtained in practical and scalable quantities through LCCTP are of growing interest as tuneable building blocks for the fabrication of nanostructured materials.⁵ Accordingly, it was of significant interest to determine if optically active xPMCP can be easily produced using (S_C, S_{Hf}) -1 and (R_C, R_{Hf}) -1. Thus, as shown in Table 1, the LCCTP of HD was next investigated using

run	1	HD (equiv)	$ZnEt_2$ (equiv)	$t_{\rm p}$ (h)	yield (g)	$M_{\rm n}^{\ d}$ (kDa)	$M_{\rm w}^{\ d}$ (kDa)	\overline{D}^{d}	% 1,3 ^e	% cis ^e	% trans ^e	$\alpha_{ m D}^{26f}~(m deg)$
1	(S_{C}, S_{Hf})	100 ^a	0	21	1.04	16	17.6	1.09	98.6	38.5	61.5	+11.2
2	(S_{C}, S_{Hf})	150 ^b	0	19	0.86	21	23.4	1.10	98.8	42.7	57.3	+7.5
3	$(S_{\rm C}, S_{\rm Hf})$	486 ^c	10	25	1.35	3.8	4.3	1.12	98.9	35.0	65.0	+11.9
4	$(R_{\rm C}, R_{\rm Hf})$	486 ^c	10	24	1.51	3.4	3.9	1.13	98.9	35.1	64.9	-12.2
5	$(S_{\rm C}, S_{\rm Hf})$	486 ^c	10	24	1.30	3.7	4.1	1.13	98.9	36.9	63.1	+12.2
6	$(R_{\rm C}, R_{\rm Hf})$	486 ^c	10	24	1.55	3.6	4.1	1.13	98.8	35.2	64.8	-11.7

Table 1. LCP and LCCTP of HD^a

^{*a*}LCP performed using 75 μ mol of 1 in 5 mL of PhCl at 268 K. ^{*b*}LCP performed at 243 K. ^{*c*}LCCTP performed using 44 μ mol of 1 in 5 mL of toluene at 268 K. ^{*d*}Determined by gel permeation chromatography. ^{*e*}Determined by NMR (see Figures S5–S10 and ref 6 for stereochemical microstructure ¹³C resonance assignments). ^{*f*}(*c* = 2.00, CHCl₃).



Figure 3. Partial ¹³C{¹H} NMR (100 MHz, CDCl₃, 298 K) spectra of PMCP and I-PMCP from (a) run 1 and (b) run 6 of Table 1, respectively.

 (S_{C}, S_{Hf}) -1 as pre-initiator, B as co-initiator, and 10 equiv of $ZnEt_2$ as the source of surrogate propagators (see Scheme 1).^{2b} Gratifyingly, the cis/trans, isotactic PMCP obtained in run 3 of Table 1 was found to be nearly the same as before but with slightly higher % trans and % 1,3 content.¹⁸ Significantly, however, while the M_n value of this LCCTP product is now only ca. 4 kDa, a narrow D value of 1.12 was still achieved. Furthermore, in keeping with the trend established with LCP, the small decrease in % cis content appears to correlate once again with a slight increase in specific optical rotation. It is also interesting to note that the substantial reduction in DP_n that occurred in going from the LCP to the LCCTP of HD did not have any significant unexpected impact on the magnitude of the optical rotation displayed by the cis/trans, isotactic PMCP materials of Runs 1 and 3. Furthermore, by switching to $(R_{C}R_{Hf})$ -1 as the pre-initiator, the LCCTP of HD under identical conditions now provided virtually the same cis/trans, isotactic PMCP product as of run 3 but with a change in sign of the specific optical rotation being observed (see run 4, Table 1). In addition to confirming that optically active PMCP products of either handedness can be readily obtained by LCCTP using either $(S_{C},S_{Hf})-1$ or $(R_{C},R_{Hf})-1$, the nearly identical structures, properties, and specific rotations of the PMCP materials of runs 3 and 4 strongly suggest that the observed optical activities are not due to contamination by potential trace amounts of undetectable chiral species that are the by-products of polymerization quenching and work-up.

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As a final study, LCCTP of HD was conducted again according to runs 3 and 4, but now excess equivalents of molecular iodine (I_2) were added at the end of the polymerization time rather than use of a protic quench and workup. As expected on the basis of our previous reports,^{2d,5} runs 5 and 6 now produced optically active, iodo-terminated cis/trans, isotactic PMCP with the same low molar mass of $M_{\rm p}$ = 4 kDa, while maintaining a narrow molecular weight distribution of D = 1.13. Figure 2b presents the ¹H NMR (400 MHz, CDCl₃, 298 K) spectrum of (-)-I-PMCP obtained from run 6 in which the integrated ratio of the ¹H resonance for the iodo-terminated end-group relative to that for the methyl endgroup established that quantitative end-group functionalization had occurred. Furthermore, the ¹³C{¹H} NMR (100 MHz, CDCl₃, 298 K) spectrum of this material that is shown in Figure 3b confirmed the preservation of the cis/trans, isotactic PMCP microstructure that is nearly indistinguishable from all other materials. It can be noted that the increase in the appearance and intensity of small additional ¹³C resonances in these new I-PMCP materials is in keeping with similar results obtained with unfunctionalized PMCP of low DP_n value, and these can be attributed to resonances for penultimate and endgroup repeat units.^{2b,18} The reduction in molar mass also results in reductions in the glass transition and melting results in reductions in the glass transition and method products vis-à-vis the corresponding values for PMCP of higher DP_n obtained through LCP (cf. $T_g = -55$ °C, $T_m = 49$ °C for (-)-I-PMCP of run 6 vs $T_g = -10$ °C and $T_m = 98$ °C for (+)-PMCP of run 3).^{10a} One somewhat unexpected result, however, is the observation that the specific optical rotations of these new I-PMCP materials are essentially the same as for the corresponding unfunctionalized PMCP products (cf. runs 3 and 4 vs runs 5 and 6 in Table 1).

In summary, it can be noted that the only previous report of xPMCP appearing in the literature is for a low molecular weight hydroxy-terminated PMCP (HO-PMCP) material with a broad polydispersity that was produced in a non-living fashion and in racemic form using an achiral catalyst.²⁵ In the present work, we have been able to demonstrate that optically active, low molar mass, end-group-functionalized cis/trans, isotactic PMCP can now be easily produced in a programmed fashion through LCCTP using a readily accessible, homochiral C_1 -symmetric caproamidinate hafnium pre-initiator that can be synthesized in short order and in either enantioform from commercially available chiral amines. To put the practicality of using this enantioselective LCCTP process over LCP to access scalable quantities of the present and future new optically active xPMCP materials in perspective, the following analysis is very revealing. Specifically, to prepare 100 g of (+)-I-PMCP with a M_n of 4 kDa, 14 g of (S_C, S_{Hf}) -1 and 22 g of B are required if LCP of HD is utilized. However, for the same quantity of product, LCCTP of the same amount of monomer now only requires 0.07 g of (S_C, S_{Hf}) -1 and 0.11 g of B if 100 equiv (relative to 1) of ZnEt₂ are used. Clearly, the latter process becomes viable at even larger scales, and more so with further increases in ZnEt₂ equivalents. As a result, it is fair to say that the door is now wide open for exploring the material science and technology of a broad range of optically active, chiral liquid crystalline xPMCP materials. Efforts are now underway to extend these studies to the enantio- and stereoselective synthesis of other optically active main-chain chiral polyolefins and xPAOs,²⁶ as well as exploring the use of (S_{C},S_{Hf}) -1 or (R_{C},R_{Hf}) -1, and related homochiral, configurapubs.acs.org/acscatalysis

tionally stable, C_1 -symmetric group 4 metal cyclopentadienyl amidinate derivatives, for other catalytic or stoichiometric asymmetric transformations.²⁷

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.0c02104.

Details for the synthesis and characterization of (S_{C},S_{Hf}) -1 and (R_C,R_{Hf}) -1; details for polymerization of 1-hexene and 1,5-hexadiene and the isolation and characterization of poly(1-hexene) and (+)- and (-)-poly(methylene-1,3-cyclopentane) materials, including NMR spectra and GPC traces (PDF)

X-ray crystallographic information for (S_C, S_{Hf}) -1 (CIF) X-ray crystallographic information for (R_C, R_{Hf}) -1 (CIF)

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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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(3) For LCCTP, $DP_n = \{[monomer]_0 - [monomer]_t\}/\{[active]_0 + (m \times n)[surrogate]_0\}$, where, *m* is the number of molar equivalents of surrogate employed, and *n* is the number of equivalent alkyl groups on the surrogate that undergo reversible chain transfer (e.g., n = 2 in the case of a dialkyl zinc compound, ZnR₂) and $D \approx 1 + (k_{ct}/k_p)$.

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