

Abstract

The focus of the research presented in this thesis is the synthesis of functional polymers and construction of controlled molecular architectures through a polymerization process referred to as ring-opening metathesis polymerization (ROMP). A brief overview of polymer chemistry as well as ring-olefin metathesis polymerization is discussed in introductory Chapter 1.

Chapters 2 and 3 discuss new synthetic routes to polyacetylene and polyacetylene block-copolymers from cyclooctatetraene and a new ruthenium olefin metathesis catalysts. Polyacetylene is an intractable material, as are most organic conducting polymers. Chapter 3, however, introduces a novel route to soluble telechelic polyenes and polyacetylene block-copolymers.

The construction of organic overlayers on semiconductor surfaces is important in the area of anti-fouling coatings as well as in organic electronic applications. Chapter 4 introduces a new route to polymer-covered silicon surfaces through a covalent Si-C linkage. ROMP of norbornene from a surface-attached ruthenium catalyst produces uniform polynorbornene overlayers with controlled thickness ranging from 10 Å to 5.5 μm . The work discussed in Chapter 5 elaborates on surface-initiated ROMP by constructing thin-film top-contact field effect transistors with a polynorbornene dielectric layer.

Chapter 6 explores the synthesis of polar-functionalized linear polymers from cyclopentene and cycloheptene derivatives. The challenge of polymerizing low-ring strain monomers *via* ROMP is also discussed. A method to *a priori* discern a monomer's ability to undergo ROMP is outlined in this chapter as well.

Chapters 7 and 8 describe the synthesis of both *regioregular* and *stereoregular*

polar-functionalized linear ethylene vinyl alcohol (EVOH) co-polymers by the ROMP of rationally designed, symmetric monomers. These polymers were made with the goal of producing materials with enhanced oxygen barrier properties. Controlling material architecture imparts a dramatic effect on both the solution and solid state morphologies of EVOH and the synthetic challenges and results are discussed.

Finally, Chapter 9 complements Chapters 7 and 8, and investigates the reason behind enhanced oxygen barrier properties of EVOH through molecular dynamics simulations. For EVOH polymers that differs only by the syn or anti orientation of neighboring diols, a clear difference is observed for the hydrogen bonding clusters. Moreover, the free volume accessible to any solute molecules is extremely low identified by a probe radius of less than 0.6 Å.