NONLINEAR POLYMERIC ARCHITECTURES VIA OLEFIN METATHESIS

Thesis by

Irina A. Gorodetskaya

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To my grandmother Yadviga

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ABSTRACT

The research presented in this thesis focuses on application of different forms of olefin metathesis, in conjunction with judicious choices of catalysts and monomers, to the construction of hyperbranched and cyclic macromolecules. This multifaceted reaction is briefly reviewed in Chapter 1, along with ruthenium-based metathesis catalysts and applications of olefin metathesis in polymer synthesis.

Hyperbranched polymers are curious materials which feature multiple end groups and possess a host of desirable physical properties; potential applications stemming from the unique properties of these macromolecules include their use as viscosity lowering additives and analyte carriers. In general, the major drawbacks faced by the classical, AB_n monomer-based hyperbranched polymers are the limited availability of specially designed monomers, harsh synthetic conditions, and poor control of the required step-growth polymerization methods. A very mild, simple, and modular, olefin metathesis-based hyperbranched polymerization route, which addresses some of these challenges, is presented in Chapter 2. This method utilizes the cross metathesis selectivity of the functional group tolerant N-heterocyclic carbene ruthenium catalyst towards different types of alkenes, and it can be applied to the polymerization of many easily prepared AB_n monomers. Moreover, the same method can be used to post-synthetically functionalize such polymers for realization of their substrate carrying potential. Chapter 3 describes one functionalization example—a pyrene analyte is attached to a metathesis derived hyperbranched polymer. This modification of the polymer provides insight into its solution structure relative to a linear analog. In addition, molecular weight control of the metathesis hyperbranched polymerization is discussed in detail in Chapter 4. The careful choice of the catalysts loading and the use of a multifunctional core are found to be important parameters in preparation of polymers which span a range of molecular weights.

Even well-established materials, such as polyethylene, can benefit from olefin metathesis and the unusual polymeric architectures it can efficiently create. For example, a cyclic polymer which lacks end groups, as opposed to having many end groups like a

hyperbranched polymer, is expected to possess unique physical properties. The preparation of cyclic and linear polyethylenes and the study of their relative rheological properties are described in Chapter 5. The polymerization methodology outlined in this Chapter takes advantage of ring-expansion metathesis polymerization—a facile method for the synthesis of cyclic macromolecules. Some efforts directed at molecular weight control of this cyclic polymerization are also discussed.

Taken together, the findings presented in this thesis emphasize the utility of olefin metathesis for the preparation of nonlinear polymers. The unusual polymeric architectures available through this chemical transformation may lead to a host of new materials with unique properties.

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