Living Polymerization

DOI: 10.1002/anie.201004709

Programmable Modulation of Co-monomer Relative Reactivities for Living Coordination Polymerization through Reversible Chain Transfer between "Tight" and "Loose" Ion Pairs**

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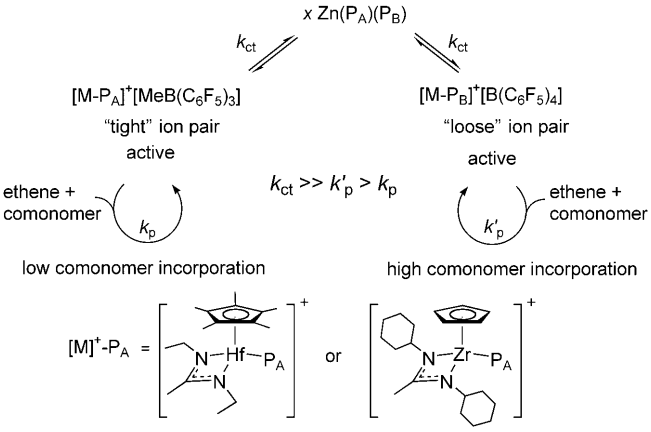
With annual global production exceeding 1.4×10^8 metric tons, it is safe to conclude that modern civilization will remain inseparably tied to polyethene- and polypropene-based materials for the foreseeable future.[1] This dependency should grow even further as new fundamental forms (or grades) of polyolefins are discovered and commercialized to fill existing technological voids.[2] To aid these efforts, we have been pursuing a strategy that seeks to identify and harness, through external control, dynamic reversible processes that are competitive with chain-growth propagation as a means by which to greatly increase the number of new materials that can be obtained with a single catalyst.[3] Herein, we now report the successful extension of living coordinative chain-transfer polymerization (LCCTP)[3–6] to include rapid and reversible chain (polymeryl-group) transfer between two populations of "tight" and "loose" propagating ion pairs, as mediated by an excess amount of a dialkyl zinc species ZnR_2, which provides additional "surrogate" chain-growth centers.[4] This approach enables the controlled modulation of comonomer relative reactivities for ethene/α-olefin and ethene/cycloalkene copolymerization. The ability to control the relative amounts of the two types of ion pairs now permits the programmable production of a broad spectrum of new polyethene-based materials in a straightforward fashion through the activation of a single precatalyst with varying ratios of two cocatalysts under otherwise identical conditions.

We have previously documented the requisite criteria, features, and key advantages of LCCTP as a practical work-around solution to the "one-polymer-chain-per-metal" restriction of traditional living coordination polymerization (Scheme 1).[3,4] For these studies, [Cp*HfMe$_2${N(Et)C(Me)N(Et)}] (**1**; Cp* = η^5-C_5Me_5) was employed as the precatalyst in combination with one equivalent of the borate cocatalyst [PhNHMe$_2$][B(C_6F_5)$_4$] (**2**) in toluene to generate the ion pair [Cp*HfMe{N(Et)C(Me)-N(Et)}][B(C_6F_5)$_4$] (**3**). This ion pair served as an active initiator for the LCCTP of ethene, propene, longer-chain α-olefins, and α,ω-nonconjugated dienes in the presence of excess molar equivalents of $ZnEt_2$ or AlR_3 (R = Et, *n*Pr, *i*Bu) to establish a population of surrogate sites that engage in rapid and reversible chain transfer with the active transition-metal propagating centers.[4,7,8]



Scheme 1. Proposed mechanism of living coordinative chain-transfer copolymerization between tight and loose ion pairs for modulating the comonomer relative reactivities of ethene and 1-hexene or cyclopentene. P_A and P_B are polymeryl groups of chain length A and B, respectively.

In the present study, we conducted the LCCTP copolymerization of ethene (E) and 1-hexene (H) at an ethene pressure of 5 psi at 25 °C and in *neat* 1-hexene to avoid the possible formation of a gradient-copolymer microstructure.[9] According to the methods of Spitz et al.,[10] the comonomer feed ratio at this temperature and pressure was determined to be: $x_E/x_H = 0.0216$ for $x_E = 0.0211$ and $x_H = 0.979$; x_E and x_H are the molar fractions of ethene and 1-hexene, respectively. With $ZnEt_2$ (10 equiv, relative to **3**) as the surrogate and a polymerization time of 30 min, the poly(E-*co*-H) material (sample 1) obtained after acid hydrolysis of the initially formed Zn(polymeryl)$_2$ intermediate was shown by gel permeation chromatography (GPC) to have a monomodal molecular-weight distribution, with $M_n = 30.0$ kDa and D ($=M_w/M_n$) = 1.13 (Table 1; M_n = number-average molecular weight, M_w = weight-average molecular weight).[9] Detailed copolymer compositional analysis of a ^{13}C NMR spectrum of sample 1 (150 MHz, 1,1,2,2-$C_2D_2Cl_4$, 90 °C) indicated a 1-hexene-incorporation level of 74.4 %, which is a remarkably high value in comparison to those reported for other poly-(E-*co*-H) materials.[9,11,12] On the other hand, when

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[**] Funding for this project was provided by the NSF (0848293).
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201004709.

Table 1: LCCTP data for the copolymerization of ethene (E) and 1-hexene (H) with the precatalyst **1**.[9]

Poly(E-*co*-H)	Cocatalyst **2**/**5**	Yield [g]	M_n [kDa][a]	D[a]	T_m [°C][b]	T_c [°C][b]	T_g [°C][b]	% H[c]	r_H[c]	r_E[c]	$r_H \times r_E$
sample 1	1:0	10.0	30.0	1.13	–	–	−46.3	74.4	0.102	51	5.20
sample 3	2:1	4.5	21.5	1.07	–	–	−52.3	62.6	0.0464	42	1.93
sample 4	1:1	3.7	17.6	1.06	–	–	−61.2	38.5	0.0148	75	1.11
sample 5	1:2	3.0	16.3	1.05	–	20.4	–	17.8	0.00443	207	0.92
sample 6	1:4	1.5	12.0	1.10	82.8, 67.3	73.5	–	8.0	0.00159	523	0.83
sample 2	0:1	1.2	9.7	1.15	90.5, 72.0	80.7	–	6.9	0.00098	605	0.59

[a] M_n and D values were determined by GPC. [b] Melting, crystallization, and glass-transition temperatures were determined by DSC. [c] The molar percentage of 1-hexene incorporation and the comonomer relative reactivities r_H and r_E were determined by ^{13}C NMR spectroscopy.

the ion pair $[Cp^*HfMe\{N(Et)C(Me)N(Et)\}][MeB(C_6F_5)_3]$ (**4**), prepared in situ from equimolar amounts of **1** and the borane $B(C_6F_5)_3$ (**5**), was used as the active initiator, the poly(E-*co*-H) material (sample 2) that was obtained under otherwise identical LCCTP conditions to those used for the synthesis of sample 1 was uniquely different, with $M_n = 9.7$ kDa, $D = 1.15$, and only 6.9% 1-hexene incorporation (Table 1). For both samples, no evidence of irreversible termination through hydrogen-atom-transfer processes could be discerned by NMR spectroscopy, and according to all criteria, including a kinetic evaluation, each of these copolymerizations leading to sample 1 and sample 2 can be classified as being living in character.[13] Not surprisingly, however, the physical properties of the two poly(E-*co*-H) materials were strikingly different. Characterization of sample 1 by differential scanning calorimetry (DSC) revealed an amorphous state over a broad temperature range that was further associated with a very low T_g value of −46.3 °C (Table 1). In contrast, the significantly more ethene rich material, sample 2, exhibited a high degree of crystallinity, with two associated melting endotherms, $T_m = 72.0$ and 90.5 °C, and a single crystallization exotherm, $T_c = 80.7$ °C.

It is now well-established that the strength of the ion-pairing interaction between a cationic transition-metal complex that is an active species for the coordination polymerization of ethene or α-olefins, and a discrete counteranion, such as $[MeB(C_6F_5)_3]^-$ and $[B(C_6F_5)_4]^-$, derived by cocatalyst activation of a neutral precatalyst, can have a substantial influence on activity, stereoselectivity, and the extent of comonomer incorporation.[14] On the basis of this existing body of research, the present results obtained with initiators **3** and **4** for the LCCTP copolymerization of ethene and 1-hexene can be rationalized by a mechanism in which the active species derived from **3** propagates with the $[B(C_6F_5)_4]^-$ counteranion as a "loose" ion pair, for which a more electropositive and more sterically accessible transition-metal center translates into a higher activity and degree of 1-hexene incorporation (Scheme 1). Similarly, the active species derived from **4** is assumed to propagate as a "tight" ion pair in which a closer (stronger) interaction of the metal center with the $[MeB(C_6F_5)_3]^-$ counteranion provides a greater barrier to 1-hexene incorporation, along with a decrease in activity. Indeed, the M_n values and total yields of the sample 1 and 2 poly(E-*co*-H) products (Table 1) are in keeping with such a scenario where the much higher degree of activity for the copolymerization mediated by **3** relative to that of the copolymerization mediated by **4** is readily apparent. Furthermore, a dramatic change in the comonomer relative reactivities derived by ^{13}C NMR spectroscopy for ethene and 1-hexene, r_E and r_H, respectively (Table 1), was observed when **3** was exchanged for **4** as the initiator for LCCTP, while all other polymerization parameters remained unchanged, including, most importantly, the comonomer feed ratio.[9]

Having identified the two limiting cases represented by samples 1 and 2, we rationalized that it might be possible to synthesize a spectrum of different grades of poly(E-*co*-H) materials by simply adjusting the relative ratio of the initial concentrations of **3** and **4** ($[\mathbf{3}]_0$ and $[\mathbf{4}]_0$) within a mixed-initiator system—if the rate for reversible chain transfer, ν_{ct}, involving the single cationic active propagating species $[Cp^*Hf(P_A)\{N(Et)C(Me)N(Et)\}]^+$, is significantly faster than the rates of propagation, ν_p and ν'_p. Under these kinetic conditions, LCCTP should provide monomodal and narrow molecular-weight distributions[7] for the poly(E-*co*-H) materials, but the degree of 1-hexene incorporation, as manifested by changes in the values for r_E and r_H, should now be set by the relative initial populations of the tight and loose ion pairs (Scheme 1).

In practice, different populations of the tight and loose ion pairs derived from **3** and **4** were readily established by activating precatalyst **1** with a mixture of the two cocatalysts **2** and **5**, whereby $[\mathbf{1}]_0 = [\mathbf{2}]_0 + [\mathbf{5}]_0$. Table 1 presents the collective data obtained for samples 1 and 2 together with data for four additional poly(E-*co*-H) materials, samples 3–6, which were obtained under identical conditions with different initial ratios of the tight and loose ion pairs. The key values of yield (activity), M_n, molar percentage of 1-hexene incorporation,

Figure 1. Poly(E-*co*-H) samples 1, 3, 4, 5, 6, and 2 (from left to right) obtained by LCCTP according to Table 1.

r_H, and $r_H \times r_E$ were all found to decrease in the predicted fashion with an increase in the population of the tight-ion-pair propagating species derived from **4** relative to that of the loose ion pair derived from **3**.[9] Importantly, GPC analysis of the new samples confirmed that all these materials were monodisperse and characterized by very narrow molecular-weight polydispersities (Table 1, column 5). Furthermore, the properties of the isolated poly(E-*co*-H) materials changed with increasing ethene content (Table 1, columns 6–8). The physical differences between these materials are perhaps best captured by a side-by-side comparison of the six samples (Figure 1).

To establish the possible generality of applying LCCTP with loose and tight ion pairs to obtain a range of different grades of polyethene-based materials, we conducted a similar investigation of ethene (E) and cyclopentene (CP) copolymerization. For this study, we used $[CpZrMe_2\{N(Cy)C(Me)N(Cy)\}]$ (**6**; $Cp = \eta^5\text{-}C_5H_5$, Cy = cyclohexyl)[8c] as the precatalyst, since we had shown previously that successful LCCTP copolymerization of ethene and cyclopentene with $ZnEt_2$ as the surrogate is possible with the sterically more open initiator species derived from **6** by activation with the borate **2**.[4c] Furthermore, this previous study served to establish that the α-iodo-terminated copolymers, α-I-poly(E-*co*-CP), can be obtained in quantitative yield through iodinolysis of the Zn–C bonds of the initially formed $Zn(polymeryl)_2$ intermediate upon the addition of a slight excess of I_2 as a solution in toluene.[4c,15,16] In the present study, these α-I-poly(E-*co*-CP) samples were further converted into the corresponding triphenylphosphonium-terminated materials, α-[I][Ph_3P]-poly(E-*co*-CP), by heating as a solution in dimethylformamide (DMF) with an excess of PPh_3 at 110 °C for 3 days.[9,18,19] A significant advantage of the α-[I][Ph_3P]-poly(E-*co*-CP) products is that an excellent qualitative picture of copolymer composition can be readily obtained through the use of matrix-assisted laser-desorption time-of-flight (MALDI-TOF) mass spectrometric analysis.[17] As originally demonstrated by Byrd et al.,[18] the attachment of a terminal cationic triphenylphosphonium moiety greatly enhances the utility of MALDI-TOF for characterization of the molecular-weight distributions and molecular-weight indices of polyolefin samples. On the other hand, without extensive standardization, it is not possible to extract quantitative values for molecular-weight indices and copolymer compositions from these MALDI-TOF data.[17–19]

Three α-I-poly(E-*co*-CP) materials were synthesized by the LCCTP copolymerization of ethene and cyclopentene with three different populations of loose and tight ion pairs derived from **6** by activation with: 1) only the borate catalyst **2** (Table 2, entry 1), 2) a 1:1 mixture of the two cocatalysts **2** and **5** (entry 2), and 3) only the borane cocatalyst **5** (entry 3). In each case, the LCCTP copolymerization of ethene and cyclopentene was performed with 50 equivalents of $ZnEt_2$ and 3000 equivalents of CP (relative to **6**) in toluene at 25 °C and at an ethene pressure of 5 psi.[9] GPC analysis of the three isolated α-I-poly(E-*co*-CP) materials confirmed monomodal and narrow molecular-weight distributions, whereby the yield (activity) and M_n values once again decreased as the concentration of the tight-ion-pair propagating species increased.

Table 2: Data for α-I-poly(E-*co*-CP) materials obtained by the copolymerization of ethene (E) and cyclopentene (CP) by LCCTP with the precatalyst **6**.[9]

Entry	Cocatalyst **2**/**5**	Yield [g]	M_n[a] [kDa]	D[a]	M_n[b] [kDa]	% CP[b]
1	1:0	2.3	2.58	1.22	1.35	15.6
2	1:1	2.1	2.46	1.14	1.11	11.4
3	0:1	1.7	2.32	1.10	0.99	8.7

[a] Determined by GPC analysis. [b] Determined by ^{13}C NMR spectroscopic end-group analysis (% CP is the molar percentage of cyclopentene incorporation).

^1H NMR spectra provided no evidence that chain termination had occurred by β-hydrogen-atom transfer, which once again validated the living character of these LCCTP copolymerizations. Finally, ^{13}C NMR spectroscopic microstructural and end-group analyses revealed that cyclopentene was enchained

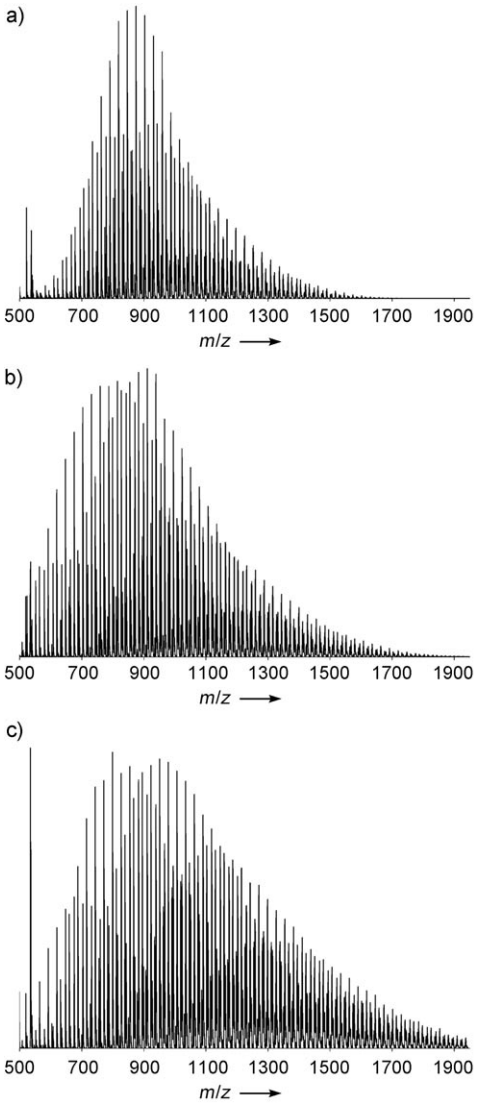

Figure 2. MALDI-TOF spectra of the α-[I][Ph_3P]-poly(E-*co*-CP) materials described in Table 2, a) entry 3, b) entry 2, and c) entry 1.

exclusively in a 1,2-fashion, and that the level of cyclopentene incorporation decreased as the population of tight ion pairs increased (Table 2).[20] The observed discrepancies between the GPC-based M_n values and those obtained by ^{13}C NMR spectroscopic end-group analysis are probably due to intrinsic deficiencies in polymer standards and GPC columns for low-molecular-weight analyses. Indeed, the MALDI-TOF data obtained for the three α-[I][Ph_3P]-poly(E-*co*-CP) samples (Figure 2) showed molecular-weight distributions that were very much in line with the M_n values derived by NMR spectroscopy. Significantly, however, these MALDI-TOF data also establish unequivocally that LCCTP involving tight and loose ion pairs can indeed be used to modulate ethene and cyclopentene comonomer relative reactivities in a programmed fashion, as evidenced by the qualitative increase in the molar percentage of cyclopentene incorporation as the population of the loose ion pair increased relative to the population of the tight ion pair (Figure 2 a–c).

In conclusion, LCCTP coupled with fast and reversible chain transfer between tight and loose ion pairs has been validated as a successful strategy for greatly extending the range of new polyolefin materials that can be obtained by copolymerization with a single initiator. Additional investigations are currently in progress to explore the extent and limits of this new methodology, including the synthesis polyolefin materials with programmed "blocky" copolymer architectures.[3,6]

Received: July 30, 2010
Published online: October 27, 2010

Keywords: ion pairs · living coordination polymerization · polyolefins · reversible chain transfer · transition metals

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[7] In brief, for LCCTP, $X_n = \{[\text{monomer}]_0 - [\text{monomer}]_t\} / \{[\text{active}]_0 + (m \times n)[\text{surrogate}]_0\}$, in which X_n is the number-average degree of polymerization, 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, ZnR_2). Furthermore, to a first approximation, the molecular-weight polydispersity index $D(=M_w/M_n)$ is approximately equal to $1 + k_p/k_{ct}$, in which k_{ct} and k_p are the rate constants for reversible chain transfer and propagation, respectively (see: Refs. [3–6] and A. H. E. Müller, R. Zhuang, D. Yan, G. Litvinenko, *Macromolecules* **1995**, *28*, 4326–4333).

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