Synthesis of Butene−Ethylene and Hexene−Butene−Ethylene Copolymers from Ethylene via Tandem Action of Well-Defined Homogeneous Catalysts

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Recent progress in the chemistry of well-defined organometallic catalysts has made a significant impact in the manufacture of polyolefins.[1] An ever-growing menu of metal−ligand combinations exists to control the activity, copolymerization aptitude, and stereoselectivity of the catalytic site.[2] Mechanistic and theoretical studies provide insight into the interactions between the substrate, metal, and ancillary ligands and how subtle electronic and steric factors come together to determine the final catalytic performance.[2]

Given the accumulated understanding of these catalysts, it is reasonable to expect that multiple sites could be coordinated to offer a performance inaccessible by a single catalyst.[3] Within this concept, we recently reported the use of tandem catalysis to produce branched polyethylene from a single feedstock of ethylene.[4,5] Mixtures of $(C_5H_5B\text{-}OEt)_2ZrCl_2$ (**1**)[6] and $[(\eta^5\text{-}C_5Me_4)\text{-}SiMe_2(\eta^1\text{-}NCMe_3)]TiCl_2$ (**2**) produce branched polyethylene from ethylene when activated with methylaluminoxane (MAO). In this process, **1**/MAO produces linear 1-alkenes which insert into the growing polyethylene chain at the **2**/MAO site.[7]

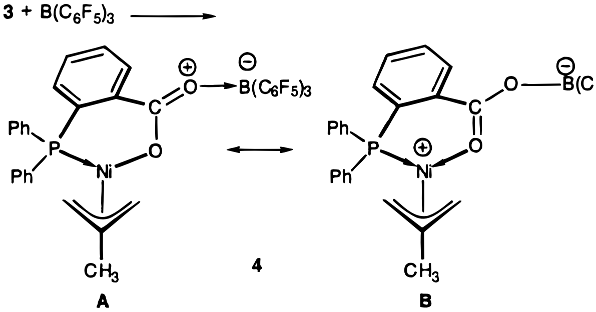
Combinations such as **1**/**2**/MAO suffer from two limitations. First, it is known that the catalytic activity of metallocene and boratabenzene-based catalysts depends on the ratio of MAO to transition metal.[2,8] As a result, one cannot obtain a linear relationship between the molar ratio of the *precatalysts* and the incorporation of branches onto the backbone. Second, since oligomerization catalysts generate a statistical distribution of 1-alkenes,[6] the precise polymer structure cannot be determined using simple spectroscopic techniques.[9] These complications could be circumvented by use of well-defined initiators and if the branches were derived from a single 1-alkene source. In this paper we report how such a tandem catalysis system can be created for the synthesis of poly(ethylene-*co*-1-butene) or polyethylene with ethyl and butyl branches.[10]

Table 1. Dimerization of Ethylene by **4**[a]

entry	*P* (atm)	*T* (°C)	activity[b]	percent 1-butene[c]	percent 1-hexene[c]	percent 2-alkenes[c]	percent dimers[c]
1	1	0	20	>99			
2	1	20	56	89	8		3
3	1	65	140	64	12	8	16
4	3	0	290	90	6		4
5	3	20	430	71	8	4	17
6	3	65	560	36	7	14	41
7[d]	3	20	630	89	8		3

[a] [**4**] = 125 μmol/L in toluene. Reaction time is 1 h. [b] Kg ethylene consumed per mole of catalyst per hour. [c] Mole percent determined by ^1H NMR spectroscopy. [d] [**4**] = 12.5 μmol/L.

While *single-component* ethylene oligomerization catalysts have been reported,[11] these either require MAO as activator or do not achieve activities toward ethylene comparable to metallocene-type polymerization catalysts. Keim recently reported the synthesis and reactivity of $[(C_6H_5)_2PC_6H_4C(O)O\text{-}\kappa^2P,O]Ni(\eta^3\text{-}CH_2CMeCH_2)$ (**3**).[12] Based on the work by Piers,[13] we discovered that addition of one equivalent of $B(C_6F_5)_3$ to **3** yields $[(C_6H_5)_2PC_6H_4C(OB(C_6F_5)_3)O\text{-}\kappa^2P,O]Ni(\eta^3\text{-}CH_2CMeCH_2)$ (**4**), as shown in eq 1.



(1)

The molecular structure of **4** (Supporting Information) shows a square-planar arrangement of ligands on Ni and a strong B−O interaction (d(B−O) = 1.541(5) Å), which is intermediate between that of a B−O single bond and a dative bond.[14] The C−ONi distance (1.240(5) Å) is characteristic of a C−O double bond, while the C−OB distance (1.289(5) Å) is more indicative of a single bond; both measurements are consistent with resonance contribution **B** in eq 1.

Compound **4** is considerably more active toward ethylene than **3**.[12] From Table 1, we note that at 0 °C and 1 atm of C_2H_4, **4** affords exclusively 1-butene (entry 1). Increasing temperature and

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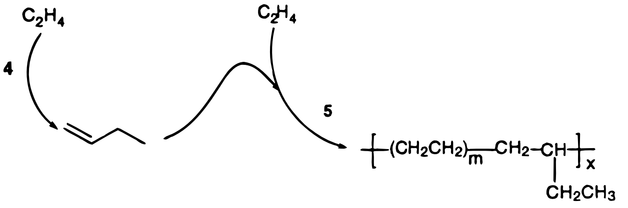
Table 2. Polymerization Data[a]

entry	**4**/**5**	activity[b]	% branching[c]	M_w ($\times 10^{-3}$)[d]
1	0.00	140	0	329
2	0.09	156	1.4	157
3	0.27	121	2.1	152
4	0.44	112	3.1	184
5	0.62	126	4.7	347
6	0.70	93	3.5	191
7	0.89	126	4.8	126
8	1.00	159	7.5[e]	63
9	1.78	83	9.9[e]	102
10	2.00	78	10.9[e]	88

[a] Polymerization conditions: $T = 20$ °C; $P(C_2H_4) = 3$ atm; [Ti] = 1.25 mmol/L; solvent, toluene; reaction time, 10 min. [b] Units of Kg (total mol of metal)$^{-1}$ h^{-1}. [c] Determined by ^{13}C NMR spectroscopy; see ref 9a for details. [d] Determined by GPC. [e] Includes contribution from butyl branches.

Scheme 1



monomer pressure results in an increase in overall ethylene consumption and loss of selectivity. In addition to 1-butene, one observes varying amounts of 1-hexene as well as isomerization products, of which 2-butene is predominant (trans content: 66% at 65 °C; 72% at 20 °C), and 2-alkyl-1-alkenes (dimerization products). The ratio of 1-hexene to 1-butene increases with temperature (from 0.09 at 20 °C to 0.19 at 65 °C) but remains relatively invariant as a function of pressure (entries 2 vs 5 and 3 vs 6, Table 1). Running the reactions under more dilute conditions keeps the 1-hexene/1-butene ratio constant and discourages the formation of 2-alkenes and dimers (entry 7). No activity was observed for **3** under any of the conditions in Table 1.

To complement the reactivity of **4** we targeted {[(η^5-C_5Me_4)-$SiMe_2$(η^1-$NCMe_3$)]TiMe}{$MeB(C_6F_5)_3$} (**5**) since, like **2**/MAO, it is effective in copolymerizing 1-alkenes with ethylene,[7] it is generated by addition of $B(C_6F_5)_3$ to [(η^5-C_5Me_4)$SiMe_2$(η^1-$NCMe_3$)]$TiMe_2$,[15] and it has an activity of 140 Kg/(mol•h) under our experimental conditions.

Addition of ethylene to a solution containing **4** and **5** results in the formation of high molecular weight polymers with monomodal molecular weight distributions (Table 2). In these reactions the total quantity of ethylene consumed equals ±5% the weight of polymer obtained. Under the appropriate conditions, this system can generate polymers with exclusively ethyl branches (Scheme 1). The ^{13}C NMR spectrum of the material obtained under the conditions in entry 4, Table 2, shows the presence of branches due to 1-butene insertion (Figure 1a). Increasing the Ni/Ti ratio results in the appearance of branches due to 1-hexene. Figure 1b shows the data obtained from the sample in entry 8, Table 2. Significantly, the simplicity of polymer structure allows for the percentage of ethyl and butyl branches in the polymer to be determined[9a] and, as shown in Figure 2, the percent of 1-butene/1-hexene in the polymer correlates well against the Ni/Ti ratio.

In summary, compound **4** is readily formed by treating **3** with $B(C_5F_6)_3$ and it displays increased activity toward ethylene as well as a propensity for 1-butene formation, relative to **3**. Since **4** and **5** display complementary reactivity, it is possible to coordinate their action to produce poly(ethylene-*co*-1-butene) from ethylene. MAO is no longer required and the branching in the polymer structure depends linearly on the ratio of the two precatalysts. The overall process behaves predictably and shows that well-defined homogeneous catalysts can be coordinated to generate polymer architectures from a single monomer feedstock that are not readily obtained by the action of a single catalyst.

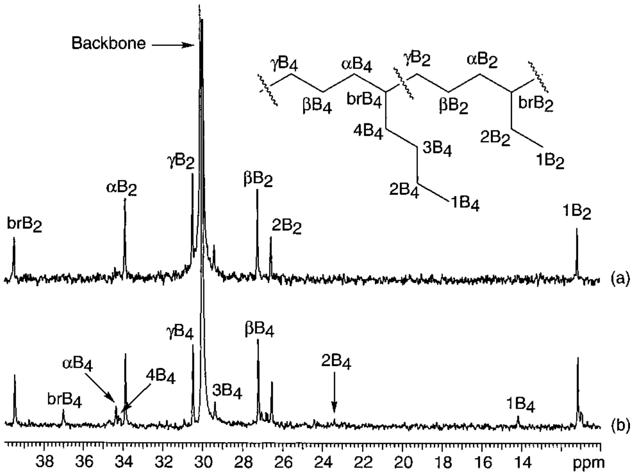


Figure 1. ^{13}C NMR spectra of polymers obtained with (a) Ni/Ti = 0.44 and (b) Ni/Ti = 1.0. Chemical shift assignments were made according to ref 9a.

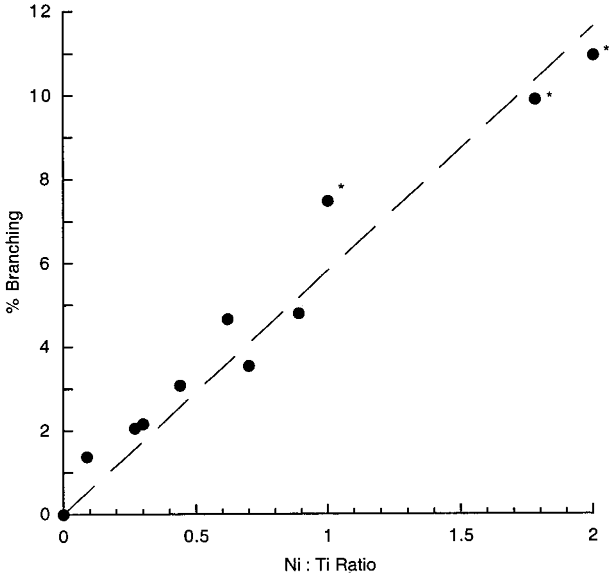


Figure 2. Percent branching in polymer as a function of the **4** to **5** ratio. An asterisk denotes observation of butyl branches.

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Supporting Information Available: Complete details for the synthesis of **4**, the oligomerization and polymerization reactions, and the crystallographic study of **4** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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