# Part I
# Introduction

*Green Polymerization Methods: Renewable Starting Materials, Catalysis and Waste Reduction*
Edited by Robert T. Mathers and Michael A. R. Meier

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# 1
# Why are Green Polymerization Methods Relevant to Society, Industry, and Academics?

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## 1.1
## Status and Outlook for Environmentally Benign Processes

In June 1992, the ''Rio Declaration on Environment and Development'' (*Rio declaration*) of the United Nations Conference on Environment and Development (UNCED) announced in Principle 1 [1] that human beings are at the center of concerns for sustainable development and that they are entitled to a healthy and productive life in harmony with nature. Since the Rio declaration, the necessity for *sustainable development* has become obvious [2]. Most frequently, sustainable development is defined as development that meets the needs of the present without compromising the ability of future generations to meet their own needs [3]. Much has happened since then and the principles of *green chemistry* [4] are now known and applied by chemists worldwide. Recently, Paul T. Anastas stated in his keynote speech at the 2010 ACS (American Chemical Society) national meeting in San Francisco: ''Building a sustainable world is the most taxing intellectual exercise we have ever engaged in. It is also the most important for the future of our world'' [5]. Thus, great challenges remain and in the field of green chemistry there are plenty of possibilities in the future for innovation and environmentally friendlier consumer products.

As the use of polymers is becoming increasingly more common for many applications in modern society, *polymer science* is able to make diverse contributions to the rapidly growing field of green chemistry. In particular, polymer science offers manifold possibilities for the sustainable use of renewable raw materials. Even though utilizing renewable resources to meet current needs without creating adverse health or environmental impacts can be challenging, renewable resources offer potentially less toxic products as these resources can be expected to be biodegradable and, more importantly, biocompatible. However, we are fully aware that this is a generalization and a careful case by case evaluation is absolutely necessary! Moreover, nature offers a great synthetic potential to the polymer chemist, and it is up to us to develop new methods to incorporate renewable resources into polymeric materials. This development has to begin now in order to be ready to apply these methods industrially in a few decades, as fossil reserves continue to

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deplete and become more expensive. Equally important, we need more sustainable routes toward known polymeric products in order to avoid waste, contamination, high energy consumption, and many other environmental concerns. In the United States, the *National Research Council*, in its report entitled ''Sustainability in the Chemical Industry: Grand Challenges and Research Needs,'' has advocated that all areas of the chemical industry focus on long-term strategies to minimize toxicity and environmental impact while creating sustainable processes [6].

Therefore, we are certain that this edited volume will assist in *training a future generation* of scientists and engineers to consider green chemistry and sustainability within the field of polymer science as the most beneficial long-term strategy. Because these peer-reviewed chapters come from departments of polymer science, chemical engineering, chemistry, and materials science, we anticipate that this volume will build upon previous polymer science [7, 8] and green chemistry [9] books to provide a *state-of-the-art resource for industry and academia*. Moreover, this variety clearly reflects the need for collaboration between these (and other) disciplines to reach our final goal of *sustainability*. Specifically, new catalytic and biomimetic methods, alternative reaction media, and the utilization of renewable resources are described in this edited volume. Additionally, these discussions cover emerging areas in condensation, controlled free radical, anionic, cationic, and metathesis polymerizations. Based on the excellent contributions in this volume, which originate from a number of science and engineering venues, we can only assume that the idea of a *green polymerization method* will continue to be an important part of polymer science for many years.

## 1.2 Importance of Catalysis

In 1836, Berzelius described his newly coined concept of ''*catalysis*'' and ''*catalytic power*'' in an article for *The Edinburgh New Philosophical Journal* entitled ''Considerations respecting a New Power which acts in the Formation of Organic Bodies''. He described these new idioms as ''a power, which is capable of effecting chemical reactions in unorganized substances, as well as organized bodies'' [10]. Years later, Karl Zeigler and Giudio Natta received the 1963 Nobel Prize for catalysis research related to polyolefins. More recently, Nobel prizes have been awarded for asymmetric catalysis (2001) and olefin metathesis catalysts (2005).

At the present time, refined ideas regarding catalysis have become very common in science and engineering disciplines, as evidenced by the large number of journal articles devoted to this subject each year. From an industrial standpoint, catalysts have played an integral role in the manufacture of chemical raw materials [11], polyolefins [12], and many other polymeric materials. To gain a perspective on the importance of catalysis in *green polymer chemistry*, it is helpful to mention that during the formulation of the principles of green chemistry [4], catalysis was described as a foundational pillar [13]. Since that time, major advances in organocatalysis and biocatalysis have continued to emerge as complementary methods to traditional

metal-based catalysts [14]. As a result, this edited volume contains an emphasis on catalytic processes that includes metal-based catalysts, organocatalysts, and biocatalysts.

Considering the expense of developing or licensing particular catalysts, why are catalysts such an integral part of green chemistry? Certainly, the ability to avoid stoichiometric amounts of reagents or recycle catalysts on heterogeneous supports promotes atom economy and reduces waste [15]. The efficiency is normally measured by *turnover numbers (TONs)*, the number of catalytic cycles or catalyst activity (kg polymer/mol catalyst·h). To accurately understand the amount of waste produced in relation to the amounts of the starting materials, it is helpful to consider the well-known E-factor [16] value for reactions. The *E-factor* concept quantifies the amount of waste produced (in kilograms) during a reaction compared with kilograms of the desired product. The ideal E-factor would be zero, but many reactions do not result in 100% conversion, show side reactions, necessitate protecting groups, or require (toxic) solvents. Several contributions in this volume contain discussions of alternative reaction media. Another compelling reason to incorporate catalytic processes is the ability to utilize *renewable resources* in ways that would not otherwise be possible. For instance, catalytic methods to convert glycerol into acrylic acid or to make cyclic carbonates with $CO_2$ represent some of the numerous examples of non-petroleum based monomer synthesis in this volume.

## 1.3 Brief Summaries of Contributions

Creating *sustainable polymers* presents a significant multidisciplinary challenge and this volume represents a diverse effort to utilize a broad range of renewable resources such as lignin, triglycerides, polysaccharides, monoterpenes, furans, lactides, and natural rubber. The methods represented are also diverse. In the first section of the book, some authors report on utilizing renewable resources directly. For example, Michael Meier describes new advances in the use of renewable feedstocks based on plant oils, showing that plant oils are a perfectly suitable renewable resource for the polymer industry. In Chapter 3, Alessandro Gandini summarizes the versatility of furans as monomers in the synthesis of resins, conjugated polymers, and reversible cross-links. Francois Jerome and Joel Barrault examine processes for converting glycerol into functional monomers. Their chapter discusses the integration of biomass with heterogeneous catalysis.

In the second section, the focus involves *sustainable reaction conditions* that reduce waste or eliminate petroleum solvents. In this regard, methods for integrating petroleum-based polymerizations with renewable starting materials are mentioned by Stewart Lewis and Robert Mathers, who provide a current review of monoterpenes in cationic and ring-opening polymerizations. Debasis Samanta, Katrina Kratz, and Todd Emrick discuss controlled and living polymerizations in water as an important method for synthesizing bio-synthetic hybrid materials.

Their chapter highlights possibilities for decreasing volatile organic solvents. Marc Dube and Somaieh Salehpour show that biodiesel is a very useful polymerization solvent for free-radical polymerizations. Fatty acid methyl esters are definitely an alternative to conventional petroleum based solvents.

The third section focuses on *catalytic process*es to synthesize monomers and polymers. Donald Darensbourg, Adriana Moncada, and Stephanie Wilson nicely summarize the ring-opening polymerization of renewable carbonates made from 1,3-propanediol. These six-membered cyclic carbonates, for instance, are suitable monomers for thermoplastic elastomers and biomaterials. Jan Becker and Andrew Dove detail the synthesis and polymerization of lactides using organocatalysts. Julian Thimm and Joachim Thiem assess polysaccharides as a major component of biomass. In Chapter 11, Nicolay Tsarevsky reviews the synthesis of macromolecules with biodegradable linkages using controlled radical polymerization.

In the fourth section, *biomimetic method*s and *biocatalysis* are discussed. Tatsuo Kaneko discusses the use of phenolic biomonomers in developing high-performance liquid crystalline polymers. Andreas Heise and Inge van der Meulen focus on recent advances in enzymatic polymer synthesis related to polyesters, polyphenols, polyanilines, and green media for enzymes. Judit Puskas, Chengching Chiang, and Mustafa Sen summarize green cationic polymerizations using biotechnology. Specifically, they describe the biosynthesis of natural rubber.

We hope that this book will be of value to its readers and promote the concepts of green chemistry and sustainability within polymer science. Last but not least, we would like to express our sincere thanks to all authors for their excellent contributions to this edited volume.

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