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Continuous Production of Ethylene-Based Diblock Copolymers Using Coordinative Chain Transfer Polymerization

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Introduction. Polyolefins are by far the largest volume class of synthetic polymers today due to their excellent mechanical properties, the inexpensive nature of olefinic monomers, and their ease of production.[1] The majority of commercially available polyolefins are based on either homopolymer or random copolymer architectures. Well-defined olefin block copolymers (BCPs) have recently become available as a result of tremendous advances in living olefin polymerization.[2] With catalysts that operate with negligible chain transfer or termination, block copolymers can be formed using sequential monomer addition techniques. These BCPs represent an evolutionary advance in polyolefin product design, with the promise of decoupling longstanding property correlations and enabling use in applications previously inaccessible to olefin-based materials. However, these materials have not yet found widespread commercial utility, likely due to high costs associated with living polymerization methods and poor processability of the monodisperse materials.

While much of the work in the field has focused on suppressing chain transfer reactions, we have found that certain chain transfer processes can be quite useful in preparing olefin BCPs. For example, ethylene/α-olefin multiblock copolymers with both hard and soft blocks can be formed using a dual catalyst "chain shuttling" system.[3] In this process, polymer chains are transferred reversibly between catalysts with different copolymerization characteristics. The mechanism governing this process, called coordinative chain transfer polymerization (CCTP), is shown in Scheme 1.[4] CCTP operates by fast exchange between "growing" and "dormant" species and is similar to many mechanisms utilized to control free-radical polymerization processes.[5] This behavior was first observed in a single catalyst system in the early 1990s by Samsel,[6] and other CCTP systems were summarized in a recent review.[4]

In these polymerizations, CCTP occurs by exchange of a growing polymer chain on a catalyst (CAT^+) with a dormant chain residing on a chain shuttling agent (CSA) (Scheme 1). The polymer chains are then extended through normal propagation reactions. If the rate of exchange is fast relative to propagation (i.e., $k_{ex}[CSA] > k_p[monomer]$), the reaction can produce a polymer with a very narrow molecular weight distribution, which is a characteristic of living polymerization. These catalysts typically undergo normal chain termination pathways (such as β-hydride elimination or chain transfer to monomer) that dictate the molecular weight of the polymer in absence of added CSA (Scheme 1). Most of the published CCTP systems operate only at room temperature or below where polymer precipitation is problematic, resulting in broadened molecular weight distributions.[4] However, for catalysts capable of making very high molecular weight polymers at sufficient temperature to maintain polymer solubility, CCTP offers great potential for synthesis of high molecular weight linear BCPs.

Although the number-average molecular weight (M_n) may increase linearly with polymer production in the early stages of polymerization, the value cannot exceed what is attainable in absence of added CSA, the base molecular weight, M_{n0}. Thus, as M_n approaches M_{n0} at higher polymer/CSA ratios, M_n no longer increases linearly. Similarly, the molecular weight distribution (M_w/M_n) is approximately 1 in the early stages of chain growth but approaches 2 as M_n approaches M_{n0}. A CCTP system therefore appears to be living under certain reaction conditions, namely when M_n is much lower than M_{n0} or at low polymer/CSA ratios. It follows that synthesis of BCPs using

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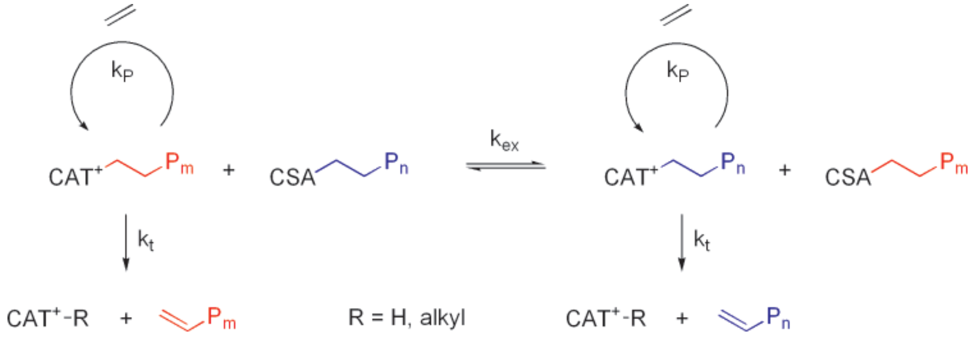
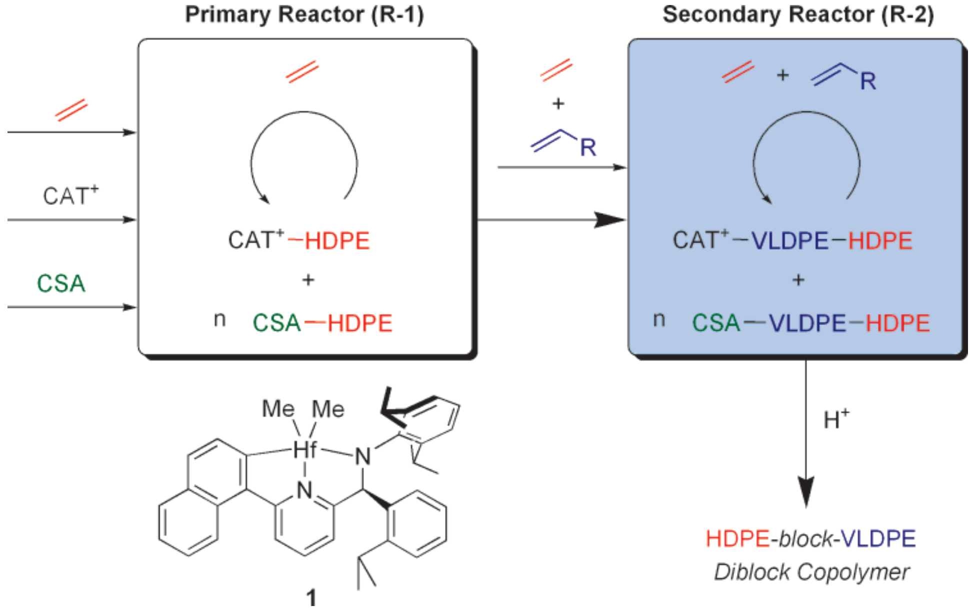
Scheme 1. Competing Mechanisms in Coordinative Chain Transfer Polymerization: Propagation, Chain Transfer, and Chain Termination Mechanisms



Scheme 2. Reactor Schematic for Preparation of Diblock Copolymer Using CCTP in a Series of CSTRs



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CCTP requires the rate of propagation to be sufficiently high relative to that of chain termination (i.e., high M_{n0}) to ensure that the majority of polymer chains are growing by the CCTP process.

As noted above, most of the previous CCTP systems lose their "living-like" properties before desirable high molecular weight polymers can be achieved, typically around $M_n = 4000$ g/mol.[4] This restriction unfortunately severely limits their use in one of the most attractive applications of a living polymerization: formation of BCPs via sequential monomer addition. In contrast, the catalysts used in our dual catalyst system operate in a high-temperature process (>100 °C)[3] and overcome the M_{n0} limitations of systems reported in the literature.[4] With this knowledge, we also reasoned that it should be possible to form BCPs from a single catalyst through sequential monomer addition. We tested this possibility by operating a CCTP system in a series of continuous stirred tank reactors (CSTRs).[7]

Results and Discussion. BCP synthesis from living polymerization is typically carried out in batch processes. In the simplest case, one monomer is added and polymerization is carried out to complete conversion, and then the process is repeated with a second monomer. In batch copolymerizations, the situation is often complicated by the different reactivities of the two monomers. This preferential monomer consumption creates a composition drift during chain growth and therefore a tapered copolymer composition. In contrast, a continuous reactor process is controlled at steady state, thereby ensuring a homogeneous copolymer composition. Therefore, a diblock prepared in a series of CSTRs has precise block junctions and homogeneous compositions of each block. The reactors are operated independently, facilitating control of the copolymer compositions from each reactor. A schematic for this reaction is shown in Scheme 2. In this case, effective CCTP gives a polymer with precisely two blocks per chain, instead of the statistical multiblock architecture afforded by dual catalyst chain shuttling systems.[3]

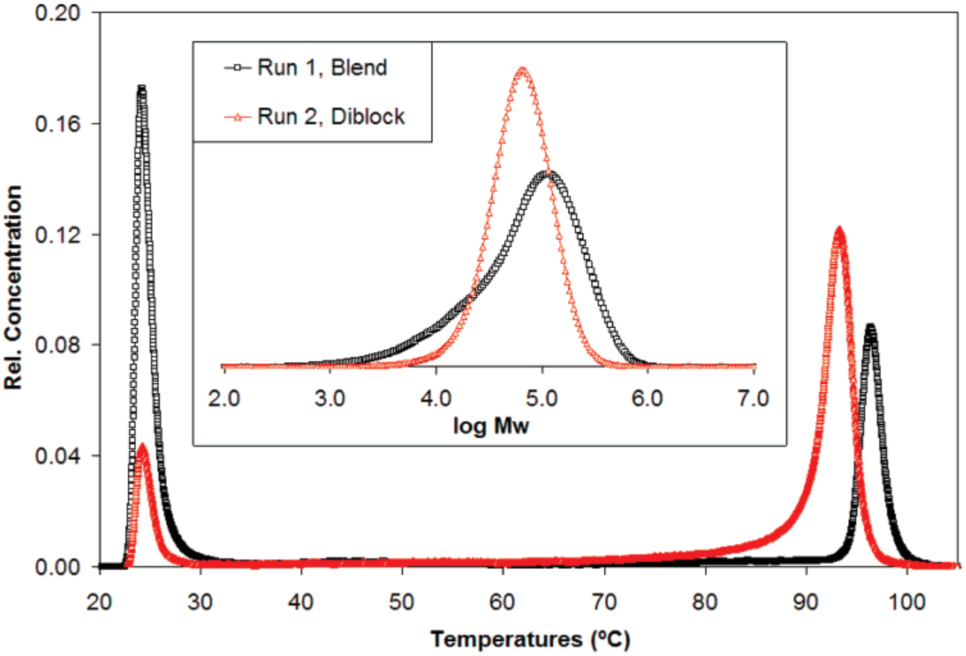
To demonstrate this technology, we targeted a copolymer with blocks of both high-density polyethylene (HDPE, $\rho \sim 0.94$ g/cm^3) and very low-density polyethylene (VLDPE, $\rho \sim 0.88$ g/cm^3). Full experimental details can be found in the Supporting Information. We chose the pyridylamide precatalyst **1**[8] for this study due to its high comonomer reactivity, high M_{n0}, and demonstrated CCTP ability.[3] We initially began the experiment by preparing a comparative dual-reactor physical blend sample to determine suitable reactor compositions (run 1 in Table 1). Production was begun in the primary reactor (R-1), where comonomer composition and hydrogen were controlled to give a copolymer with the desired density (0.937 g/cm^3) and melt index (1.1 dg/min). After production had stabilized, the R-1 effluent was sent to the secondary reactor (R-2) and production was continued. Additional catalyst was required in R-2 to maintain polymerization, as much of the catalyst from R-1 was no longer active upon exiting the reactor. The feed composition in R-2 was modified to give a resin with an overall melt index of 1 dg/min and density of 0.899 g/cm^3. Production rates were controlled in the two reactors such that 68% of the production

Table 1. Polymer Characterization Data from Continuous Coordinative Chain Transfer Polymerization

	R-1 product[a]		dual-reactor product										
run	ρ (g/cm^3)	I_2 (dg/min)	ρ (g/cm^3)	I_2 (dg/min)	M_n[b] (kg/mol)	M_w/M_n[b]	Zn/Hf ratio[c]	chains per Zn[d]	chains per Hf[d]	ATREF peak (°C)	ATREF solubles (wt %)	T_m[e] (°C)	ΔH[e] (J/g)
1	0.937	1.1	0.899	1.0	25.9	4.42	0		191	96.4	55.9	126	104
2	0.948	20	0.899	3.9	44.5	1.67	153	2.5	380	93.3	13.2	122	104

[a] Product isolated from first reactor before beginning production in the second reactor. [b] Measured by GPC relative to polystyrene standards and converted to polyethylene equivalents. [c] Molar ratio of zinc to hafnium in the final product. [d] Chains per Zn was calculated by using the zinc feed and polymer production rates and the number-average molecular weight of the resulting copolymer corrected for comonomer content. Similarly, chains per Hf was estimated by using the total catalyst metal feed. [e] Determined by differential scanning calorimetry.

Chart 1. Comparison of GPC (Inset) and ATREF Traces from Run 1, a Physical Blend (□), and Run 2, a Diblock Copolymer (Δ)



occurred in R-2 for an overall production rate of 4 kg/h. The density of the material produced in R-2 can be estimated at 0.88 g/cm^3 using the reciprocal density relationship.[9]

The diblock sample (run 2, Table 1) was produced using the reactor conditions established for preparation of the blend. The comonomer composition and production rate were maintained at the same value as in run 1, but instead of adding hydrogen to R-1, diethylzinc was used as an CSA to achieve the desired melt index ($I_2 = 20$ dg/min, equivalent to a M_n value of ∼15−20 kg/mol). As in the previous case, this material, along with fresh catalyst,[10] was fed to R-2, and production was continued. The reactor compositions and production rates were controlled to give a polymer with the same overall density (0.899 g/cm^3) as the final polymer from run 1. No additional chain transfer agent was added to R-2. The material collected from R-2 had a melt index of 3.9 dg/min, indicating a higher molecular weight than the R-1 product. This is consistent with the expected chain extension reaction from the CCTP process.

A number of methods provide data consistent with the diblock nature of this new copolymer, including molecular weight, thermal behavior, and solution solubility behavior. The GPC traces in Chart 1 (inset) reveal a broad molecular weight distribution, $M_w/M_n = 4.42$, for the dual reactor blend sample from run 1. The sample displays a broad molecular weight distribution despite the fact that a resin with a melt index of 1 dg/min was prepared in each reactor. This broadness is expected for this pyridylamide catalyst, as the activation mechanism generates multiple active sites.[11]

On the other hand, the sample produced with DEZ added to the first reactor displays an overall M_w/M_n of 1.67. The narrowing of the distribution indicates that the polymerization has CCTP characteristics. The theoretical molecular weight distribution from an ideal "living" polymerization in a series of two CSTR reactors[12] is given by the following equation, where f_1 and f_2 are the mass fractions of polymer comprising the two blocks:

$$M_w/M_n = 2(1 - f_1 f_2)$$

The theoretical lower limit of the molecular weight distribution in run 2 is therefore 1.57. The sample from run 2, with observed $M_w/M_n = 1.67$, indicates that the sample contains a large fraction of polymer chains with the anticipated diblock architecture. The estimated number of chains per zinc and hafnium are also indicative of a high level of CCTP. The M_n of the diblock product corresponds to just over 2 chains per zinc but 380 chains per hafnium. This copolymer also provides a highly unusual example of a polyolefin produced in a continuous process with a molecular weight distribution less than that expected for a polymer prepared with a single-site catalyst.

The comonomer composition distributions of these two materials were analyzed using analytical temperature rising elution fractionation (ATREF) (Chart 1).[13] Analytical temperature rising elution fractionation, or ATREF, is a technique that fractionates semicrystalline copolymers as a function of crystallization temperature. The physical blend displays a peak at 96

°C with an area of 39 wt % and a soluble fraction of 56 wt %. This behavior is consistent with a physical blend of HDPE and VLDPE. The ATREF trace from the run 2 diblock sample reveals a peak at a slightly lower temperature, 93 °C, with no evidence of a shoulder at higher temperature that would indicate uncoupled HDPE. In contrast to the blend, the majority of this sample, 84 wt %, elutes at this high temperature, while only 13 wt % of the sample is soluble at room temperature.[14] This ATREF behavior can only result from a BCP architecture with a very homogeneous block structure. The melting behavior of the two resins also reveals structural differences. The physical blend has a peak melting temperature (T_m) of 126 °C with a heat of fusion of 104 J/g, consistent with the high-density fraction of the sample. The diblock sample from run 2 has similar crystallinity, with heat of fusion of 104 J/g, reflecting the similar compositions of the two samples. However, the diblock sample displays a lower peak melting temperature, with $T_m = 122$ °C. This depression of peak melting temperature is also consistent with a BCP architecture.[15]

Conclusion. The polymer synthesis shown in Scheme 2 represents a powerful example of the use of CCTP for synthesis of olefin-based BCPs in a continuous process.[16] This diblock copolymer has a well-defined block structure containing no more than two blocks per chain, in sharp contrast to the statistical multiblock composition produced by our dual catalyst process.[3] These materials are also very different from those made by living polymerization techniques, as the distribution of residence times gives a distribution of molecular weights in each block. The overall molecular weight distribution of copolymers from continuous CCTP is narrower than that of a typical single-site polymer, a result of running the reaction in a series of CSTRs.

This continuous CCTP technique, which produces multiple chains per catalyst, is amenable to preparation of large quantities of BCP; the material described above was produced at a rate of 4 kg/h! Living polymerization systems described in the literature[2] are performed in non-continuous batch or semibatch processes and typically yield much smaller quantities of BCPs (<50 g) from reactions that proceed over the course of several hours. This CCTP scheme also produces multiple chains per catalyst, an advantage over stoichiometric living polymerization systems. The block composition can easily be varied by changing the production rate in either reactor, while the comonomer content of either block can be tailored by varying the feed compositions or even introducing another catalyst into one reactor (as long as the new catalyst also does CCTP). The continuous process also ensures a homogeneous copolymer composition within each block, in sharp contrast to materials produced in batch or semibatch processes which have tapered compositions. We are currently expanding the process capabilities for this continuous CCTP system and exploring applications for these new ethylene-based olefin block copolymers.

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Supporting Information Available: Text giving complete experimental details for dual-reactor operation, polymer characterization details with additional data, and the complete derivation of the theoretical molecular weight distribution from living polymerization in a series of CSTRs, tables of process conditions for the primary and secondary reactor, and a chart showing a comparison of melting behaviors. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) The reciprocal density relationship $\rho = 1/(f_1/\rho_1 + f_2/\rho_2)$ was used to estimate the resulting overall density of the desired polymer blend.

(10) In both reactions, fresh catalyst was required to reach the desired productivity in the second reactor (R-2). This added catalyst will initiate a new polymer chain without a HDPE block. However, since we make about 400 chains/total catalyst, the relative number of new chains introduced by this addition is very low (<0.25% of the chains).

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