

## Highly Branched Polyethylene Oligomers via Group 4-Catalyzed Polymerization in Very Nonpolar Media

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### Introduction

Since Ziegler's and Natta's milestone discoveries in the 1950s, polyethylenes (PE's) have become some of the most versatile and extensively used plastics worldwide, with global production expected to reach nearly 100 million tons in 2018, valued near \$183 billion. Group 4 transition metals play a central role as catalysts in producing these materials with great efficiency and selectivity. Nevertheless, these catalysts are markedly ineffective in producing polyethylenes with large densities of  $-(\text{CH}_2)_x\text{CH}_3$  backbone branches having  $x \geq 5$  as LDPE (low-density polyethylene) or highly branched polyethylenes (HBPEs) with low molecular mass ( $M_n < 1200$  g/mol) (Figure 1). Low Mn HBPEs are structurally very similar to poly( $\alpha$ -olefins) (PAOs), which are the major synthetic lubricant oils with huge global market ( $> 2$  Mt demand in 2015). However, the high cost of PAOs (due to the complex multi-step synthesis/purification process) has been a major barrier to their widespread adoption in the fast-growing energy efficiency lubrication industry. In contrast, HBPEs offer great potential as synthetic lubricants if an efficient, cost-effective catalytic method for their synthesis could be developed.

**Figure 1. Polyethylene categories and microstructural branching characteristics**

	HDPE	LLDPE	LDPE	Low $M_n$ HBPE
Microstructure				
Catalyst	Ziegler-Natta, Phillips	Ziegler-Natta, Single-site (Ti, Zr)	ICI radical process	CGCZrR <sup>+</sup> (this work)
Branch type	Trace	Short (C1~C5), Long (C6, C8)	Short (C1~C5), Long ( $\geq$ C6)	Short (C2, C4), Long ( $\geq$ C6)
Predicted global production in 2018	~45 MT	~30 MT	~25 MT	

### Materials and Methods

All manipulations of air-sensitive materials were performed with standard Schlenk techniques and glassware. Hydrocarbon solvents were then vacuum-transferred from Na/K alloy. PAO4 base oil used in this study was provided by Valvoline Inc. a 150-mL glass

pressure vessel was used for ethylene homo- and copolymerizations. NMR spectra were recorded on Varian UNITY Inova-500 (FT, 500 MHz, <sup>1</sup>H; 125 MHz, <sup>13</sup>C) and Agilent DD2-HCN600 (FT, 600 MHz, <sup>1</sup>H; 150 MHz, <sup>13</sup>C). NMR experiments on air-sensitive samples were conducted in Teflon valve-sealed sample tubes (J-Young). Elemental analyses (CHN) were performed by Midwest Microlab, Indianapolis, Indiana.

### Results and Discussion

This catalytic system was specially designed for use in an unconventional solvent for ethylene polymerization processes—a saturated hydrocarbon. Here we report the synthesis of low Mn HBPEs from inexpensive, abundant ethylene as the main feedstock using a single-site organozirconium precatalyst [1-Me<sub>2</sub>Si(3-ethylindenyl)(<sup>t</sup>BuN)]ZrMe<sub>2</sub> (CGCZrMe<sub>2</sub>) activated with the saturated hydrocarbon-soluble perfluoroarylborate cocatalyst, (para-n-octylphenyl)<sub>3</sub>C<sup>+</sup>B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup> (B<sub>1, n-octyl</sub>). Notably, the 25 °C activation and polymerization proceeds efficiently in nonpolar, non-coordinating methylcyclohexane with activity as high as 4627 kg·(mol Zr)<sup>-1</sup>·h<sup>-1</sup>·atm<sup>-1</sup> and branch densities as high as 61 and 93 branches/1000C for homo- and 1-hexene co-polymerizations, respectively. Control experiments, spectroscopic experiments and DFT studies argue that this unprecedented activity and branch-directing selectivity reflect heretofore unrecognized aspects of the cationic catalyst-counteranion pairing in such non-polar/non-coordinating media. Furthermore, this catalytic system is highly tunable, enabling precise tuning of branch density and identity (ethyl, n-butyl,  $-(\text{CH}_2)_n\text{CH}_3$ ,  $n \geq 5$ ) by adjusting reaction parameters. The products are tribologically promising alternative candidates to synthetic lubricants.

### Significance

To the author's knowledge, this is the first example of highly branched polyethylenes produced by organo-group 4 transition metal catalyzed ethylene polymerization and is realized via unprecedented solvent effects and a soluble, structurally/functionally well-defined borate cocatalyst. The HBPE oligomers can be made in large quantities with this catalytic system using cheap, abundant ethylene as the primary feedstock, and exhibits superior tribological performance vs. commercial synthetic lubricant oil PAO4 in terms of viscosity stability with temperature, film formation ability, and friction loss metrics, thus offering great potential for low-cost access to high-performance synthetic lubricant oils.

### References

1. Yanshan Gao, Jiazhen Chen, Yang Wang, David Pickens, Alessandro Motta, Q. Jane Wang, Yip-Wah Chung, Tracy Lohr and Tobin J. Marks. *Nature Catalysis*, in press (2018).
2. Tobin J. Marks; Yanshan Gao; Tracy L. Lohr; Matthew Christianson; Jerzy Klosin; Edmund M. Carnahan; Andrew Young. *U.S. Provisional Patent Application*. 62/650,462 (2018).
3. Tobin J. Marks; Yanshan Gao; Tracy L. Lohr. *U.S. Provisional Patent Application*. 62/626,879 (2018).