

Appendix A
Towards AB_n-Based Hyperbranched Polyethylene

Facile access to different polymeric architectures of chemically well-established macromolecules can expand their applications. Moreover, comparative studies of polymers with the same chemical composition but different chain structure can contribute to a better understanding of polymer physics and aid in the design of new materials. In particular, the large volume, industrial polymers, such as polyethylene (PE) or polypropylene (PP), stand to benefit from structural changes since their simple aliphatic backbones do not allow other types of alterations. For example, the vast array of properties demonstrated by PE is based on the amount and extent of branching that is introduced into its main chains during the polymerization. However, the structure and functionality of this polyolefin are also very difficult to manipulate in a precise manner, because of PE's chemical simplicity and the lack of any kind of anchoring or repeat unit-defining functional groups.

Olefin metathesis is a reaction ideally suited for the construction of model polyolefins since it joins well-defined monomers via an alkene functionality, which can be “erased” at will by subsequent hydrogenation. In fact, ADMET has previously been used for precise branch placement in an ethylene/propylene copolymer model study.¹ Moreover, Chapter 5 of this thesis includes a discussion on the synthesis of previously unattainable cyclic PE via ring-expansion metathesis polymerization. However, to the best of our knowledge, hyperbranched PE with a well-defined AB_n unit has never been prepared via olefin metathesis or any other method.^{2,3,4}

Scheme A1 outlines a route to hyperbranched polyethylene via ADMET of a specially designed monomer **3**, followed by hydrogenation. The general method for this polymerization is based on the selectivity of catalyst **A** (Figure A1) towards different types of alkenes, which is described in Chapter 2 of this thesis. However, the AB_n monomer design described in Chapter 2 must be adjusted for the preparation of hyperbranched PE. To be able to reduce the polymerization product to the bare aliphatic backbone of polyethylene, ester linkages must be avoided. Therefore, the acrylate “B” functionalities have to be exchanged for vinyl ketones.

The desired monomer **3** was prepared in three simple steps from commercially available, inexpensive dimethyl glutaconate. However, its polymerization with **A** stalled, presumably due to the very slow rate of metathesis of the very electron-deficient vinyl

ketones. Nevertheless, according to ^1H NMR analysis, this polymerization proceeds to some extent when a more active and stable, phosphine free catalyst **B** is employed under dilute conditions (Figure A2).⁵ The optimization of polymerization conditions with **B** is currently underway and appears promising.

Scheme A1. Synthetic route towards the hyperbranched polyethylene via ADMET.

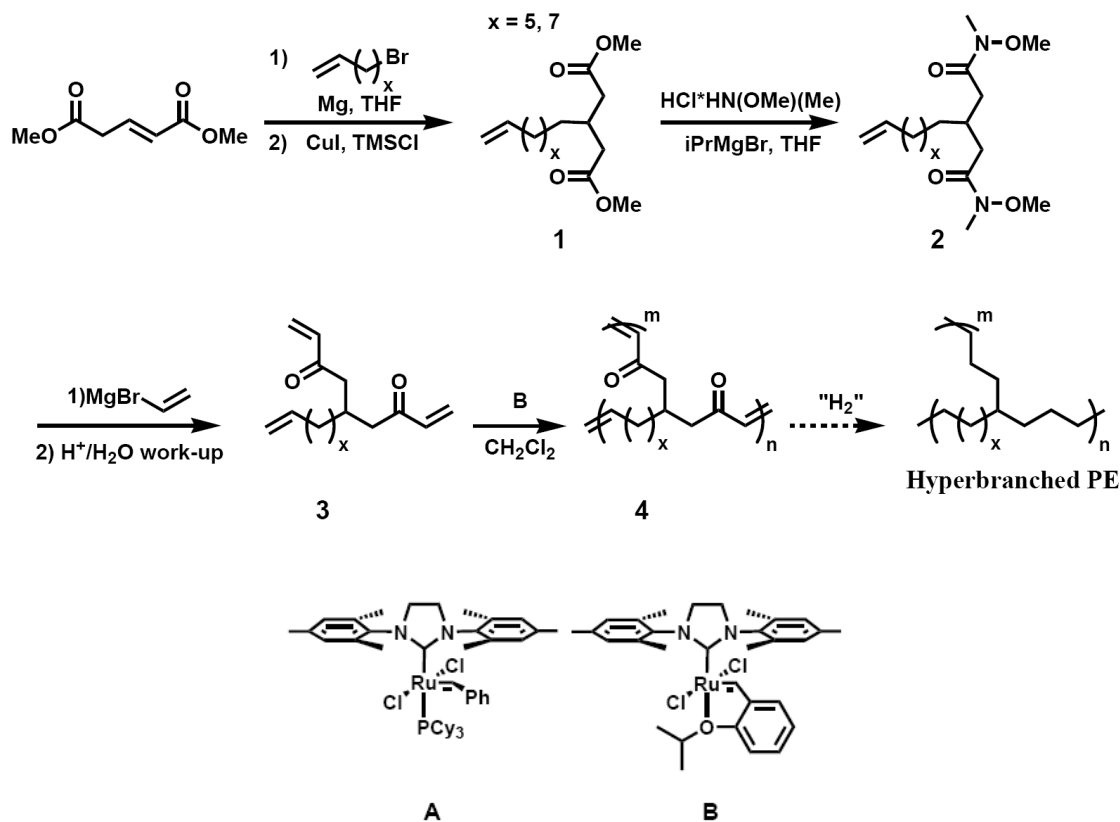


Figure A1. Hyperbranched ADMET catalysts.

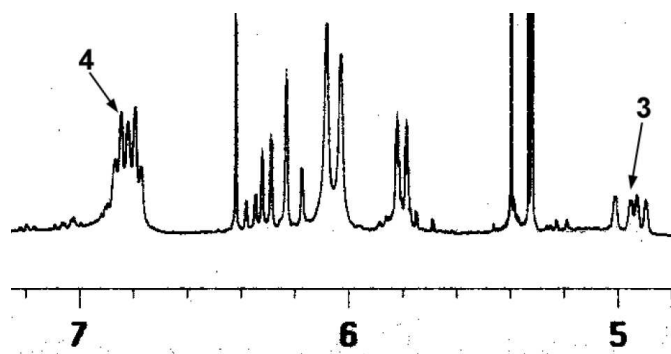


Figure A2. ^1H NMR evidence for polymerization of **3** to **4**.

Experimental Procedures

Materials and Instrumentation. All reagents were purchased from Aldrich at the highest available purity grade and used without further purification. NMR spectra were obtained using a Varian Mercury-300 spectrometer; samples were dissolved in CD₂Cl₂.

(1). A dry, 50 mL, round bottom flask equipped with a stir bar was charged with magnesium turnings (2.0 g, 82.3 mmol) and purged with argon for 15 min. 15 mL of dry THF was added to this reaction vessel and the mixture was heated to 50 °C. After the reaction mixture was stirred at 50 °C for another 15 min, a few drops of magnesium-activating 1,2-dibromoethane were added to the flask, and the solution was checked for gas evolution. Once it was established that the addition of C₂H₄Br₂ produced gas, 10-bromo-1-decene (4.2 g, 19.2 mmol) was slowly added to the vessel. The reaction solution was stirred for 3 hours at 50 °C before being transferred to a dry, 100 mL, round bottom flask charged with CuI (0.37 g, 1.9 mmol), 25 mL of dry THF, and a stir bar. The resulting suspension was stirred at room temperature until the dark color persisted (~ 2 min) before being cooled to -78 °C. After the consecutive addition of TMSCl (2.8 g, 25.7 mmol) and dimethyl glutaconate (1.0 g, 6.3 mmol), the mixture was stirred at -78 °C for 2 h and allowed to warm to room temperature. A solution of NH₄Cl (sat. aq.) was then added to the reaction flask and the solution was stirred for ~ 1 h until it became clear (bright orange in color). The products were extracted in EtOAc three times. The combined organic layers were washed with brine and dried over anhydrous MgSO₄. The solution was then filtered, concentrated, and purified by silica gel chromatography. Elution with 1 to 5 % EtOAc in hexane afforded 1.23 g of **1** (x = 7; 65 % yield). NMR (300 MHz, CD₂Cl₂, ppm): δ 5.82 (m, 1H), 5.02–4.90 (m, 2H), 3.63 (s, 6H), 2.33–2.31 (m, 4H), 2.03 (m, 2H), 1.37–1.27 (m, 15H). ¹³C NMR (300 MHz, CD₂Cl₂, ppm): δ 173.45, 139.88, 114.37, 51.85, 38.84, 34.54, 34.36, 32.68, 30.15, 30.01, 29.97, 29.68, 29.52, 27.09. HRMS(FAB+) *m/z*: 299.2213 [M+H].

(2). **1** (1.23 g, 4.12 mmol) was combined with N,O-dimethylhydroxylamine hydrochloride (1.21 g, 12.4 mmol) in 9 mL of dry THF. The reaction mixture was cooled to -20 °C, a 2M solution of isopropylmagnesium chloride in THF (12.4 mL) was added

dropwise to the flask, and the solution was stirred for additional 30 min. A saturated aqueous solution of NH_4Cl was added to the reaction mixture, and it was allowed to warm to room temperature. Thereafter, the mixture was diluted with Et_2O , and the products were extracted with Et_2O three times. The combined organic layers were dried over anhydrous MgSO_4 , filtered, and concentrated. Purification by silica gel chromatography, eluting with 25 to 50 % EtOAc in hexane afforded 1.24 g of oil **2** ($x = 7$; 84 % yield). NMR (300 MHz, CD_2Cl_2 , ppm): δ 5.82 (m, 1H), 5.01–4.90 (m, 2H), 3.66 (s, 6H), 3.12 (s, 6H), 2.41–2.37 (m, 4H), 2.03 (m, 2H), 1.39–1.21 (m, 15H). ^{13}C NMR (300 MHz, CD_2Cl_2 , ppm): δ 174.09, 139.91, 114.33, 61.66, 36.72, 35.06, 34.75, 34.36, 31.81, 30.33, 30.13, 30.02, 29.70, 29.53, 27.38. HRMS(FAB+) m/z : 357.2747 [M+H].

(3). **2** (0.35 g, 0.98 mmol) was dissolved in 5 mL of dry THF, and the solution was cooled to $-78\text{ }^\circ\text{C}$. A 1M solution of vinylmagnesium bromide in THF (10 mL) was added to the reaction flask, and the mixture was allowed to warm to room temperature. The resulting solution was then slowly poured over a saturated aqueous solution of NH_4Cl , and the products were extracted with CH_2Cl_2 three times. The combined organic layers were consequently washed with saturated aqueous solutions of NaHCO_3 (once) and NaCl (once), before being dried over anhydrous MgSO_4 , filtered, and concentrated. Purification by silica gel chromatography, eluting with 5 to 20 % EtOAc in hexane, afforded 115 mg of oil **3** ($x = 7$; 40 % yield). NMR (300 MHz, CD_2Cl_2 , ppm): δ 6.38–6.17 (m, 4H), 5.89–5.75 (m, 1H), 5.81 (dd, $J = 10.2\text{ Hz}$, $J = 1.6\text{ Hz}$, 2H), 5.03–4.91 (m, 2H), 2.58–2.40 (m, 4H), 2.03 (m, 2H), 1.39–1.18 (m, 15H). ^{13}C NMR (300 MHz, CD_2Cl_2 , ppm): δ 200.62, 139.87, 137.35, 128.37, 114.40, 44.49, 35.22, 34.75, 34.39, 31.01, 30.27, 30.01, 29.71, 29.54, 27.35. HRMS(FAB+) m/z : 291.2336 [M+H].

Notes and References

- (1) Sworen, J. C.; Smith, J. A.; Wagener, K. B.; Baugh, L. S.; Rucker, S. P. *J. Am. Chem. Soc.* **2003**, *125*, 2228-2240.
- (2) Pseudo-hyperbranched polyethylene has been prepared via "chain-walking" methods, which employ transition metal catalysts and are described in references 3 and 4. However, these methods produce statistical, random branching with no defined AB_n monomers in the backbone.
- (3) Guan, Z.; Cotts, P. M.; McCord, E. F.; McLain, S. J. *Science* **1999**, *283*, 2059-2062.
- (4) Sunder, A.; Heinemann, J.; Frey, H. *Chem. Eur. J.* **2000**, *6*, 2499-2506.
- (5) Choi, T.-L.; Lee, C. W.; Chatterjee, A. K.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 10417-10418.