DOI: 10.1002/anie.200906658

Aufbaureaktion Redux: Scalable Production of Precision Hydrocarbons from AlR_3 (R = Et or *i*Bu) by Dialkyl Zinc Mediated Ternary Living Coordinative Chain-Transfer Polymerization**

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In 1952, Karl Ziegler[1] introduced the Aufbaureaktion, a process by which the controlled oligomerization of ethene can be accomplished using triethylaluminum (TEA) as a chain-growth initiator at high pressure but relatively low temperature (cf. 100 °C, 100 bar). Commercial success of the Ziegler process, as it is now commonly known, is secured by the ability to provide a pseudo-Poisson distribution of long-chain linear α-olefins (LAOs) of the general formula $H_2C{=}CH\text{-}(CH_2)_nCH_3$ ($n = 1$–15) and the corresponding saturated terminal alcohols $HOCH_2(CH_2)_{n+1}CH_3$ through direct chemical transformations of the $Al[(CH_2)_{n+2}CH_3]_3$ intermediates.[2] In 2006 alone, global production of LAOs stood at four million metric tons, with 55 % of this volume being targeted for lubricants, plasticizers, detergents, additives, and fine chemical products.[3,4] Unfortunately, no Aufbaureaktion for the controlled oligomerization of propene or long-chain α-olefins using TEA or other trialkyl aluminum species AlR_3 as chain-growth initiators has ever been developed.[5] Accordingly, the potential technological value of new classes of hydrocarbon-based products that might be available from such processes on a commodity volume scale remains unknown. Herein, we report a new fundamental strategy, termed ternary living coordinative chain-transfer polymerization (t-LCCTP), for production of precision hydrocarbons (PHCs) through the living oligomerization and co-oligomerization of propene and long-chain α-olefins. PHCs represent a new class of polyolefins that are distinguished by having programmable and architecturally discrete carbon–carbon bonded frameworks, very low (e.g. oligomeric) molecular weights, and extremely narrow molecular weight distributions. With foreseeable benefits to society of PHCs as green and sustainable synthetic base stock oils and waxes for a broad range of technological applications, the ability of t-LCCTP to provide scalable volumes of these materials in a simple atom-economical and cost-effective manner from existing commodity AlR_3 reagents at ambient temperatures is highly comparable to the original Ziegler process.

Recently, we reported that the living coordinative chain-transfer polymerization (LCCTP) and copolymerization of ethene, propene, long-chain α-olefins, and α,ω-nonconjugated dienes could be achieved using $[(\eta^5\text{-}C_5Me_5)Hf(Me)\{N(Et)C(Me)N(Et)\}][B(C_6F_5)_4]$ (**1**) as the active transition-metal initiator for chain-growth propagation, along with multiple stoichiometric equivalents (relative to **1**) of diethylzinc (DEZ) that serve as surrogate chain-growth centers.[6] A fundamental requirement for successful LCCTP of these monomers is that the rate and rate constant, ν_{ct} and k_{ct}, respectively, for reversible (polymeryl group) chain transfer between the active transition-metal propagating centers and the inactive surrogate main-group-metal species must be far greater than the corresponding kinetic parameters ν_p and k_p for transition-metal-mediated propagation to insure that all active (A) and surrogate (S) species appear to propagate at the same rate. Within this kinetic scheme, the number-average degree of polymerization X_n for the final polyolefin product is defined by $X_n = ([\text{monomer}]_0 - [\text{monomer}]_t)/[A + nx\,S]_0$, where x is the initial number of molar equivalents of main-group-metal alkyl species relative to the transition-metal initiator and n is the number of alkyl groups of the surrogate species that engage in rapid and reversible chain transfer (e.g. $n = 2$ for DEZ).[7,8] An extremely narrow Poisson molecular weight distribution for the polyolefin product is also expected for the case where $k_{ct} \gg k_p$, since, to a first-order approximation, the polydispersity index D is defined by $D = M_w/M_n \approx 1 + k_p/k_{ct}$, where M_w and M_n are the weight-average and number-average molecular weight indices, respectively.[9] Typically, values of D for polyolefins obtained from LCCTP using **1** and DEZ are 1.04–1.09.[6]

Since the final yield of polyolefin product obtained through LCCTP is now virtually dependent upon only the initial amount of DEZ employed, this process circumvents the critical 'one-polymer-chain-per-metal-center' criterion of traditional living coordination polymerization that has proven to be an insurmountable liability for the scalable production of precision polyolefins and PHCs.[6,10] On the other hand, from a cost and safety perspective, the transport and handling of industrial volumes of DEZ is still problematic, and accordingly, the existing dependence of the current LCCTP process on this reagent could prove to be an Achilles heel limiting the successful commercialization of PHCs and PHC-based products. In this respect, TEA and triisobutylaluminum (TIBA), which are produced on a commodity scale from aluminum metal, dihydrogen, and ethene and isobutene, respectively, are significantly less expensive and substantially less pyrophoric than DEZ.[11] An additional advantage of these AlR_3 compounds over DEZ in terms of product yield is realized if

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[**] Funding for this work was provided by the NSF (0848293).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200906658.

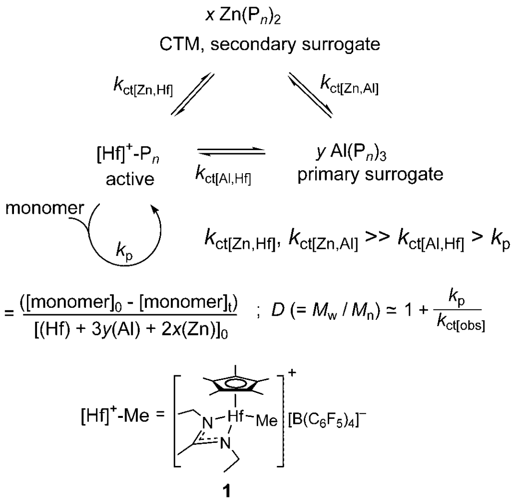
all three alkyl groups can equally engage in rapid and reversible chain transfer.

The upper half of Table 1 summarizes the results of LCCTP of propene using **1** and multiple equivalents of DEZ, TEA, and TIBA conducted according to our reported procedure.[6,12] Entry 1 serves as a frame of reference in which **1** and 20 equivalents DEZ in toluene provided, after 2 h at 0 °C and 5 psi propene, an atactic polypropene (a-PP) material for which the yield and M_n value are consistent with both ethyl groups of DEZ being accessible and engaged in rapid and reversible chain transfer with the active transition-metal propagating species (cf. $D = 1.04$). Upon replacing DEZ with TEA (Table 1, entry 2), very similar results were obtained under identical conditions, and again, on the basis of yield and the value of M_n, it can be concluded that all three ethyl groups of TEA were successfully engaged in reversible chain transfer. Furthermore, end-group analysis of this a-PP sample by ^{1}H NMR spectroscopy (600 MHz, 1,1,2,2-[D$_2$]tetrachloroethane, 90 °C) revealed the absence of terminal vinyl resonances owing to irreversible β-hydrogen transfer chain termination, thereby providing significant support for the living character of this polymerization. However, the larger D value of 1.19 for the material obtained with TEA is indicative of a smaller rate constant for hafnium–aluminum polymeryl group exchange relative to that for hafnium–zinc chain transfer, or more specifically, $k_{ct[Zn,Hf]} > k_{ct[Al,Hf]}$ according to Scheme 1. With TIBA (Table 1, entry 3), an increase in both temperature and time (cf. 20 °C for 4 h) was required to obtain any appreciable quantity of a-PP product. Unfortunately, efforts to increase the scale of this reaction through use of 100 equivalents TIBA revealed that an exceedingly long polymerization time of 16 h at 20 °C was required to provide only a small amount of product that further had an undesirable D value of 1.21 (Table 1, entry 4). Finally, it must be noted that with TIBA, a long induction period of at least one hour was always observed prior to the onset of LCCTP, and the possible origin of this phenomenon is the subject of ongoing investigations.

Table 1: Results for LCCTP and t-LCCTP of propene.[12]

Entry	AlR$_3$		DEZ	t_p	T_p	Yield	M_n[b]	D[b]
	R	[equiv][a]	[equiv][a]	[h]	[°C]	[g]	[kDa]	
				LCCTP				
1	–	–	20	2	0	4.2	8.75	1.04
2	Et	20	–	2	0	3.9	5.21	1.19
3	*i*Bu	20	–	4	20	4.6	6.00	1.19
4	*i*Bu	100	–	16	20	2.6	0.82	1.21
				t-LCCTP				
5	Et	10	10	2	0	4.4	7.31	1.02
6	*n*Pr	10	10	2	0	2.0	2.88	1.05
7	*i*Bu	10	10	2	0	1.2	1.84	1.07
8	*i*Bu	18	2	4	20	3.1	4.53	1.04
9	*i*Bu	190	10	72	20	88.0	0.58[c]	1.10
10[d]	*i*Bu	18	2	4	20	0.8	1.27	1.10
11[d]	*i*Bu	20	–	4	20	1.4	2.31	1.46

[a] Molar equivalents relative to **1**. [b] Determined by GPC analysis. [c] Determined by NMR spectroscopic end-group analysis. [d] t-LCCTP carried out in the presence of 500 equiv 1-octene.



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Scheme 1. Ternary living coordinative chain transfer polymerization of α-olefins employing **1** as the active chain-growth initiator, AlR$_3$ (R = Et, *n*Pr, or *i*Bu) as primary surrogate chain-growth species, and ZnEt$_2$ as both a secondary surrogate and as a chain-transfer mediator (CTM). P$_n$ is a polymeryl group that is produced after multiple α-olefin insertions involving **1**. All other parameters are defined in the main text.

To improve upon preliminary results obtained for AlR$_3$-mediated LCCTP of propene using **1**, we became intrigued by the idea of adding a third component, such as DEZ, that could act as a secondary surrogate chain-growth species, and more importantly as a chain-transfer mediator (CTM), to greatly enhance the overall rate of chain transfer between the active hafnium species and the primary surrogate aluminum centers by the mechanism proposed in Scheme 1. Critical to the success of this proposal for t-LCCTP, in which three different metal species must engage synergistically in ternary fashion, is that the relative rates and rate constants for polymeryl group exchange amongst all the metals, as well as that for chain-growth propagation at hafnium, must be of the following order: $(\nu_{ct}, k_{ct})_{[Zn,Hf]}, (\nu_{ct}, k_{ct})_{[Zn,Al]} \gg (\nu_{ct}, k_{ct})_{[Al,Hf]} > (\nu_p, k_p)_{[Hf]}$. Under this condition, similar approximate first-order relationships for X_n and D should hold; namely: $X_n = ([\text{monomer}]_0 - [\text{monomer}]_t)/[(\text{Hf}) + 2x(\text{Zn}) + 3y(\text{Al})]_0$ and $D \approx 1 + k_p/k_{ct[obs]}$, where $k_{ct[obs]}$ is the overall apparent rate constant for chain transfer.

On the basis of existing literature precedent, it was not at all obvious that DEZ could be used to realize the goal of t-LCCTP according to Scheme 1. On the one hand, there is ample evidence in support of rapid alkyl-group exchange in solution between two different main-group-metal alkyl species, such as between trialkyl borane compounds (BR$_3$) and dialkyl zinc reagents (ZnR$_2$), as well as more specifically between DEZ and TEA in benzene.[13,14] Moreover, it is well known that both DEZ and trimethylaluminum (TMA) can each serve independently as chain-transfer agents for either the heterogeneous Ziegler–Natta or homogeneous coordination polymerization of ethene and propene.[6,8,15–17] On the other hand, to our knowledge, no data has yet been presented that might serve to either indicate or substantiate the possible existence of synergistic interactions for reversible coordinative chain-transfer polymerization of ethene, propene, or longer-chain α-olefins as mediated by two different main-group-metal alkyl species. Indeed, substantial evidence to the contrary appears to exist in the case of dialkyl zinc and trialkyl aluminum chain-transfer agents. More specifically, it is well known that significant amounts of TMA are present as a residual component of methylaluminoxane (MAO), which is used as an activating cocatalyst for coordination polymerization.[18] However, in investigations of DEZ-mediated CCTP of ethene reported by Gibson and co-workers[8] in which the bis(imino)pyridine iron complex $[\{2,6\text{-}(\mathrm{MeC{=}N}\text{-}2,6\text{-}i\mathrm{Pr_2C_6H_3})_2\mathrm{C_5H_3N}\}\mathrm{FeCl_2}]$ is activated with a large excess of MAO, there is no evidence for an odd-carbon-numbered series of linear *n*-alkanes as a coproduct alongside the observed even-carbon-numbered series. This finding strongly suggests that rapid chain transfer between residual TMA and either DEZ or the active iron-centered propagating species must not be a competitive process in this system.[7] Furthermore, as part of an investigation into the possible origins of unusual copolymerization results encountered with the use of DEZ as a chain-transfer agent in combination with traditional heterogeneous Ziegler–Natta catalysts activated using TIBA, Chadwick and co-workers[16] reported that a 1:1 mixture of DEZ and TIBA in hexane solution undergoes spontaneous decomposition to yield a gray metallic precipitate and unidentifiable solution-phase products. Our present studies employing mixtures of these two reagents in toluene, however, failed to produce any evidence for such behavior. Finally, our intended use of DEZ for t-LCCTP as both a secondary surrogate and as a CTM is mechanistically quite distinct from its role as a chain-shuttling agent for transferring a polymeryl group between two different active transition-metal propagating species, as originally introduced by Arriola and co-workers[17] for the production of blocky poly(ethene-*co*-octene) by a nonliving process.

Gratifyingly, as the results presented in the lower half of Table 1 demonstrate, introduction of DEZ into the $\mathrm{AlR_3}$-mediated LCCTP of propene, conducted with **1** in toluene at 0 °C for 2 h and 5 psi, had a desired favorable influence on the values for all the key parameters of yield, M_n, and *D*. More specifically, when 10 equivalents each TEA and DEZ were initially employed, both the yield and M_n values of the isolated a-PP were found to be consistent with extremely rapid and reversible chain transfer amongst all three metal species, and remarkably, the polydispersity of this material was shown to be extremely narrow, with a *D* value of only 1.02 (Table 1, entry 5). Similar results were obtained when tri(*n*-propyl)aluminum and TIBA were employed as the primary surrogates (Table 1, entries 6 and 7, respectively). Moreover, end-group analysis by ^{13}C NMR spectroscopy (150 MHz) unequivocally established that all three alkyl groups of $\mathrm{AlR_3}$ (R = *n*Pr and *i*Bu) and the two ethyl groups of DEZ were incorporated into the respective a-PP materials at the theoretical level and ratio in each case.[12,19] While the exact nature of the mechanistic pathways and presumed bimetallic intermediates involved in the various chain-transfer processes presented in Scheme 1 have not yet been elucidated, the beneficial synergistic (catalytic) role played by the $\mathrm{ZnR_2}$ species initially present is evidenced in the above results by the fact that reversible hafnium–aluminum polymeryl group exchange is clearly no longer the rate-determining process dictating molecular weight polydispersity.[20] Finally, it can be noted that as the size of the R group in $\mathrm{AlR_3}$ increases in the order Et < *n*Pr < *i*Bu, a commensurate decrease in the apparent overall rate of t-LCCTP that further tracks with a slight steady increase in *D* values was observed (cf. Table 1, entries 5–7). Although the origin (or origins) of these trends are under further investigation, it is reasonable to presume that they arise from differences in the rates for initial chain transfer.

With preliminary support for t-LCCTP according to Scheme 1 secured, we next sought to address the critical question of whether practical scalable production of PHCs could be achieved using only a minimal amount of DEZ. Thus, although further optimization is still in progress, entry 8 of Table 1 and the data reproduced in Figure 1 conclusively demonstrate that with only 10 mol % DEZ (relative to $\mathrm{AlR_3}$) serving as a CTM and secondary surrogate, the t-LCCTP of propene can be effectively and efficiently achieved using 18 equivalents TIBA as the primary surrogate in toluene under near ambient conditions (20 °C, 5 psi) to produce a-PP material of very narrow polydispersity (*D* = 1.04). Once again, ^{1}H NMR spectroscopy further confirmed the living character of this t-LCCTP process. Moreover, as entry 9 of Table 1 and Figure 2 reveal, quite remarkably, this living oligomerization of propene by t-LCCTP with **1** could be substantially and successfully scaled in volume by employing 190 equivalents TIBA with as little as 5 mol % (10 equiv) DEZ in toluene at the same temperature and pressure to provide 88 g of the new PHC-based "white" oil represented by a-PP with a targeted low molecular weight and very narrow polydispersity (cf. M_n = 580 Da, *D* = 1.10). Most telling regarding the significance of this result is that, to obtain an equal quantity of this new PHC material through traditional living coordination polymerization, 179 g **1** would have been required as compared to the 0.3 g quantity that was employed for t-LCCTP in the present example! Equally important is the fact that this t-LCCTP of propene was carried out at ambient temperature over a period of 72 h with only a very slight

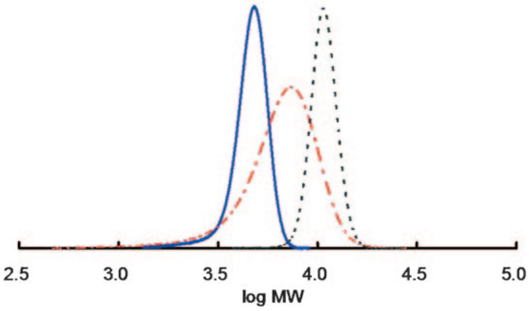

Figure 1. Molecular weight distributions for a-PP products obtained from the LCCTP of propene according to entry 3 (red dashed curve) and t-LCCTP of propene according to entry 8 (blue solid curve) of Table 1. The molecular weight distribution for a polystyrene standard (M_n = 11.3 kDa; *D* = 1.02) is shown as the black dotted curve.

Figure 2. A new PHC-based a-PP "white" oil of low molecular weight ($M_n = 580$ Da) and very narrow polydispersity ($D = 1.10$) prepared by t-LCCTP according to entry 9 of Table 1.

increase in termination that is responsible for the small degradation in product polydispersity (see also Figure S7 in the Supporting Information).

As a final note, entry 10 of Table 1 serves to establish that t-LCCTP can also be successfully extended to copolymerizations, where in the present case 10 mol% DEZ in combination with 18 equivalents TIBA (relative to **1**) efficiently provided a PHC material comprised of a targeted low molecular weight random copolymer of propene and 1-octene of very narrow polydispersity ($M_n = 820$ Da; $D = 1.10$). Once again, in the absence of DEZ, standard LCCTP provides a similar material, albeit one of inferior polydispersity (cf. $D = 1.46$; Table 1, entry 11).[12] In both cases, 1-octene was incorporated at a level of approximately 24 mol% as determined by ^{13}C NMR spectroscopic structural analysis.

In summary, the present results serve to validate the concept of t-LCCTP of propene and α-olefins as a viable process for accessing a large variety of PHCs in scalable bulk quantities. Importantly, this process employs much less expensive and much less pyrophoric AlR_3 reagents as the primary surrogate chain-growth centers in combination with only a relatively small amount of DEZ (e.g., 5 mol%, unoptimized). As the initial product of t-LCCTP before acidic quench is an $Al(P_n)_3$ species (Scheme 1), a variety of simple chemical transformations can be envisioned to additionally yield a broad range of end-group-functionalized PHCs. In this respect, after a wait of nearly 60 years, a new Aufbaureaktion has been introduced for the practical and scalable living oligomerization of propene and longer-chain α-olefins.

Received: November 25, 2009

Keywords: chain transfer · homogeneous catalysis · hydrocarbons · polymerization · zinc

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