

Phenyl-Terminated Polyolefins via Living Coordinative Chain Transfer Polymerization with ZnPh_2 as a Chain Transfer Agent

Mark A. Wallace, Aaron A. Burkey, and Lawrence R. Sita*



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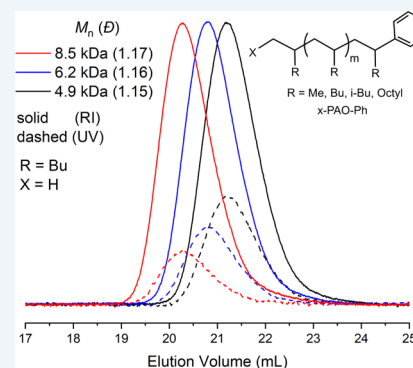
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ABSTRACT: Living coordinative chain transfer polymerization (LCCTP) of α -olefins, including propene, 1-hexene, 1-decene, and 4-methyl-1-pentene, using the Hf pre-initiator **1**, the borate co-initiator **B1**, and excess equivalents of diphenylzinc (ZnPh_2) as a chain transfer agent, provides excellent yields of the corresponding phenyl-terminated polyolefins with tunable degree of polymerization (DP_n) and very symmetric and narrow molecular weight distribution (e.g., $\bar{D} \leq 1.1$). Reactive quenching of ZnPh_2 -mediated LCCTP with molecular iodine (I_2) further provides orthogonally difunctionalized α -iodo, ω -phenyl polyolefins (x-PAO-Ph). The use of diethylzinc (ZnEt_2) in place of ZnPh_2 under otherwise identical conditions provides the corresponding ethyl-terminated polyolefin products (x-PAO-Et) with nearly the same DP_n and $\bar{D}$ values. A mechanism is proposed for R' group transfer from ZnR'_2 and polymeryl (P) group transfer from ZnP_2 during LCCTP that involves nucleophilic attack on a coordinated olefin and avoids formation of a Hf-R' bonded intermediate. These results serve to further advance LCCTP for the production of next-generation polyolefins.

KEYWORDS: living, chain transfer, polymerization, polyolefin

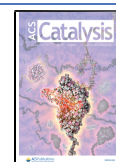


Polyolefins, which are largely obtained through the transition-metal catalyzed (coordinative) polymerization and copolymerization of ethene, propene, and a few higher carbon-numbered linear and branched α -olefins, are remarkable in the range of materials that are now available in support of a diverse array of products and applications.¹ Nonetheless, there remains the need and desire to develop the next generation of polyolefins that can continue to support the technological needs of society while also serving to reduce future environmental impact by being more amenable to recycle and upcycle.² Given the very small pool of industrially relevant olefin monomers, the quest for these next-generation polyolefins must ultimately rely on the conceptualization and validation of new combinations of transition-metal catalysts and polymerization processes in which they operate.³ The latter should also be highly versatile for the production of new fundamental forms and families of different “grades” of polyolefins in a programmable way, and importantly, in a manner that is not supply- or cost-prohibitive. Herein, we now report the ability to use excess equivalents of commercially available diphenylzinc (ZnPh_2) as a chain transfer agent (CTA) for the living coordinative chain transfer polymerization (LCCTP) of a variety of α -olefins to produce excellent yields of ω -phenyl terminated and α -iodo, ω -phenyl difunctional polyolefins.^{4,5} Most importantly, LCCTP provides a work-around solution to the “one-chain-per-active-site” limitation on scalability that is the intrinsic liability of all traditional living polymerizations.⁶ By varying the initial number of equivalents of ZnPh_2 employed, we further document the

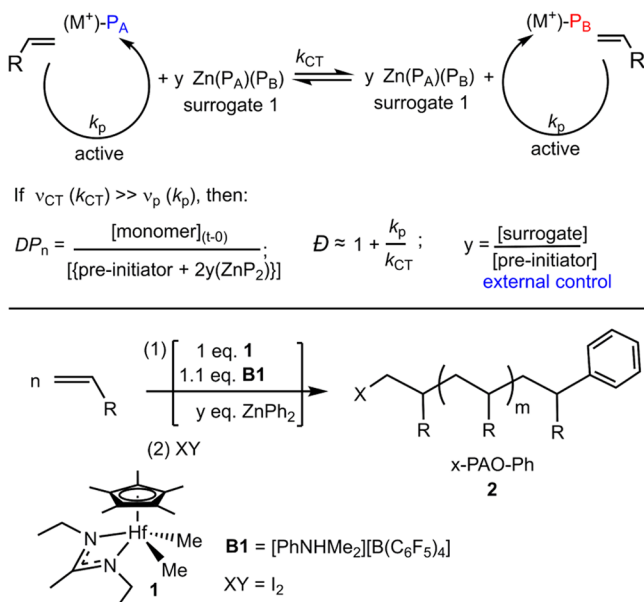
ability to program different targeted DP_n values while maintaining a very narrow molecular weight distribution (MWD). Finally, end-group-functionalized polyolefins (x-PAOs) that can be obtained through LCCTP in practical and scalable quantities are providing the key building blocks for several different classes of polyolefin block copolymers and molecular conjugates, several of which adopt highly ordered canonical and noncanonical periodic nanostructures in the condensed state.⁷ Accordingly, the results, conclusions, and hypotheses of the present report serve to contribute further to the advancement of LCCTP for designing and producing next-generation polyolefins.

Over the past decade, we have been pursuing the design, development, and application of the LCCTP of ethene and α -olefins as a highly versatile process by which to obtain a wide structural variety of new forms of polyolefins.^{4,7} More to the point, the top half of Scheme 1 summarizes the mechanism of LCCTP in which a population of transition-metal species that are active for chain-growth propagation are in fast dynamic exchange with a much larger population of inactive main-group-metal polymeryl species that serve as “surrogate” chain

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Scheme 1. (Top) Mechanism for Two-State Living Coordinative Chain Transfer Polymerization and (Bottom) Production of α -x, ω -Ph Difunctional Polyolefins (x-PAO-Ph)



growth centers. In the absence of chain termination, and under conditions where the rate and rate constant for reversible chain transfer between the active and surrogate species, ν_{CT} , (k_{CT}), are far greater in magnitude than the corresponding kinetic parameters for chain-growth propagation, ν_p , (k_p), both populations of active and surrogate species will appear to propagate at the same rate, and all of the desired aspects of a living polymerization can be maintained. These features include having a tunable number-average degree of polymerization (DP_n) and a very narrow MWD as defined by a dispersity index, $\bar{D} = M_w/M_n \approx 1 + k_p/k_{CT}$, where M_n and M_w are the number- and weight-average molecular weight indices, respectively.^{6,8} However, a large burden of scale-up cost is now carried by that of a relatively inexpensive commodity main-group-metal alkyl, such as diethylzinc ($ZnEt_2$), triethylaluminum ($AlEt_3$), or a mixture of the two, that is initially present in an excess amount at the start of LCCTP, relative to the more “exotic” transition-metal pre-initiator and expensive borate co-initiator. If all of the alkyl groups on the main group metal surrogate can be shown to be productively engaged in reversible chain transfer,^{4f} an added benefit of LCCTP as currently practiced is that it can be used for the successful targeting and production of practical quantities of low to ultra-low molecular weight polyolefin products with $\bar{D}$ values typically being ≤ 1.1 . Indeed, the ability to rapidly generate a family of different grades with nonoverlapping MWDs for a specific polyolefin structure by simply varying the initial number of equivalents of the main-group-metal alkyl is providing a new synthetic tool by which to establish and validate chain length-dependent trends in physical properties of “precision” polyolefins. A further bonus of LCCTP is that reactive quenching with a variety of inexpensive X–Y reagents can be used to directly provide end-group-functionalized poly(α -olefinates) (x-PAOs).⁷ Finally, we have more recently reported the first example of enantioselective LCCTP that can be used for the production of optically active x-PAOs.^{4g,h} On the other hand, to date, the entire body of work with LCCTP

has utilized only the aforementioned main-group metal alkyl reagents, which mechanistically constrains one end of the polyolefin product remaining unfunctionalized.

For the broader scope of controlled and nonliving coordinative chain transfer polymerization (CCTP), which includes Dow’s “chain-shuttling” process,^{10–12} a few examples of main group metal CTAs that incorporate a functional group have been documented in the scientific literature for providing access to α -monofunctional and α,ω -difunctional polyolefin products.¹³ However, these CCTP systems and functionalized CTAs: (1) are constrained by a limited range of olefin monomers that can be employed (e.g., exclusive to ethene only or co-polymerizations with ethene), (2) require multistep syntheses of the functionalized CTA, (3) have not been validated for near-quantitative utilization of all functional group components of the CTA,¹⁴ and (4) are based on strategies for the in situ generation and utilization of functionalized CTAs that are of ill-defined structure. Finally, although claims can be found in the patent literature for the general use of aryl-substituted zinc compounds as CTAs for CCTP, we could find no corroborating experimental results that were provided in support of any of these claims.¹⁵

To the best of our knowledge, there has only been one report of the use of $ZnPh_2$ to produce a phenyl-terminated polyolefin through coordination polymerization.¹⁶ In this case, $ZnPh_2$ was simply employed in combination with δ -TiCl₃ for preparation of a traditional heterogeneous Ziegler–Natta catalyst that provided isotactic polypropene for which a ¹³C NMR spectrum showed evidence for a certain degree of phenyl group termination. Gibson and co-workers¹⁰ also screened a large number of main-group organometallic reagents as potential CTAs in their seminal investigations of transition-metal catalyzed nonliving CCTP of ethene, and these authors stated, “ $ZnPh_2$ shows no evidence for chain transfer”. More recently, Tonks and co-workers¹⁷ reported that $ZnPh_2$ is ineffective as a CTA for ethene polymerization using a combination of an (α -diimine)NiBr₂ complex and methylaluminumoxane (MAO) as the active catalyst. Observation of a sharp decrease in polymerization activity with increasing equivalents of $ZnPh_2$ employed further led these investigators to conclude that irreversible phenylation of the transition-metal active species was occurring. It is also important to note that in this study, no spectroscopic evidence for the formation of ω -phenyl-terminated polyethene was provided.

The bottom half of Scheme 1 summarizes the experimental procedures implemented in the present report for the LCCTP of α -olefins using the previously reported cyclopentadienyl, amidinate (CPAM) hafnium pre-initiator, (η^5 -C₅Me₅)[N(Et)-C(Me)N(Et)]Hf(CH₃)₂ (**1**), and the “activating” borate co-initiator, [PhNH(CH₃)₂][B(C₆F₅)₄] (**B1**).^{4a} To begin, it is important to note that all of the polyolefin products were characterized by gel permeation chromatography (GPC) to obtain the molecular weight indices M_n , M_w , and $\bar{D}$ using a calibration curve based on 13 commercial narrow polystyrene (PS) standards.¹⁸ However, a reanalysis of these PS standards using our GPC system and the derived calibration curve consistently provided slightly lower M_n values and slightly higher $\bar{D}$ values vis-à-vis those provided by the vendor [cf. PS-6: M_n = 4740 Da, $\bar{D}$ = 1.03 (stated values) vs M_n = 4124 Da, $\bar{D}$ = 1.16 (our values)]. It is reasonable to conclude that this variance is simply due to differences in the specific instrument parameters used, which includes the number and type of SEC columns employed, and this information is being provided for

Table 1. LCCTP of α -Olefins

run ^a	equivalents (monomer) ^d	ZnR ₂ ' (equiv)	AlEt ₃ (equiv)	yield (g)	M _n ^f (Da)	M _w ^f (Da)	$\bar{D}$ ^f
1	1900 (H)	R' = Et (20)		3.2	4640	5370	1.16
2	1900 (H)	R' = Et (5)		2.8	14 840	17 570	1.18
3	1900 (H)	R' = Ph (20)		3.0	4880	5600	1.15
4	1900 (H)	R' = Ph (15)		3.0	6160	7170	1.16
5	1900 (H)	R' = Ph (10)		3.1	8490	9910	1.17
6	1900 (H)	R' = Ph (5)		3.0	16 050	19 140	1.19
7 ^b	1900 (H)	R' = Ph (20)		3.1	4700	5390	1.15
8	1900 (H)	R' = Ph (2)	12	3.0	4860	5960	1.23
9	1900 (4M1P)	R' = Ph (20)		2.7	4530	5340	1.18
10	1900 (D)	R' = Ph (20)		4.5	5770	6760	1.17
11 ^c	C3 ^e	R' = Ph (20)		2.2	4830	5530	1.14

^aPolymerization performed using 20 μ mol of **1** and 22 μ mol of **B1** in 5 mL of toluene at 0 °C for 24 h. ^bPolymerization was quenched using an excess of I₂. ^cPolymerization time was 3 h. ^dH = 1-hexene, 4M1P = 4-methyl-1-pentene, D = 1-decene, and C3 = propene. ^ePropene was introduced and maintained at 5 psi pressure. ^fDetermined by GPC (THF, 40 °C, calibration curve based on 13 polystyrene standards).

the benefit of the reader in assessing the magnitude of the $\bar{D}$ values reported for the new polyolefin products.

Table 1 provides details for the LCCTP of 1-hexene that was conducted using different equivalent amounts of ZnR₂' (R' = Et and Ph) and AlEt₃ as CTAs. To begin, runs 1 and 2 were performed using 20 and 5 equiv of ZnEt₂, respectively, under our standard conditions to obtain atactic poly(1-hexene) (aPH) reference samples.¹⁸ Next, run 3 was conducted using 20 equiv of ZnPh₂ in place of ZnEt₂, and this produced an excellent 94% yield of aPH that was determined to have M_n, M_w, and $\bar{D}$ values very similar to that of run 1 (see Table 1). In fact, as Figure 1 reveals, the two samples are nearly

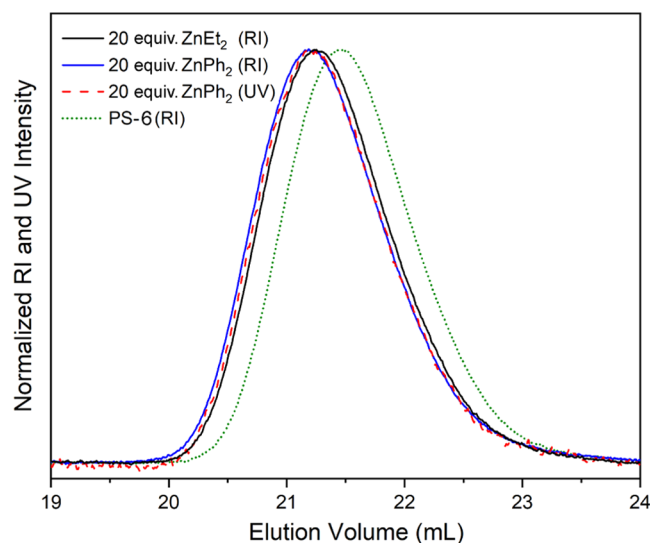


Figure 1. GPC traces for poly(1-hexene) produced using LCCTP at 0 °C in toluene and **1** as a pre-initiator, **B1** as a co-initiator, and 20 equiv of ZnR₂' (R' = Et, Ph) according to runs 1 and 3 of Table 1. The GPC trace of a polystyrene standard (PS-6) is provided for comparison. The detector used for each trace is provided in parentheses.

indistinguishable, based on the GPC traces from the RI detector alone. However, the aPH from run 3 also now presented a GPC trace using the UV detector (λ 260 nm) that perfectly matched the RI trace when the signal intensities of the two detectors were normalized in magnitude (cf. red dashed vs blue solid maxima in Figure 1). A comparison of the two aPH samples from run 1 and run 3 with the GPC trace for

the PS-6 standard (cf. green dotted maximum in Figure 1) provides compelling evidence that both polymerizations are living when either ZnEt₂ or ZnPh₂ was employed as the CTA. This conclusion is further supported by a comparison of the ¹H and ¹³C{¹H} NMR spectra for the two aPH samples in which the absence of vinyl and vinylidene resonances indicates that chain termination by β -hydrogen atom transfer did not occur (see Figures S1 and S3). Finally, these data strongly indicate that both phenyl groups of ZnPh₂ are engaged in an initial and subsequent exchange with equal efficiency. In short, the substitution of ethyl by a phenyl substituent on Zn apparently has no effect on the magnitude of any kinetic parameter related to initial group transfer from Zn to Hf that might then manifest as a noticeable difference in the MWD profile and dispersity index. Based on the widely accepted bimetallic mechanism for group exchange, the present finding is not only very surprising but it also suggests that perhaps the current understanding of this process can be improved upon (vide infra).

As a further test of the utility of ZnPh₂ to serve as a competent chain transfer agent and source of surrogate sites, LCCTP of 1-hexene was next performed in a series of experiments in which the number of excess equivalents of this CTA were systematically varied according to runs 4–6 in Table 1. Figure 2 presents the GPC traces for the resultant aPH materials, along with that of run 3, in which the RI signal intensity for each sample has been normalized in height while the UV signal was then adjusted using the RI normalization factor. As can be seen, there is a steady progression to higher M_n values as the amount of ZnPh₂ decreases from 20 to 15 to 10 equiv while the $\bar{D}$ value and the MWD profile remain constant.^{4a} For run 6 that employed only 5 equiv of ZnPh₂, the GPC trace now shows a slight asymmetry to the lower molecular weight side, and the M_n value is slightly higher than expected, based on the established trend. However, it must be pointed out that the value of $\bar{D}$, in this case, is still very narrow (cf. 1.19 for run 6 vs the mean value of 1.16 for runs 3–5), and in the absence of the visual provided by Figure 2, it might not normally call for any discussion. However, both the slight asymmetry and higher M_n value can be interpreted as signs that a very small degree of chain termination has occurred during LCCTP. On the one hand, a close inspection of both the ¹H and ¹³C{¹H} NMR spectra for the aPH material from run 6 once again do not show any evidence for termination by β -hydrogen atom transfer (see Figure S6). On the other hand,

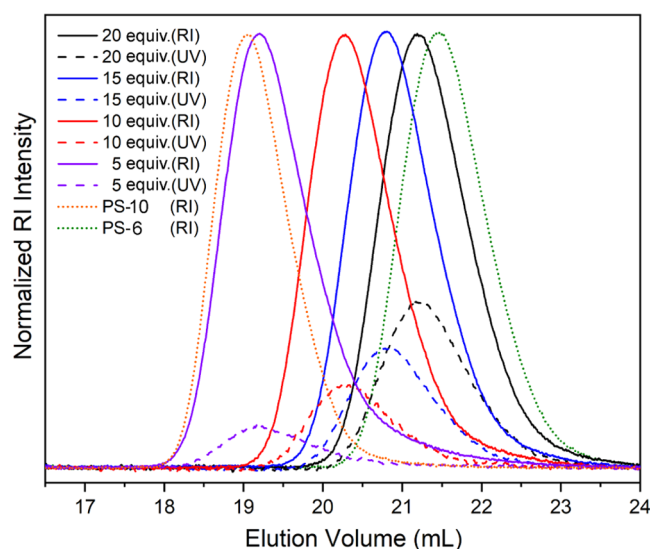


Figure 2. GPC traces for ω -Ph-terminated poly(1-hexene) produced using LCCTP at 0 °C in toluene and **1** as a pre-initiator, **B1** as a co-initiator, and different excess equivalents of ZnPh_2 according to runs 3–6 of Table 1. The detector used for each trace is provided in parentheses. The GPC traces for polystyrene standards PS-6 and PS-10 ($M_n = 22\,230$ Da, $\bar{D} = 1.02$) are provided for comparison.

observation in the latter of a very small increase in the intensities of ^{13}C resonances for 2,1-misinsertions of 1-hexene that occur during propagation appears to identify the culprit of chain termination. The question that remains, however, is whether chain termination by 2,1-misinsertion is unique to the use of ZnPh_2 as the CTA? Or is it an intrinsic feature of the active species derived from **1** and **B1**, and therefore, can be expected to occur with this particular α -olefin monomer irrespective of the nature of ZnR_2 being used? An overlay of the GPC (RI) traces for aPH obtained from runs 2 and 6 points to the latter being responsible (see Figure S16). Finally, the trend observed in Figure 2 for the steady decrease in the UV detector signal intensity for phenyl-terminated aPH as a function of decreasing equivalents of ZnPh_2 is to be expected for dilution of the aromatic chromophore by the nonabsorbing hydrocarbon polyolefin chains as the values of DP_n and M_n increase.

Two additional tests were performed to determine if ZnPh_2 can be used to seamlessly replace ZnEt_2 in the LCCTP of 1-hexene. The first of these was a repeat of the conditions of run 3, but with the change that after the end of the polymerization time, an excess amount of molecular iodine (I_2) was added to quench the polymerization to produce an α -iodo, ω -phenyl difunctional aPH product (see run 7 in Table 1).⁷ Gratifyingly, an analytical and spectroscopic characterization (see Figures S7 and S14) of the material obtained confirmed that quantitative end-group functionalization had occurred in the manner depicted in Scheme 1. A second test was also carried out to determine if a small amount of ZnPh_2 can be an effective polymeryl group mediator for the more complex case of three-state LCCTP when a large excess of AlEt_3 is used as the primary source of surrogate chain growth centers. As previously reported,^{4c} a much smaller rate constant for reversible polymeryl group transfer between Al and Hf results in a much broader MWD and larger $\bar{D}$ value. However, due to very fast and reversible $\text{Zn} \rightleftharpoons \text{Al}$ and $\text{Zn} \rightleftharpoons \text{Hf}$ exchange, a very small amount of ZnEt_2 in the initial AlEt_3 used, can restore a

much narrower MWD by effectively serving to catalyze faster polymeryl group exchange between Al and Hf.^{4c,j,14} Once again, this expectation was met with a 2:12 mixture of $\text{ZnPh}_2/\text{AlEt}_3$ as CTA as revealed by the molecular weight indices recorded for the aPH material obtained for run 8 in Table 1. Figure 3 presents a comparison of the GPC traces (RI and

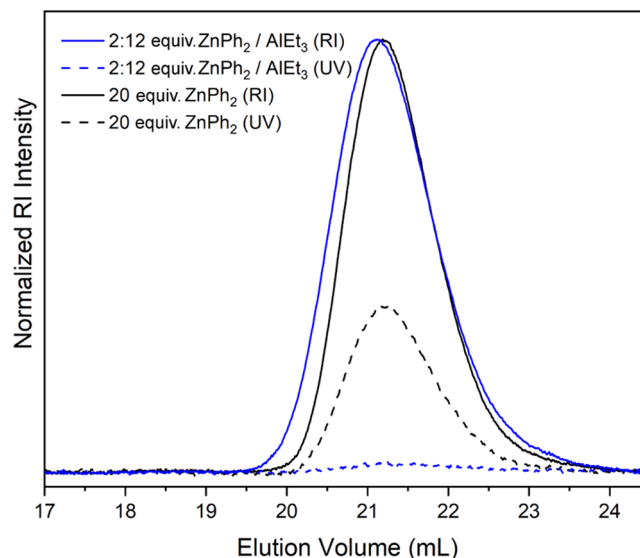


Figure 3. GPC traces for a three-state LCCTP of 1-hexene at 0 °C in toluene using **1** as a pre-initiator, **B1** as a co-initiator, and a 2:12 mixture of ZnPh_2 and AlEt_3 (blue) and two-state LCCTP under identical conditions using 20 equiv of ZnPh_2 (black) according to runs 8 and 3, respectively, in Table 1.

UV) of this material with that of aPH obtained under identical conditions but using 20 equiv of ZnPh_2 of CTA (run 3). These data further establish the seamless ability to effectively use either ZnEt_2 or ZnPh_2 reagents for two- and three-state LCCTP. By corollary, if rapid Ph group transfer is occurring between ZnPh_2 and AlEt_3 in the CTA mixture prior to the start of three-state LCCTP, then perhaps the bigger revelation is that $\text{Al}(\text{Et})_{3-n}(\text{Ph})_n$ species must also be effective CTAs for the production of ω -Ph polyolefins.

As a last synthetic consideration, the utility of using LCCTP with ZnPh_2 to produce a much larger variety of phenyl-terminated polyolefins was explored in a preliminary fashion by executing runs 9–11 of Table 1. Thus, the same number of monomer equivalents with 4-methyl-1-pentene (4M1P) and 1-decene (D) in runs 9 and 10, respectively, served to produce the corresponding phenyl-terminated atactic poly(4-methyl-1-pentene) (ω -Ph-aPMP) and phenyl-terminated atactic poly(1-decene) (ω -aPD) in excellent yields in each case (see Table 1). In the case of propene (C3), LCCTP was conducted under 5 psi of this gaseous monomer at 0 °C using an initial 20 equiv of ZnPh_2 and a shorter polymerization time (cf. 3 vs 24 h) to provide a high yield of phenyl-terminated atactic polypropene (ω -aPP) with a very narrow dispersity (cf. $\bar{D} = 1.14$ in Table 1). Analytical and spectroscopic characterization of all of these new polyolefin materials were fully consistent with quantitative phenyl end-group incorporation (see Figures S9–S11, S14, and S15). Figure 4 provides a side-by-side comparison of the GPC traces (RI and UV) for these three ω -Ph polyolefins.¹⁸ Once again, the decrease in the intensity of the UV signal in the order aPP > aPMP > aPD is in keeping with the expected dilution of the phenyl group chromophore relative to the

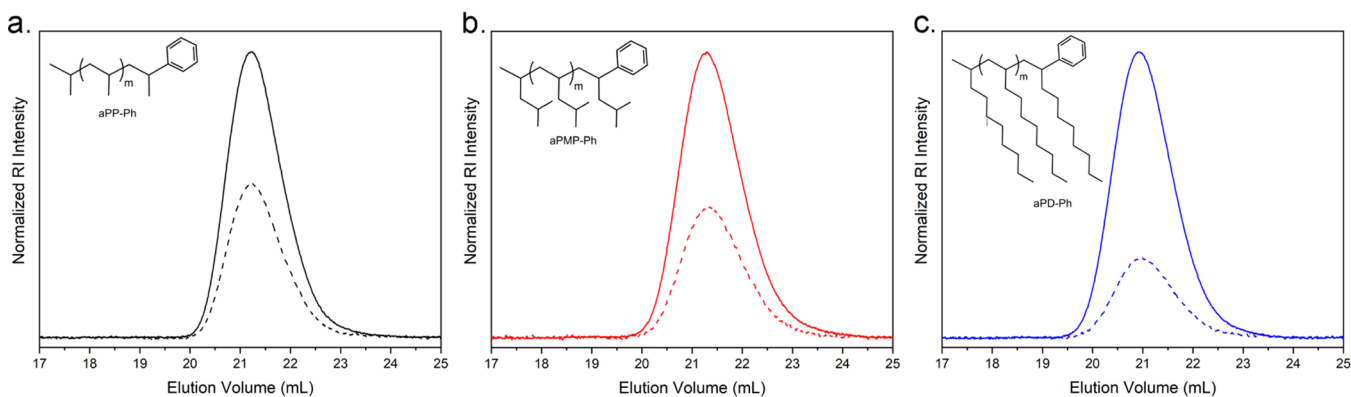


Figure 4. GPC traces for (a) ω -Ph atactic polypropene (aPP-Ph), (b) ω -Ph atactic poly(4-methyl-1-pentene) (aPMP-Ph), and (c) ω -Ph atactic poly(1-decene) obtained according to runs 9–11 of Table 1 with solid line for RI detector and dashed line for UV detector.

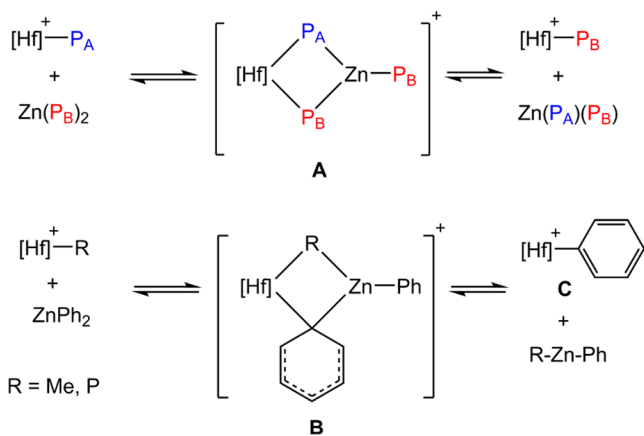
nonabsorbing hydrocarbon fraction of the polyolefin. Finally, it can be mentioned that ethene is also an excellent monomer for LCCTP with ZnPh_2 to provide phenyl-terminated polyethene (ω -Ph-PE), as well as α -iodo, ω -Ph PE that is obtained by reactive quenching with I_2 . However, given the greater challenges associated with controlling the much higher reactivity of this monomer, the limited solubility of the PE products, and the need for additional analytical and spectroscopic methods to properly characterize these materials, a detailed full account of the results of these additional studies will be presented elsewhere.¹⁹

On the one hand, perhaps the absence of any prior scientific evidence for the ability of ZnPh_2 to serve as a highly efficient chain transfer agent in either LCCTP or CCTP should not be surprising if one's expectations are based on the widely proposed mechanism for how group transfer in these processes is thought to proceed. More to the point, Scheme 2 presents the traditional view of bimetallic polymeryl group exchange that is believed to occur through a four-membered ring intermediate A.^{10–13} However, while there is plenty of spectroscopic and structural evidence for alkyl group exchange occurring through dinuclear μ -alkyl bridging interactions,²⁰ to the best of our knowledge, the literature is devoid of any

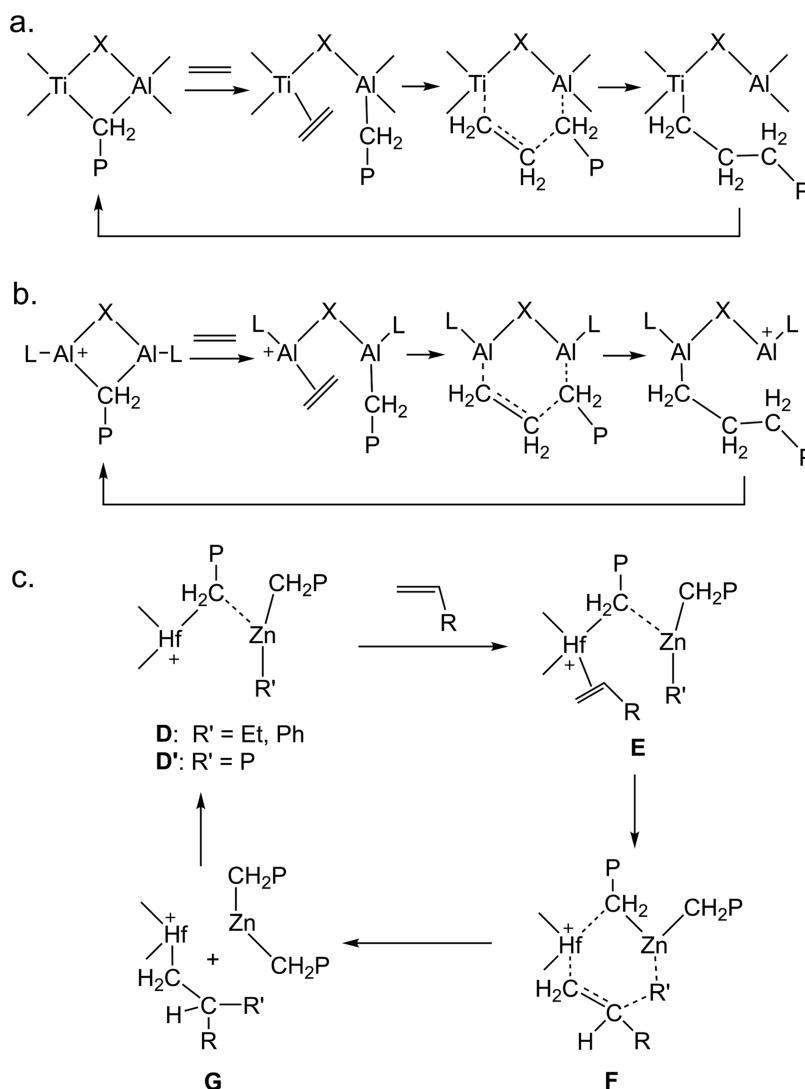
similar study or evidence of aryl group exchange occurring between a transition-metal complex and a main-group organometallic through the formation of a bimetallic μ -aryl bridging interaction of the type displayed in intermediate B and that leads to the formation of the transition-metal-aryl bonded exchange product C. Indeed, the closest experimental support for the latter type of bimetallic μ -aryl bridging interaction can be found in the crystallographic analysis of ZnPh_2 in which the dimeric structure, $[\text{PhZn}(\mu\text{-Ph})]_2$, is observed in the solid state.²¹ Variable temperature 1D and 2D NMR spectra and density functional theory (DFT) computational results also support the formation of bimetallic adducts involving the $\text{Hf-C}_{\text{sp}^2}$ bond of a naphthyl substituent of a Hf pyridyl-amido ion-pair complex and a $\text{Zn-R}'$ ($\text{R} = \text{Me}$ or Et) bond of ZnR'_2 .²² Returning to Scheme 2, perhaps the biggest issue with adopting the bimetallic group exchange mechanism in the case of LCCTP using ZnPh_2 as a CTA arises with product C. That is, to the best of our knowledge, there has never been a report in the scientific literature that provides compelling experimental or theoretical results in support of the ability of a transition-metal complex serving as either a precatalyst or a catalyst in which a M-Ph bond engages in the initiation of the coordinative polymerization of olefins that proceeds through either a 1,2- or 2,1-migratory insertion mechanism.²³

The results of the present report clearly show that ZnEt_2 and ZnPh_2 can be used interchangeably in the two- and three-state LCCTP of α -olefins to provide polyolefin products that are nearly indistinguishable with regards to molar mass, MWD profile, and dispersity. The latter CTA also provides excellent yields of polyolefin products with near-quantitative incorporation of an ω -Ph end group, irrespective of the steric nature of the α -olefin and polyolefin side chains. It is difficult, if not impossible, for us to reconcile these results as arising through the bimetallic group exchange mechanisms of Scheme 2, and we have accordingly looked for reasonable alternatives. To begin, we have considered the possibility that if bimetallic exchange according to Scheme 2 occurs, then neither the initial $\text{Ph} \rightleftharpoons \text{Me}$ and $\text{Ph} \rightleftharpoons \text{polymeryl}$ group exchanges, nor the migratory insertions of olefin monomer into both of the new Hf-Ph bonds that would be formed, are rate-determining processes that affect the nature of the polyolefin MWD profile. Although this kinetic and mechanistic scenario appears to be highly unlikely, we have nonetheless initiated an investigation involving structural and spectroscopic studies to document group exchange that might occur between ZnR'_2 ($\text{R}' = \text{Et}$ and

Scheme 2. (Top) Bimetallic Mechanism for Coordinative Chain Transfer between Transition-Metal Propagator and Main Group-Metal Surrogate Where P_A and P_B are Different Polymeryl Chains and (Bottom) Bimetallic Mechanism for Phenyl (Ph) Group Exchange with Transition-Metal Initiator ($\text{R} = \text{Me}$) or Propagator ($\text{R} = \text{Polymeryl}$, P)



Scheme 3. Proposed Bimetallic Mechanisms for Coordinative Polymerization and Group Transfer: (a) ref 25, (b) ref 26, and (c) This Work^a



^aP = polymeryl.

Ph) and ion pair initiators and living polymeryl species derived from **1** and **B1**.²⁴ We have also experimentally ruled out the possibility that simple olefin monomer insertion into the Zn–R' bonds proceeds as a first step to provide Zn(CH₂CHRR')₂, which is not expected to manifest large differences for R' = Et vs Ph. However, in truth, we are fundamentally skeptical about the general validity of the bimetallic mechanism for chain transfer proceeding via structure **A** in Scheme 2 on the basis of steric arguments. Here, we note that while often invoked, we have not found any report in the literature in which definitive experimental support has been provided to show that group exchange can proceed through the formation of two simultaneous μ -bridging polymeryl groups in the fashion required.

From the very early days of the discovery and development of heterogeneous Ziegler–Natta catalysts for the coordination polymerization of ethene, propene, and other α -olefins, various bimetallic mechanisms for propagation involving a transition-metal center working in concert with a main-group-metal alkyl component have been proposed, and some of these are attractive alternatives to the generally accepted Cossee and

Arlman mechanism involving the migratory insertion of a polymer chain into a coordinated olefin proceeding at a single transition-metal center.^{25,26} For instance, Natta and Mazzanti²⁵ proposed the bimetallic mechanism of Scheme 3a in which the monomer that is coordinated to the electrophilic Ti center formally undergoes nucleophilic attack at one end of the olefin ligand by the polymeryl group residing on Al that results in chain growth extension. More recently, computational studies of aluminum-based catalysts for polyethylene have identified plausible bimetallic mechanisms for propagation that involve the intramolecular transfer of a polymeryl group from a neutral Al center onto one end of ethene that is coordinated to a cationic Al center according to Scheme 3b.²⁷ Of course, the mechanism for the oxymercuration and amidomercuration of olefins is also proposed to proceed through nucleophilic attack on the olefin ligand of a Hg⁺(η^2 -olefin) intermediate.²⁸ Based on these considerations, we propose the alternative bimetallic mechanism for alkyl, phenyl, and polymeryl group transfer that is presented in Scheme 3c, which is shown after one cycle starting with the initial ZnR'₂ (R' = Et or Ph) has already occurred. One main feature of this mechanism is that it

requires much less steric congestion about both metal centers by avoiding a four-centered intermediate. In addition, the bimetallic adduct that arises through complexation of $\text{Zn}(\text{R}')\text{-}(\text{P})$ to form one μ -polymeryl interaction between Hf and Zn can potentially serve to enhance the electrophilicity of the transition-metal center in structure **D**. In turn, complexation of monomer to this species is facilitated and the partial positive charge that develops on this coordinated ligand in **E** lowers the energy barrier for subsequent nucleophilic attack of a R' group ($\text{R}' = \text{Et}$ or Ph) from Zn directly onto one end of the olefin through the six-membered ring transition state **F** to formally complete chain extension at Hf and simultaneously transfer a polymeryl group to Zn according to **G**. The two components from this last step can then reform a new bimetallic adduct **D'** and start the process over. Of course, one of the major attractive features of this hypothesis is that it also avoids the formation of a Hf- R' bonded intermediate.

In summary, we present experimental results which show that ZnPh_2 can seamlessly replace ZnEt_2 as the chain transfer agent and the source of surrogate centers in the LCCTP of α -olefins to provide ω -Ph-terminated polyolefins, and optionally, α -iodo, ω -Ph difunctional polyolefins for a structural variety of olefin monomers.⁴¹ Both new classes of polyolefins are expected to be useful in the post-polymerization synthesis of a spectrum of new polyolefin-based materials with an expanded range of applications. In addition to the aforementioned mechanistic studies, we are now engaged in exploring the full scope of employing different ZnAr_2 reagents, where Ar is a functionalized arene or polycyclic arene group. Finally, a computational investigation that can help to more firmly establish our proposed alternative mechanism for bimetallic group exchange and propagation is currently in progress. The results of all of these follow-up studies will be reported in due course.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acscatal.1c02038>.

Experimental details, including complete spectroscopic data (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Lawrence R. Sita – Laboratory for Applied Catalyst Science and Technology, Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742, United States; [orcid.org/0000-0002-9880-1126](mailto:lsita@umd.edu); Email: lsita@umd.edu

Authors

Mark A. Wallace – Laboratory for Applied Catalyst Science and Technology, Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742, United States

Aaron A. Burkey – Laboratory for Applied Catalyst Science and Technology, Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742, United States; Materials Science and Engineering Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, United States

Complete contact information is available at:

<https://pubs.acs.org/doi/10.1021/acscatal.1c02038>

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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