

Synthesis of Branched Polyolefins Using a Combination of Homogeneous Metallocene Mimics

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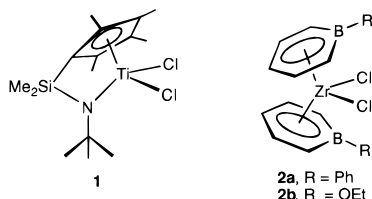
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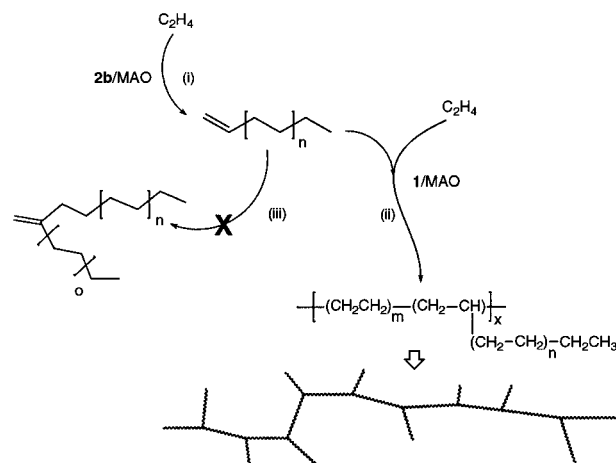
Metallocene catalysts¹ have made a profound impact on polyolefin technology.^{2,3} These catalysts are formed by reaction of a group 4 metallocene, such as Cp₂ZrCl₂ (Cp = C₅H₅), with a coactivator, of which methylaluminoxane (MAO) is most typical. Modification of ligand environment on the precatalyst (i.e., by linking with an intraannular bridge⁴ or by introducing sterically bulky substituents on the Cp ring) leads to different specificities of the active species and ultimately controls important product properties such as stereoregularity and molecular weight. Non-Cp ligands can also be used in this context and catalysts derived from [(η⁵-C₅Me₄)SiMe₂(η¹-NCMe₃)]TiCl₂ (**1**)⁵ are excellent for copolymerizing ethylene with 1-alkenes such as 1-hexene or 1-octene.⁶ This reactivity allows for the synthesis of branched polyethylene and can be used to adjust the processing ability of the bulk material.⁷

The substitution of boratabenzene ligands⁸ for Cp as a strategy to build metallocene mimics is currently of interest because the selectivity of the resulting catalysts can be controlled by choice of the exocyclic substituent. Solutions of [C₅H₅B-N(*i*-Pr)₂]₂ZrCl₂ and MAO react with 1 atm of ethylene to give polyethylene,⁹ but under similar conditions [C₅H₅B-Ph]₂ZrCl₂ (**2a**) gives a mixture of 2-alkyl-1-alkenes (vinylidene olefins).¹⁰ For [C₅H₅B-OEt]₂ZrCl₂ (**2b**) and MAO, the addition of ethylene results in the formation of 1-alkenes.¹¹



It occurred to us that the reactivities of activated **1** and **2b** complement each other and that their combination in a single reactor would lead to the formation of branched polyethylene using ethylene as the only monomer. The overall strategy for

Scheme 1



the proposed tandem catalyst is shown in Scheme 1.^{12,13} Ethylene reacts with **2b**/MAO to produce 1-alkenes in situ (step i). The role of **1**/MAO is to polymerize ethylene and incorporate the 1-alkenes into the growing chain (step ii). For this strategy to be successful, the reactivity of the two metal sites toward ethylene must be well-matched, the catalysts must not interfere with each other chemically, and the stirring rate must ensure efficient mass transfer. It is also important to prevent dimerization of the 1-alkenes to the less reactive 2-alkyl-1-alkenes (step iii).

We have found that the reaction sequence described in Scheme 1 works. Representative polymerization data are shown in Table 1.¹⁴ On the basis of the results of multiple runs, we estimate the accuracy of these numbers at approximately $\pm 10\%$. Note that the consumption of ethylene is within the same order of magnitude for all catalysts (entries 1, 2, and 4). All attempts to use **2a**/**1**/MAO mixtures resulted in substantial formation of 2-alkyl-1-alkenes along with polymer. Best results are obtained with **2b**/**1**/MAO, for which no soluble byproducts are observed by GC/MS. Gel permeation chromatography shows that the polymers formed by **2b**/**1**/MAO exhibit a monomodal molecular weight distribution. Therefore, 1-alkenes from **2b**/MAO are quantitatively incorporated into the polyethylene chain growing out of the titanium site. As expected, a higher ethylene pressure gives higher molecular weight product (entry 5 vs 6).

Entries 7–12 show that varying the amount of MAO to a constant **2b**/**1** ratio influences product properties and overall reactivity. Conditions with less than 500 equiv of Al relative to Ti or Zr result in negligible ethylene consumption and there is an optimum MAO to **2b**/**1** ratio (entry 8). Comparison of entries 8, 18, and 19 shows that lowering the temperature results in higher polymer yields. At room temperature, Scheme 1 fails because

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Table 1. Olefin Polymerization Data^a

entry	reaction conditions					polymer properties		
	cat.	Zr:Ti:Al	[Zr] (μM)	temp ($^{\circ}\text{C}$)	<i>P</i> (atm)	activity ^b	<i>T</i> _m ^c ($^{\circ}\text{C}$)	<i>M</i> _w ^d ($\times 10^{-3}$)
1	2a	1:0:1000	830	$\sim 70^e$	1	320	115 ^f	
2	1	0:1:1000	830 ^g	$\sim 70^e$	1	450	134	29
3	2a/1	1:20:20000	21	~ 40	2	620	116 ^f	37 ^h
4	2b	1:0:1000	42	60	1	910	91 ^f	
5	2b/1	1:10:10000	8.3	60	1	1080	130	86
6	2b/1	1:10:10000	8.3	60	2	1160	127	109
7	2b/1	1:2:10000	42	60	1	950	123 ^f	
8	2b/1	1:2:2000	42	60	1	1100	118	
9	2b/1	1:2:1000	42	60	1	550	125	
10	2b/1	1:2:500	42	60	1	160	128	
11	2b/1	1:2:200	42	60	1	36		
12	2b/1	1:2:100	42	60	1	3		
13	2b/1	1:5:5000	17	60	1	990	125	68
14	2b/1	1:2:2000	42	60	1	900	124	73
15	2b/1	1:1:1000	83	60	1	620	121	74
16	2b/1	1.5:1:1000	125	60	1	440	98 ^f	
17	2b/1	2:1:1000	167	60	1	360	94 ^f	64
18	2b/1	1:2:2000	42	75	1	800	120 ^f	
19	2b/1	1:2:2000	42	90	1	590	124 ^f	

^a Conditions: solvent, toluene; reaction time, 30 min. ^b Activity in units of kg (total moles of metal)⁻¹ h⁻¹. ^c Melting point of insoluble product determined by DSC. ^d Determined by GPC vs polystyrene standards at 145 $^{\circ}\text{C}$. ^e Reaction quickly rose to approximate temperature due to exothermicity of polymerization. ^f Temperature at greatest endotherm, other transitions present. ^g Denotes [Ti] rather than [Zr]. ^h Bimodal distribution with *M*_w centered about 2000 (corresponding to 2-alkyl-1-alkenes) and 53 500 (branched polymer).

the 1-alkenes produced by **2b**/MAO precipitate out of solution before insertion into the polymer chain.

¹³C NMR spectroscopy confirms the branched structure of the products.¹⁵ Most diagnostic are the peaks at δ 38.1 and 39.6 corresponding to the methine carbons of isolated branches. Also observed are three resonances of equal intensity at δ 34.4, 27.2, and 30.4 from the methylene carbons α , β , and γ to the methine junction. Signals at δ 35.8 and 33.5, which would indicate consecutive 1-alkene insertions, were not detected. It is not possible to determine the exact branching content from simple NMR experiments because there is a distribution of branch lengths and also because some branches are sufficiently long that their methylene carbons have resonance frequencies identical to those of their backbone counterparts.

Ultimately, the dual-catalyst process of Scheme 1 should offer the opportunity to adjust product properties from the reaction conditions, and more specifically, from the ratio of catalytic species. Figure 1, which collects entries 13–17 from Table 1, shows that this is indeed the case since the melting point temperature drops as the percentage of **2b** increases. These data are consistent with more frequent branching and thus a more disordered polymer morphology.

In summary, it is possible to produce branched polymers from ethylene alone by combining the ability of **2b**/MAO to produce 1-alkenes with the ability of **1**/MAO to copolymerize ethylene with 1-alkenes.¹⁶ This combination of metallocene mimics complements the reactivity of Ni(II) diimine catalysts reported by Brookhart which produce branched polyolefins from ethylene via a β -hydride-elimination/chain-migration mechanism.^{15e,17} The dependence of polymer structure on reaction conditions is

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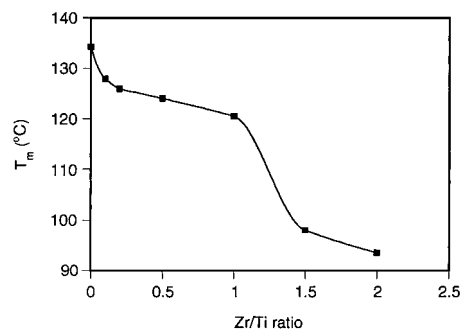


Figure 1. Dependence of the melting point (*T*_m) of the branched polyethylene on the initial ratio of **2b** and **1**.

complicated in the tandem system because **2b**/MAO produces a distribution of 1-alkenes, which are known to be less reactive with increasing molecular weight.¹⁸ A distribution of propagating species with different reactivities and selectivities should also be expected after these 1-alkenes insert into the Ti–C bond. Despite these complications, Figure 1 shows that it is possible to modify polymer properties from the initial mixture of precatalysts. Scheme 1 also constitutes a rare example of two independent catalysts working cooperatively to produce a single product.

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Supporting Information Available: Details for polymer synthesis and characterization (18 pages). See any current masthead page for ordering and Internet access instructions.

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