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Tuning Block Compositions of Polyethylene Multi-Block Copolymers by Catalyst Selection

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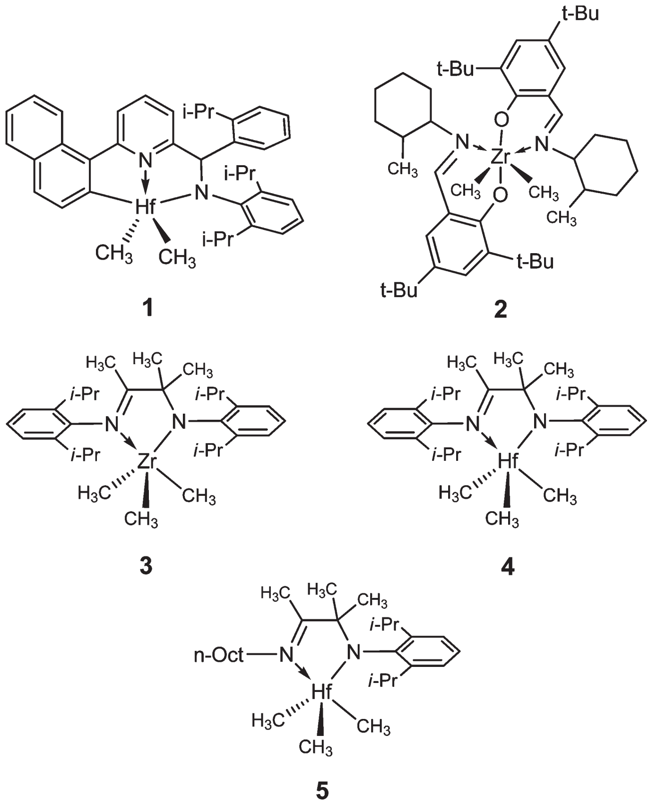
Chain shuttling, the fast exchange of growing polymer chains among catalyst centers mediated by a chain shuttling agent (CSA), has enabled the production of ethylene-based olefin block copolymers (OBCs) using coordination catalysts.[1] For example, copolymerization of ethylene and an α-olefin by certain catalyst pairs in the presence of a CSA produces an OBC with blocks that are alternately highly or lightly branched. This new polyethylene architecture, which has a statistical distribution of block lengths and blocks/chain, provides advantaged material properties[2] and can produce mesophase-separated materials with interesting optical properties.[3]

Because the catalysts in this process operate simultaneously in the reactor, the segment compositions are dependent; that is, conditions that generate a targeted level of short chain branching (SCB) for one catalyst determine the SCB level of the other. Short chain branches affect polymer properties by disrupting the crystallinity of polyethylene; accordingly, segments with less SCB are designated as "hard", whereas those with more SCB are "soft". This difference in SCB (δ) is controlled by the difference in ethylene/α-olefin selectivity of the two catalysts and the monomers' concentrations in the reactor. For the catalyst pair previously described,[1a] under reactor conditions for which **1** (Chart 1) produces 0.857 density polymer (ca. 18 mol % octene), **2** produces 0.939 density polymer (ca. 1 mol % octene). Thus, the component blocks of this polymer are near the extremes of high density polyethylene (0.94 to 0.97) and ultralow density polyethylene (0.86 to 0.90).[4] However, some polymer applications, such as those that require low processing temperatures or hydrocarbon solubility, may benefit from lower δ. Therefore, alternative chain shuttling catalysts with varying α-olefin selectivities were sought to enable production of such new OBCs. Catalysts featuring imine–amine ligands (**3**–**5**) were investigated[5] as potential chain shuttling catalysts because of their gross structural similarities to **1** and good catalytic performance.[6]

Chain shuttling polymerizations are conducted most effectively in continuous reactors,[1a] meaning that all monomers and reagents are constantly fed to the reactor, and the produced polymer is isolated from the effluent. Flows are adjusted to achieve the desired steady-state conditions, as measured by online analytical instruments and polymer analysis. Many design variables (including hard/soft ratio, density, average block length, and molecular weight) can be controlled in a chain shuttling polymerization by altering flows of monomers, catalysts, CSA, and H_2. In this work, several potential design variables are held constant to isolate the effects of varying the "hard" catalyst, selected from catalysts **2**–**5**. Therefore, the soft catalyst (**1**) and diethylzinc (DEZ) as a CSA are the same in all experiments. Furthermore, $[C_8H_{16}]/[C_2H_4]$ is held constant at 1.9, fixing the octene content of the soft block. The flow of **1** is also not varied, but the flow of the hard catalyst is adjusted to achieve the target $[C_2H_4]$. As a result, each of the resultant polymers contains about 60–70% soft block. The concentration of DEZ is also held essentially constant, although different shuttling kinetics may generate different average block lengths. Finally, the melt index of each of the OBCs is adjusted to $I_2 = 1.0$ ($M_w \approx 120$ kg/mol) by adjusting hydrogen flow.

Chart 1. Catalyst Structures



Several control experiments were performed to ensure the reliability of interpretation of polymer architecture and provide insight into the constituent block compositions. The campaign started with **2** as hard catalyst to generate the previously reported OBC with large δ (Table 1). Runs B and C are single-catalyst controls using **1** and **3** as the soft and hard catalysts, respectively. Run D is conducted in the absence of CSA to generate a blend for comparison to the OBC made in Run E.

To transition from Run E to Run F, reactor operation was continued as flow of **2** was phased out and flow of **3** phased in. Adjustments were made to flows of **3**, ethylene, and octene to reach the target $[C_2H_4]$, $[C_8H_{16}]$, and production rate. Hydrogen flow was adjusted to reach the target I_2. After the target steady-state condition was reached, that is, several consecutive measurements of polymer properties (I_2, density) and analytical measurements of $[C_2H_4]$ and $[C_8H_{16}]$ were equivalent, the product was collected. Transition from Run F to Run G proceeded in a similar fashion, transitioning from hard catalyst **3** to **4**.

The basic polymer characterization is tabulated in Table 1. All of the polymers of Runs A, E, F, and G have characteristics indicative of a blocky architecture. Despite the use of two catalysts, M_w/M_n is ~2 for all of these examples. As previously described,

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Table 1. Process and Polymer Characterization Data

run	soft cat	hard cat	mol % hard cat	eff[a]	Zn[b]	dens[c]	dens (hard)[d]	est. % soft block	M_n[e]	M_w[e]	M_w/M_n	T_m (°C)	ΔH_f (J/g)	% purge[f]
A	**1**	**2**	27	240	256	0.877	0.939	73	60	118	1.95	118	63	32
B	**1**	none	0	258	242	0.857	none	100	73	139	1.90	36	32	92
C	none	**3**	100	66	186	0.932	0.932	0	31	70	2.29	124	172	7
D	**1**	**3**	34	143	0	0.883	0.932	63	14	81	5.71	123	78	60
E	**1**	**3**	57	170	219	0.880	0.932	68	56	119	2.11	118	66	34
F	**1**	**4**	25	227	201	0.869	0.898	69	60	127	2.13	111	41	38
G	**1**	**5**	6	283	221	0.867	0.891	69	63	129	2.06	91	42	49

[a] Kilograms polymer/gram catalyst metals. [b] Residual Zn in polymer (ppm). [c] Density of the OBC (g/cm^3). [d] Estimated composition of the hard block, expressed as density. [e] Kilograms per mole. [f] Fraction of polymer that elutes at room temperature in TREF.

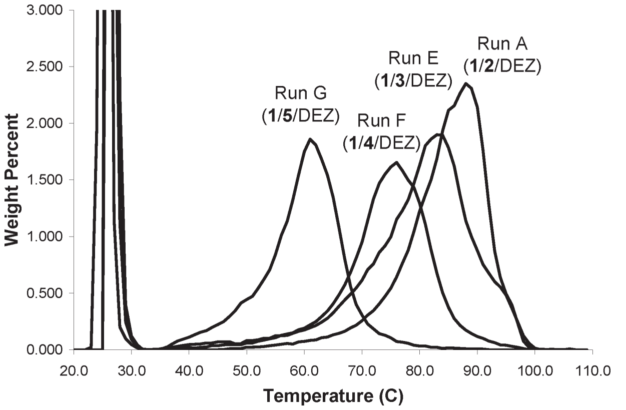

Figure 1. Temperature rising elution fractionation (TREF) data for OBCs showing the influence of α-olefin content in the hard block on polymer solubility.

this narrow molecular weight distribution is a result of the shuttling process, in which polymer chains are exchanged among multiple active catalyst sites prior to termination, leading to an averaging effect for chain termination. The comparative blend D exhibits much broader molecular weight distribution (M_w/M_n = 5.71), which confirms the blend in the absence of shuttling agent and supports the assertion that DEZ shuttling leads to blocky architectures.

Additional evidence of the blocky nature of the new polymers is provided by the melting behavior, as shown by DSC. The principle melting features are determined by the octene content in the hard block, as incorporated by the "hard" catalyst, which was varied in this study. The DSC measurements are tabulated in Table 1. Because the $[C_8H_{16}]/[C_2H_4]$ ratio was held constant and the same "soft" catalyst was used, the soft block composition should be the same in all of the polymers. Therefore, the lower T_m on progression from **2** to **3** to **4** to **5** indicates control of the hard block composition by catalyst selection. This interpretation is also consistent with the overall polymer densities in Table 1, which indicate a consistent trend in octene response.

Perhaps the most instructive analysis of these new polymers is provided by temperature rising elution fractionation (TREF) (Figure 1). The low density (soft) ethylene–octene copolymer produced by **1** under these reactor conditions is quite soluble in the eluent and easily purged at ambient temperature. However, the hard catalysts produce much more crystalline polymer that does not elute until higher temperatures. Thus, a physical blend for these 60/40 soft/hard compositions is expected to have two eluting fractions with ca. 60% in the purge fraction. In fact, this is observed for the control polymer made in Run D. However, OBCs show relatively little purge fraction with the majority of the polymer eluting at much higher temperature. This high elution temperature is a result of the covalent tether of soft polymer fraction to hard polymer fraction in the block copolymer architecture. This phenomenon has been demonstrated and described previously.[2]

Interestingly, these new polymers show a range of elution temperatures, corresponding to the octene content of the hard segments. The trend is fully consistent with the OBC characterization. That is, polymers made with more ethylene-selective hard catalysts have higher TREF elution temperatures.

As shown in Table 1, catalyst selection to tune the hard block allows one to make OBCs with control over melting point (T_m), crystallinity (ΔH_f), and solubility (% purge). This new capability expands the polymer design space for chain shuttling technology.

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Supporting Information Available: Polymerization details; synthetic procedures, NMR spectra and single crystal X-ray data for **3**, **4**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

Note Added after ASAP Publication. This Communication posted ASAP on September 15, 2010 with the wrong image for Chart 1 and Figure 1. The correct version posted on September 20, 2010.

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