

**Syntheses of Polymers with Diverse Architectures via  
Metathesis Polymerization  
and  
Investigation of Their Structure-Property Relationships**

Thesis by

Yan Xia

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For Mom, Dad, and my Wife

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## Abstract

Metathesis polymerization using highly active, functional-group-tolerant catalysts is a powerful and versatile method for polymer synthesis. This thesis focuses on the preparation of a variety of advanced polymer architectures using well-defined ruthenium-based metathesis catalysts and the study of materials properties dictated by those unique macromolecular structures.

Chapter 1 introduces olefin metathesis, metathesis polymerization, and recent developments in living/controlled polymerization and polymer functionalization. The goal is to provide a summary of the current toolbox of polymer chemists. The second part of Chapter 1 describes using these tools to synthesize different macromolecular architectures.

Chapters 2 and 3 describe ring-expansion metathesis polymerization (REMP) using cyclic catalysts. Chapter 2 focuses on catalyst development, while Chapter 3 focuses on the REMP mechanism and cyclic polymer characterization.

Chapters 4 and 5 focus on brush polymers. Chapter 4 describes the syntheses of linear and cyclic brush polymers using ring-opening metathesis polymerization (ROMP) and REMP of macromonomers (MMs), respectively. Chapter 5 describes the efficient synthesis of brush copolymers and the study of their melt state self-assembly into highly ordered nanostructures.

Chapter 6 describes the synthesis and electro-optic response of well-defined liquid crystalline (LC) gels that were made from controlled end-linking of telechelic LC



polymers. These gels possessed very fast, reversible electro-optic switching; the degree of response was closely related to network structure.

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