Living Coordinative Chain-Transfer Polymerization and Copolymerization of Ethene, α-Olefins, and α,ω-Nonconjugated Dienes using Dialkylzinc as "Surrogate" Chain-Growth Sites

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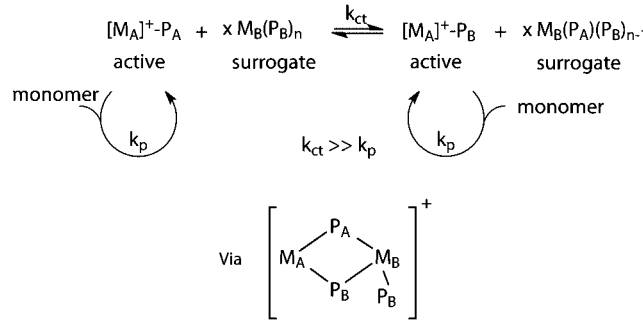
ABSTRACT: Highly efficient, rapid, and reversible chain transfer between active transition-metal-based propagating centers derived from {Cp*Hf(Me)[N(Et)C(Me)N(Et)]}[$B(C_6F_5)_4$] (Cp* = η^5-C_5Me_5) (**1a**) or {Cp*Hf(Me)[N(Et)-C(Me)N(Et)]}[$B(C_6F_5)_3$Me] (**1b**) and multiple equivalents of dialkylzinc (ZnR_2) acting as "surrogate" chain-growth sites has been achieved for establishing the *living* coordinative chain-transfer polymerization (CCTP) of ethene, α-olefins, and α,ω-nonconjugated dienes and living CCTP copolymerization of ethene with α-olefins and α,ω-nonconjugated dienes. These living CCTP processes not only provide a work-around solution to the "one chain per metal" cap on product yield currently limiting traditional living coordination polymerization of ethene and α-olefins but, in addition, provide access to practical volumes of a variety of unique new classes of precision polyolefins of tunable molecular weights and very narrow polydispersity ($M_w/M_n \leq 1.1$).

Introduction

Several transition-metal-based catalysts have been reported that can mediate the living metal-mediated coordination polymerization (also known as homogeneous, single-site Ziegler−Natta polymerization) of ethene, propene, higher α-olefins, and α,ω-nonconjugated dienes, and in some cases, these proceed with a high degree of stereocontrol (tacticity).[1,2] The commercialization of new polyolefin materials and products that takes advantage of the unique capabilities of living coordination polymerizations appears unlikely, however; at least as currently practiced.[3,4] More specifically, the same fundamental criterion of a living polymerization, namely, chain-growth propagation in the absence of irreversible chain termination, serves to establish a "one polymer chain per active metal center" cap on product yield as a critical liability. The severity of this liability sharply increases further—in terms of catalyst cost and metal recovery (removal from the product)—as the targeted number-average degree of polymerization, X_n, of the desired polyolefin product decreases. Indeed, while living coordination polymerization is ideally suited for accessing the largely unexplored material science and technology associated with architecturally well-structured "precision polyolefins" of very low to moderate molecular weights (ca. 500−10000 Da), the practical availability of significant quantities of these materials presently remains out of reach due to unfavorable weight (polymer) to weight (catalyst) ratios.[1,3−5]

An extremely attractive mechanistic proposal for providing a work-around solution to the intrinsic production liabilities of living coordination polymerization is presented by the concept of *coordinative chain-transfer polymerization* (CCTP), which employs added equivalents of a main-group metal alkyl that can serve in the capacity of "surrogate" metal chain-growth sites.[6−9] More specifically, at the heart of CCTP is highly efficient and reversible chain (polymeryl group) transfer between active transition-metal propagating centers and chain-growth-inactive main-group metal alkyl centers that proceeds according to Scheme 1.[6,10] Significantly, if the rate constant for chain-transfer exchange between the active and inactive metal centers, k_{ct}, is several times greater than the rate constant for propagation, k_p, then both the transition- and main-group metal centers will

Scheme 1



effectively appear to engage in chain-growth propagation at the same rate—while also maintaining all the desired features of a living polymerization.[7c,11] Indeed, under these conditions, X_n will be governed by both the quantity of monomer consumed and the total concentration of all polymeryl groups, P_A and P_B, that are formally engaged in active chain growth according to Scheme 1 and more precisely by $X_n = \{[\text{monomer}]_0 - [\text{monomer}]_t\}/([(M_A-P_A)^+ + n(M'_B-P_B)]_o)$, where n is the number of equivalent polymeryl groups per main-group metal [e.g., $n = 2$ for dialkylzinc (ZnR_2)]. The molecular weight polydispersity index, D ($=M_w/M_n$), will further be approximately determined by the relative magnitudes of the rate constants for these two processes according to $D \approx 1 + (k_p/k_{ct})$, where M_w and M_n are the weight-average and number-average molecular weight indices, respectively.[11] Finally, according to the mechanism depicted in Scheme 1, the quantity of polymer product is clearly no longer capped by the amount of transition-metal catalyst but rather the total molar equivalents of the much less expensive and readily available main-group metal alkyl that is employed.

Although highly desirable for beating the "one chain per metal" restriction of living coordination polymerizations, CCTP has, until now, only been successfully demonstrated in nonliving fashion for ethene polymerization and for the "chain-shuttling" copolymerization of ethene and 1-octene employing two different single-site catalysts for the production of "blocky" polyolefin copolymers.[6,7,12] Problematically, for successful realization of CCTP under living or nonliving conditions, it has already been convincingly demonstrated that substantial dif-

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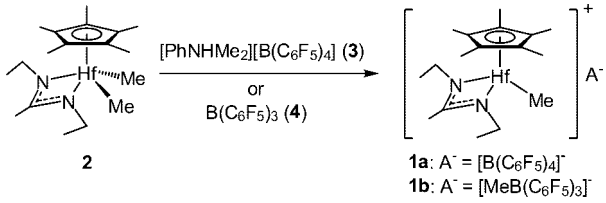
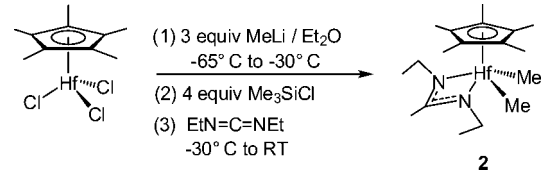
Scheme 2



Scheme 3



ficulties exist in identifying the right combinations of precatalyst, cocatalyst, main-group metal alkyl reagent, and polymerization conditions under which rapid, reversible, and highly efficient chain transfer (including chain shuttling between two different active propagating centers) can occur according to Scheme 1.[6f,8i] Indeed, given the extent and nature of these difficulties, it might reasonably be concluded that the discovery of new (living) CCTP systems can only realistically be accomplished through implementation of high-throughput screening methodology and instrumentation.[13] Further, since successful demonstration of (living) coordinative chain-transfer *homopolymerization* of longer chain α-olefins and α,ω-nonconjugated dienes, such as 1-hexene and 1,5-hexadiene, respectively, has hitherto not been reported, the task of finding a catalyst system that can engage in productive CCTP of these monomers with ethene and propene would appear to be, at the outset, an enormously daunting task.

Recently, we reported that the cationic methyl monocyclopentadienyl amidinate hafnium complex {Cp*Hf(Me)-[N(Et)C(Me)N(Et)]}[B(C_6F_5)$_4$] (Cp* = η^5-C_5Me_5) (**1a**), which is generated in situ from equimolar amounts of the neutral, dimethyl precatalyst Cp*HfMe$_2$[N(Et)C(Me)N(Et)] (**2**) and the borate cocatalyst [PhNHMe$_2$][B(C_6F_5)$_4$] (**3**) according to Scheme 2, can serve as a highly active catalyst in toluene at 0 °C for the living CCTP of propene in the presence of a large range of different initial molar equivalents (e.g., 5−200 equiv) of diethylzinc ($ZnEt_2$) to provide atactic polypropene materials of extremely narrow polydispersity (D < 1.1) and over a large tunable molecular weight range (M_n = 1000−111000).[2,9] As a demonstration of the utility of this living CCTP process for providing practical volumes of low molecular weight material, we have been able to successfully achieve a 60 g scaleup production of an atactic polypropene oligomer (M_n = 920 000 Da, D = 1.10) using only 0.165 g of the precatalyst **2**. By comparison, in the absence of living CCTP, this same amount of oligomeric material would have required 30 g of the expensive precatalyst, or a 2:1 polymer:precatalyst weight ratio! With these accomplishments in hand, we next set out to determine whether this system would be equally effective for (1) the living CCTP of ethene and higher α-olefins and (2) the living CCTP copolymerization of ethene or propene with higher α-olefins and α,ω-nonconjugated dienes. Herein, we report the successful realization of all of these objectives through documentation of living coordinative chain-transfer polymerizations and copolymerizations of these various monomers with added equivalents of $ZnEt_2$ as the main-group metal alkyl. Importantly, these living CCTPs permit access to several new categories of polyolefin homo- and copolymer materials that are characterized by tunable molecular weights and narrow molecular weight polydispersities ($D = M_w/M_n \leq 1.1$) at scales that greatly exceed those that are obtainable by classical living coordination polymerization alone.

Results and Discussion

a. Precatalyst Synthesis. We have previously demonstrated that a wide range of unique polyolefin materials and polyolefin stereochemical microstructures are now available through living coordination polymerizations of α-olefins and α,ω-nonconjugated dienes that are mediated by the class of molecularly discrete, homogeneous catalysts comprising the cationic group 4 metal complexes of general structure {(η^5-C_5R_5)M(Me)-[N(R^1)C(R^2)N(R^3)]}[B(C_6F_5)$_4$] (M = Zr and Hf).[2,9,10] For the present study involving reversible chain transfer with main-group metal alkyls, it has already been previously noted by us[9] that a reduction in nonbonded steric interactions of the supporting ligand environment of the propagating metal center within this class of catalyst is likely to be crucial for achieving a high degree of activity for the CCTP of longer chain α-olefins and α,ω-nonconjugated dienes. The incorporation of hafnium as the metal for the active propagating center is also viewed as being desirable for maintaining the living character of coordination polymerization at higher temperatures due to a documented greater thermal stability of hafnium complexes with alkyl substituents bearing β-hydrogens vis-à-vis the corresponding zirconium-based compounds.[14] On the basis of these considerations, and given the ready availability of *N*,*N*-diethylcarbodiimide that can be conveniently obtained in large quantity through dehydration of *N*,*N*-diethylurea, the precatalyst **2** was targeted for synthesis via the now-routine methodology presented in Scheme 3.[2,9] Gratifyingly, the desired compound **2** was obtained as a pale-yellow crystalline material in 65% yield after recrystallization from pentane at −30 °C, and in keeping with previous observations,[2,10,15] **2** engages in facile metal-centered racemization via "amidinate ring flipping" in solution at room temperature as evidenced by ^{1}H NMR spectroscopy.

Table 1. Living CCTP of Ethene Using 1b and ZnR_2[a]

run	$ZnEt_2$ (equiv)	t_p[b] (min)	yield (g)	M_n[c]	D[d]	T_m[e] (°C)
1	20	8	0.21	665	1.03	80
2	50	18	0.34	527	1.07	67
3	100	32	0.72	526	1.06	66
4	150	48	0.92	499	1.07	63
5	200	63	1.17	466	1.07	61
6[f]	50	21	0.24	449	1.06	56

[a] Conditions: **2** (10 μmol), **4** (10 μmol), and ZnR_2 in toluene (40 mL) at 25 °C under a positive pressure of ethene (~5 psi).[18] [b] Polymerizations were terminated at the onset of precipitation. [c] Determined by ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR end group analysis. [d] Determined by gel permeation chromatography (GPC) analysis. [e] Determined by differential scanning calorimetry (DSC) analysis. [f] Zn(i-Pr)$_2$ was used in place of $ZnEt_2$.

b. Living CCTP of Ethene. In the absence of main-group metal alkyl, introduction of ethene at ~5 psi to a toluene solution of the cationic complex **1a**, prepared in situ according to the Scheme 2, resulted in rapid precipitation of polyethene at 25 °C. To attenuate polymerization activity, an equimolar amount of the *borane* cocatalyst B(C_6F_5)$_3$ (**4**)[16] was used to generate [{Cp*HfMe[N(Et)C(Me)N(Et)]}[B(C_6F_5)$_3$Me] (**1b**) from the precatalyst **2** through methide group abstraction (see Scheme 2). As Table 1 and Figures 1−3 reveal, this modification led to successful development of highly efficient living CCTP of ethene that can be conducted in the presence of varying molar equivalents of ZnR_2 (R = Et or i-Pr). Thus, to begin, in the presence of 20 equiv of $ZnEt_2$, polymerization of ethene according to run 1 of Table 1 showed no precipitation of material until a polymerization time, t_p, of 8 min, and with more equivalents of $ZnEt_2$, this window of solution homogeneity could be extended even longer without affecting the CCTP activity (runs 1−5). Interestingly, CCTP of ethene using Zn(i-Pr)$_2$ appeared to proceed with only a slightly lower activity under

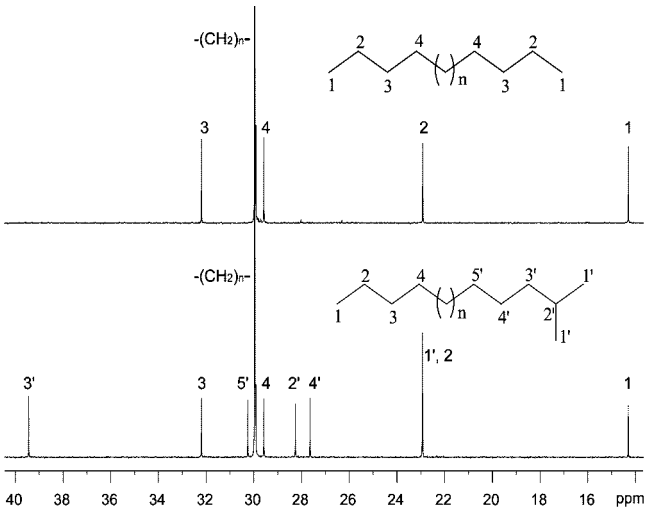


Figure 1. $^{13}C\{^1H\}$ NMR (150 MHz, 1,1,2,2-$C_2D_2Cl_4$, 90 °C) spectra of isolated polyethene from (top) run 5 and (bottom) run 6 of Table 1.

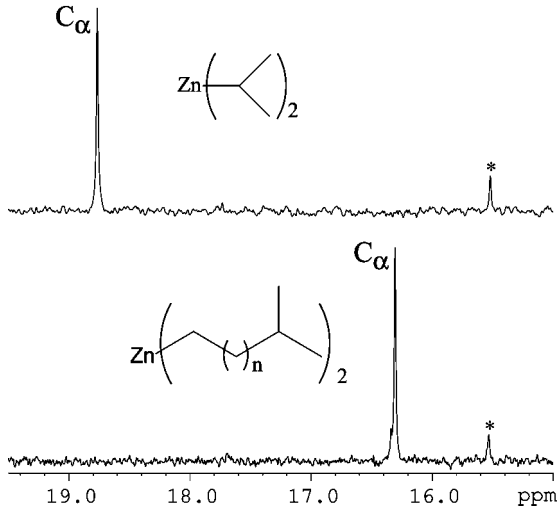


Figure 2. Partial $^{13}C\{^1H\}$ NMR (150 MHz, toluene-d_8, 20 °C) spectra showing the Zn−C_α region of (top) a mixture of **1b** and Zn(i-Pr)$_2$ in the absence of ethene and (bottom) the same mixture within 15 min after introduction of ethene. The ^{13}C resonance for a trace amount of diethyl ether is marked with an asterisk.

identical conditions (cf. runs 2 and 6). ^1H and ^{13}C NMR spectroscopies were used to quantify the nature of the end groups and M_n values after standard workup and isolation of the polyethene products, and as the ^{13}C NMR spectra for runs 5 and 6 in Figure 1 reveal, highly linear polyethene structures with well-defined end groups were observed, with the latter showing no evidence for chain termination by β-hydrogen transfer.[17] Importantly, these data also revealed that the polyethene material obtained from CCTP using 50 equiv of Zn(i-Pr)$_2$ distinctly possesses one isopropyl end group and one nonbranched end group. Indeed, the ^{13}C NMR spectra presented in Figure 2 for an NMR-scale CCTP polymerization of ethene served to verify that both of the i-Pr groups in Zn(i-Pr)$_2$ rapidly engage in chain growth of polyethene via the mechanism of Scheme 1. Figure 3 also demonstrates that the t_p-normalized M_n values for the isolated polyethene materials from runs 1−5 are proportional to $1/([\mathbf{1b}]_o + 2[ZnEt_2]_o)$ as expected for nonterminating CCTP according to Scheme 1. Finally, the living character of these CCTPs of ethene using $ZnEt_2$ are supported through a kinetic analysis involving characterization by gas chromatography of timed aliquots, each of which reveals a

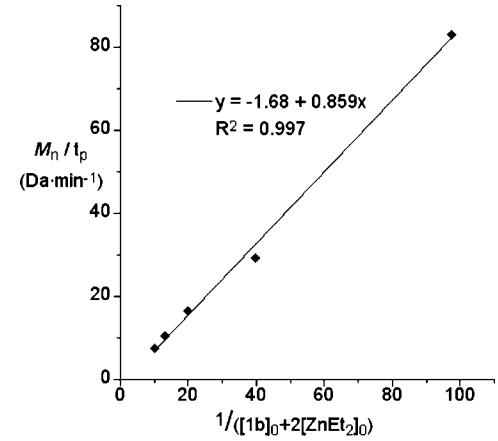


Figure 3. Dependence of time-normalized M_n values as a function of total active and surrogate metal sites for chain growth according to Scheme 1 and Table 1.

Table 2. Living CCTP of Higher α-Olefins and 1,5-HD Using 1a and $ZnEt_2$[a].

run	$ZnEt_2$ (equiv)	monomer (equiv)	t_p (h)	yield (g)	M_n	D
1	10	1-hexene (1670)	15	1.06	6650	1.06
2	20	1-hexene (1670)	15	1.08	3830	1.05
3	20	1-octene (1000)	18	0.82	3330	1.06
4[b]	10	1,5-HD (1400)	15	0.77	8020	1.04

[a] Conditions: **2** (10 μmol), **3** (10 μmol), and $ZnEt_2$ in toluene (10 mL) at −10 °C.[18] [b] Polymerization performed at 0 °C.

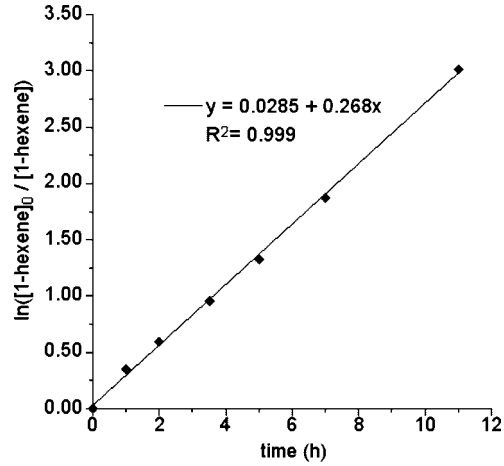


Figure 4. Kinetic analysis of the living CCTP of 1-hexene using **1b** and $ZnEt_2$.

narrow Poisson distribution of H−$[C_2H_4]_n$−H linear *n*-alkanes that are further distinguished by a linear increase in average carbon number with time.[6,18] In practical terms, for run 5 of Table 1, only 4.6 mg of precatalyst **2** was required to prepare 1.17 g of polyethene with an M_n of 466 ($D = 1.07$) under CCTP using 200 equiv of $ZnEt_2$, whereas 1.15 g of **2** would have been necessary to provide the same amount of product through standard living coordination polymerization.

c. Living CCTP of Higher α-Olefins and α,ω-Nonconjugated Dienes. With the ability to conduct living CCTP of ethene and propene[9] using $ZnEt_2$ now firmly established, it was of particular interest to determine whether this same system would be capable of the unprecedented task of achieving the living CCTP of longer chain α-olefins and α,ω-nonconjugated dienes. As Table 2 and Figure 4 demonstrate, this objective could indeed be accomplished by coupling the higher activity of **1a** with $ZnEt_2$. Thus, data for runs 1 and 2 of Table 2 confirm that the

Table 3. Living CCTP Random Copolymerization of Ethene with α-Olefins and 1,5-HD[a]

run	$ZnEt_2$ (equiv)	comonomer (equiv)	t_p (min)	yield (g)	PE content[b] (%)	M_n	D
1	20	1-hexene (1500)	60	2.79	84	13000	1.16
2	50	1-hexene (1500)	60	2.56	82	5910	1.24
3	20	1-octene (1500)	60	2.47	80	10400	1.14
4[c]	20	1-octene (1000)	60	2.60	88	12100	1.15
5	20	1-octene (1000)	30	1.60	91	8870	1.25
6	20	1,5-HD (1500)	60	2.45	85	14800	1.06
7	50	1,5-HD (1500)	60	2.34	84	6220	1.11

[a] Conditions: **2** (10 μmol), **3** (10 μmol), and $ZnEt_2$ in toluene (40 mL) at 25 °C and ethene (~5 psi).[18] [b] Polyethene (PE) content determined by NMR. [c] A 25 mL volume of toluene was used.

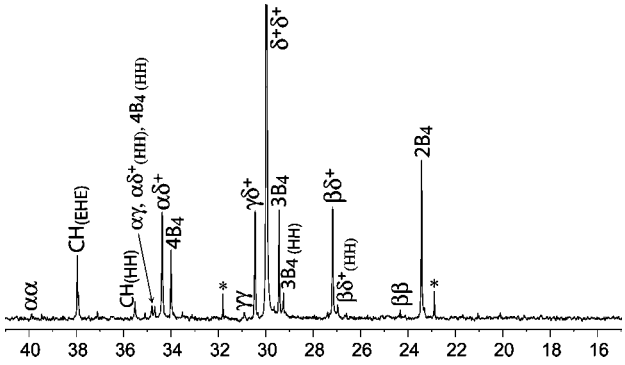


Figure 5. $^{13}C\{^1H\}$ NMR (150 MHz, 1,1,2,2-$C_2D_2Cl_4$, 90 °C) of poly(ethene-*co*-1-hexene) from run 1 of Table 3. Resonances are labeled according to previously reported structural assignments,[18,22] except those for trace hexane that are marked with an asterisk.

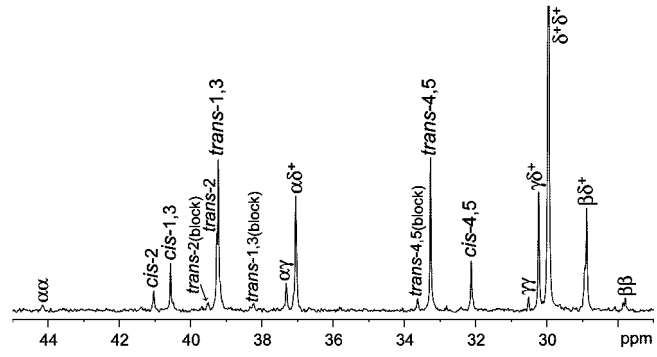


Figure 6. $^{13}C\{^1H\}$ NMR (150 MHz, 1,1,2,2-$C_2D_2Cl_4$, 90 °C) of poly(ethene-*co*-PMCP) from run 6 of Table 3. Resonances are labeled according to previously reported structural assignments.[18,23]

living CCTP of 1-hexene can be conducted in toluene at −10 °C to provide high yields of atactic poly(1-hexene) materials of narrow polydispersity ($D < 1.1$) and with M_n values that are dependent on the initial molar equivalents of main-group metal alkyl employed—but product yields that are not—as expected for the mechanism of Scheme 1. In addition, Figure 4 presents a kinetic analysis for CCTP of 1-hexene using **1b** and $ZnEt_2$ that displays a linear relationship between monomer conversion and time, and this correlation, along with end group analysis by NMR spectroscopy, unequivocally establishes the living character of polymerization[2,4,18]—which, to the best of our knowledge, represents the first example of CCTP for a longer chain α-olefin other than propene.[9] In this regard, the data of Table 2 further reveal that the living CCTP of 1-octene and 1,5-hexadiene (1,5-HD) can also be accomplished in similar fashion (runs 3 and 4). For the latter, structural analysis by ^{13}C NMR spectroscopy reveals that propagation proceeds almost exclusively by living cyclopolymerization to provide *cis, trans*-poly(methylene-1,3-cyclopentane) (PMCP) with less than 0.5% propagation occurring via noncyclized insertion of the 1,5-HD monomer that leaves pendant vinyl groups.[2b,18,19]

d. Living CCTP Copolymerizations of Ethene with α-Olefins and α,ω-Nonconjugated Dienes. With the successful living CCTP homopolymerizations of ethene, propene, longer chain α-olefins, and α,ω-nonconjugated dienes accomplished, an intriguing remaining challenge was to determine whether the living CCTP random copolymerizations of ethene with these latter different classes of monomers by a given catalyst system could be achieved.[7,20] Thus, it was somewhat surprising to find that the combination of **1a** and $ZnEt_2$ in toluene at 25 °C proved to be ideal for the living CCTP copolymerization of ethene with either higher α-olefins, such as 1-hexene and 1-octene, or α,ω-nonconjugated dienes, such as 1,5-HD, as supported by the data presented in Table 3 and Figures 5 and 6.[18] More specifically, the data in Table 3 for copolymerizations of ethene with 1-hexene (runs 1 and 2) and with 1,5-HD (runs 6 and 7) confirm that, under identical conditions, M_n values for the isolated copolymers are directly dependent on the molar equivalents of $ZnEt_2$ that are employed and with product yields once again remaining invariant. GPC of the copolymer products further revealed monomodal molecular weight distributions possessing slightly broader polydispersities—an observation that may be indicative of slower reversible chain transfer relative to propagation.[7c,11] Importantly, Figures 5 and 6 present structural analyses of the copolymers by $^{13}C\{^1H\}$ NMR (150 MHz) spectroscopy, and in each case, the comonomer is almost exclusively incorporated into the polymer backbone as isolated units and with only a trace of either consecutive comonomer dyads (e.g., H−H or HD−HD) or alternating comonomer triads (e.g., H−E−H or HD−E−HD) being observed.[18,22,23] It is also essential to point out that incorporation of 1,5-HD occurs exclusively by cyclopolymerization to produce isolated methylene-1,3-cyclopentane units. Finally, DSC analyses of all the copolymers of Table 3 revealed phase transitions that are distinct from those expected for each of the possible homopolymers. Indeed, each of the poly(ethene-*co*-PMCP) materials are characterized by well-defined M_n-dependent, first-order melting transitions (cf. T_m = 87 and 76 °C for runs 6 and 7, respectively).[18]

Conclusion

The results presented in this paper establish that living coordinative chain-transfer polymerizations and copolymerizations of ethene, α-olefins, and α,ω-nonconjugated dienes are capable of providing a work-around solution to the one chain per metal cap on product yield while providing access to unique new classes of precision polyolefins. We are presently exploring the full range of opportunities provided by these findings, including end group functionalization and well-defined polyolefin block copolymers. The results of these studies will be published in due course.

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Supporting Information Available: Experimental details, including polymer synthesis, characterization, and kinetic studies. This material is available free of charge via the Internet at http://pubs.acs.org.

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