Chapter 1
ADMET:
Functionalized Polyolefins

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ABSTRACT

The use of acyclic diene metathesis (ADMET) in the synthesis of functionalized polyolefins is discussed. The nature of polymerizations, catalysts, and techniques are briefly covered. An overview of recent functionalized ADMET polymers and major contributions to its methodology is given. This chapter will place special emphasis on the use of ADMET to synthesize increasingly complex and new morphologies, resulting in well-defined polyolefin structures and functionalized materials unlocked as a result of this powerful polymerization method. Presented are polyolefins, materials, and architectures not possible through conventional polymerization techniques.

1. INTRODUCTION

Functionalized polyolefins: incorporation of desired properties into the world's most common plastics. Currently, the production of all forms of polyethylene (PE) total above 80 million tons each year. (Piringer, Baner, & Editors, 2008) This tonnage is attributed to the availability of cheap starting materials derived from fossil fuels and now even agricultural products. Commercially produced functionalized polyolefins are synthesized by the copolymerization of ethylene and other vinyl monomers, such as vinyl acetate and acrylates. However, due to the many side-reaction products, commercially produced functionalized PE structures are not well defined and are limited by defects such as uncontrollable and random branching. ADMET is recognized as the premiere polymerization technique for synthesizing complex polyolefin structures requiring accurate placement of functionalities. (Schulz & Wagener, 2014)

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Since the emergence of Acyclic Diene Metathesis (ADMET) polymerization in the early 1990s, many sophisticated structures and functionalized polyolefins have been produced. Moieties including alcohols, acids, ketones, halogens, aromatics and others have been incorporated into PE. (Opper & Wagener, 2011) Because of the mild reaction conditions and limited number of side reactions, ADMET provides a level of control not possible in conventional techniques. Thus, ADMET is the leading polymerization technique for synthesizing complex architectures requiring accurate and precise placement of functionalities, while limiting reaction defects. Imperfections such as crosslinking and uncontrollable branching make conventionally polymerized materials difficult to study fundamentally. Vasile & Editor, 2000) These side reactions are less desirable for advanced applications where precision is required.

Elimination of defects is made possible due to increasing availability of highly-selective olefin metathesis catalysts in recent years. Although metathesis polycondensation was first hypothesized as early as the 1950s, success was not achieved until 1991 with the successful polymerization of 1,9-decadiene and 1,5-hexadiene. (K. B. Wagener, Boncella, & Nel, 1991) The advent of ADMET coincides directly with the development of novel catalysts such as Schrock's and Grubbs' catalysts, which earned their developers (along with Yves Chauvin) a shared Nobel Prize in 2005. (Harries-Rees, Chauvin, Grubbs, & Schrock, 2005) The continuing development of new, more tolerant catalysts allows for more sophisticated and functionalized polyolefin structures to be produced.

To better understand the effects of defects in PE, precision models of PE functionalized with branches have been synthesized via ADMET. More recently, high-polarity, acidic, ionic, renewable chemicals and drug moieties have been employed as branches. These precision polymers have brought new properties to polyolefins and the potential for advanced applications, such as ion transport, renewable and biodegradable plastics, as well as drug therapeutics. This chapter describes ADMET, the reaction and techniques, followed by a discussion of precision functionalized polyethylenes, with an emphasis on major contributions as well as recent literature examples.

2. ADMET

Before discussing the details of various functionalized polyolefins synthesized by ADMET, it is first necessary to give the reader a brief description of the ADMET reaction and mechanism, including considerations and limitations. This section also provides a general procedure for performing a typical polymerization.

2.1 Polycondensation of α,ω-dienes

Although polyolefins are typically produced by chain-addition reactions, yielding molecular weights into the hundreds of thousands and even millions, the ADMET mechanism is based on stepwise-condensation. (Opper & Wagener, 2011) For every metathesis event between α,ω-diene monomers, a molecule of ethylene is evolved (Figure 1a). Removal of ethylene drives the reaction forward, slowly forming dimers, trimers, tetramers, and so on. All of these olefinic molecules may react at any time, continually increasing the molecular weight. Since, the reaction is step-growth in nature, the Carothers equation applies; i.e., only at near quantitative conversion of monomer is high molecular weight polymer formed (Figure 1b). Hence, monomer purity is absolutely crucial to prevent unintended chain capping and other side reactions.