Wiley Series on Polymer Engineering and Technology
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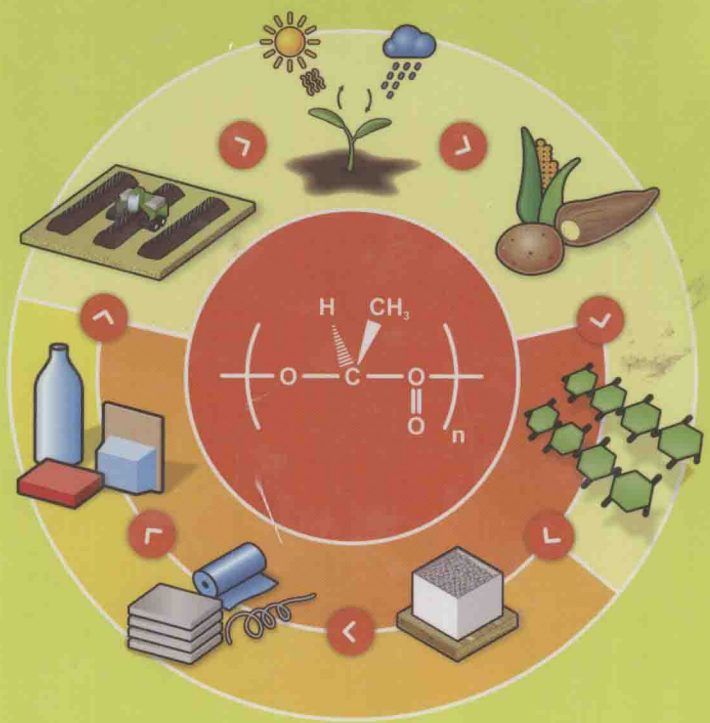
POLY(LACTIC ACID)

SYNTHESIS, STRUCTURES, PROPERTIES, PROCESSING, AND APPLICATIONS



Edited by
RAFAEL AURAS, LOONG-TAK LIM,
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WILEY

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Synthesis, Structures, Properties, Processing, and Applications

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PREFACE

Poly(lactic acid) (PLA) cannot be considered as a new polymer. As early as 1845, PLA was synthesized by Théophile-Jules Pelouze by the condensation of lactic acid [1]. In 1932, Wallace Hume Carothers et al. developed a method to polymerize lactide to produce PLA that was later patented by DuPont in 1954 [2]. Although PLA existed for several decades, its use was limited to biomedical applications (e.g., biocompatible sutures, implants, biologically active controlled release devices) due to its high cost. The low molecular weight PLA polymers obtained also hampered their wide-ranging applications. The breakthrough occurred in the early 1990s when Cargill Inc. succeeded in polymerizing high molecular weight PLA using a commercially viable lactide ring opening reaction [3, 4]. In 1997, Cargill Dow LLC, a joint venture between Cargill Inc. and The Dow Chemical Company, was formed to begin truly commercially significant production of PLA resins under the trade name NatureWorks™. This is a major landmark in PLA's history because it signifies the beginning of a large-scale use of this bio-based polymer, transforming PLA from a specialty material to a commodity thermoplastic.

The increased availability of PLA stimulated an increased in its research and development activities. A survey of the literature revealed that the number of published articles related to PLA increased exponentially over the past decade, which can be also partly attributed to the escalating "green" movement that is stimulating the use of bio-based polymers. To date, the major PLA resin suppliers have been Cargill (in the United States known as Ingeo™), Mitsui Chemicals, Inc. (in Japan known as LACEA™), Purac (The Netherlands), and Teijin Limited (in Japan known as Biofront®). Other important events that took place pertaining to PLA are summarized in Figure P.1 and Table P.1.

While the information available in the literature is massive, at the inception of this volume, no reference book could be found that coherently assembled the scientific and technological knowledge about PLA. Our main motive for editing this book was to consolidate the most relevant information on PLA into a volume that serves as a one-source reference for readers who are keen on this unique biodegradable polymer.

Organized in five parts, Part I of this book covers several important topics, including chemistry and production of lactic acid (Chapter 1) and lactide (Chapter 2), which are the essential building blocks of PLA. Different polymerization reactions for the production of PLA are covered in Chapter 3. In view of certain shortcomings of PLA, copolymerization of PLA with other monomers and stereocomplexation with optimal enantiomer lactide ratios are gaining increased popularity as ways to enhance the material properties of the resulting polymer. These topics are covered in detail in Chapters 4 and 5, respectively. These chapters set the stage for discussions in Part II of this book, in which different material properties of PLA are covered in eight separate chapters. Chain configuration, tacticity, and crystal structure are discussed in Chapter 6 to illuminate how chain structure affects the material properties of PLA and its copolymers. Chapter 7 investigates the compatibility of PLA with solvents and other polymers, an important aspect that should be considered during end-use applications. The interaction of PLA with electromagnetic radiation for probing the molecular structure and interactions are discussed in Chapter 8. The essence of spectroscopy techniques for PLA analysis, including UV–VIS, FTIR, Raman, and NMR, is reviewed in this chapter. Crystallization, thermal, and rheological properties of PLA are discussed in Chapters 9 and 10, and these

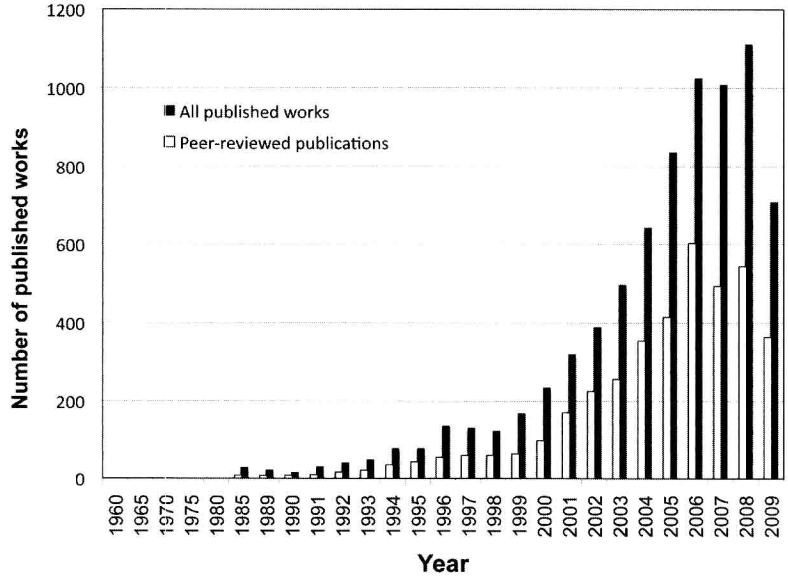

FIGURE P.1 Number of works published since 1960 based on Scholars Portal Search (accessed on 28 Dec 09) using keywords "polylactide", "poly(lactic acid)", and "polylactic acid".

TABLE P.1 Significant Events Related to PLA Production that Occurred over the Past Few Decades

2010	Jung et al. employed recombinant *Escherichia coli* to produce PLA [5]
2009	PURAC, Sulzer, and Synbra announced production of PLA from solid lactide for foamed products
2009	Galactic and Total Petrochemicals from Belgium created a joint venture, Futerro, to begin PLA production
2009	Cargill Inc. acquired full NatureWorks ownership from Teijin Limited
2008	Uhde Inventa Fischer and Pyramide Bioplastics announced large-scale production of PLA in Guben, Germany
2008	PURAC started to commercialize solid lactide monomers under PURALACT™
2007	Teijin launched heat-resistant stereocomplex PLA under Biofront™
2007	NatureWorks LLC and Teijin Limited formed 50–50 joint venture to market Ingeo™ bio-based thermoplastic resins
2005	Cargill Inc. acquired The Dow Chemical Company's share in Cargill Dow LLC 50–50 joint venture
2003	Toyota produced and developed PLA for automotive applications
1997	Formation of Cargill Dow LLC, a 50–50 joint venture of Cargill Inc. and The Dow Chemical Company, to commercialize PLA under the trade name NatureWorks™
1997	Fiberweb (now BBA, France) introduced melt-blown and spun-laid PLA fabrics under Deposa™ brand name
1996	Mitsui Chemicals, Inc. commercialized PLA produced by polycondensation route
1994	Kanebo Ltd. introduced Lactron® PLLA fiber and spun-laid nonwovens

are important to elucidate the melt processing phenomena of PLA. In the remainder of Part II, Chapters 11, 12, and 13 deal with the mechanical, permeability, and migration behaviors of PLA, respectively, and will serve as handy references for designing and engineering PLA products for various end-use applications. In Part III, seven chapters are devoted to summarizing the state of the art of processing and conversion technologies for PLA, covering topics such as extrusion and molding (Chapter 14), polymer blending (Chapters 15 and 16), foaming (Chapter 17), preparation of micro- and nanocomposites (Chapters 18 and 19), and fiber spinning (Chapter 20). One of the hallmarks of PLA polymers is that they are degradable, which has been viewed as an attractive feature for certain applications. In Part IV, six chapters are included to discuss in great detail the various degradation modes of PLA, including hydrolytic degradation (Chapter 21), enzymatic degradation (Chapter 22), thermal degradation (Chapter 23), photodegradation (Chapter 25), and biodegradation (Chapter 25). This part ends with Chapter 26 in which the life cycle assessment and the environmental footprint of PLA are objectively discussed. Finally, in Part V, various applications for PLA are discussed, including medical items (Chapter 27), packaging (Chapter 28), textiles (Chapter 29), and environment-related applications (Chapter 30). Rather than eliminating all duplicate materials between chapters, we deliberately allowed some overlap in discussions to enable the chapters to stand alone to some extent.

This volume skillfully brings together the work of many contributors who are experts in their respective research areas. This volume would not have been possible without

their help and contributions. We are indebted to them for their participation and patience during the preparation of this book and are grateful that they have entrusted us to edit their contributions as per the requirements of each chapter. We hope that readers will find this book useful. We are looking forward to receiving comments and constructive feedback regarding the content of this book [5]. Finally, we are indebted to our three academic institutions, Michigan State University, University of Guelph, and Toyohashi University of Technology, for allowing us to dedicate our effort and time to the completion of this edited book. Our most grateful thanks are to our colleagues for providing a sounding board to discuss ideas and explore new concepts about biodegradable polymers and materials in general; to our editor at John Wiley & Sons, Inc., Jonathan T. Rose, for supporting this proposal, and walking us through its completion; to Lisa Van Horn for coordinating the production of the book; and to Sanchari Sil, our project manager at Thomson Digital, for her invaluable patience to in answering our endless questions about the final proofing of the book. Overall, we could not put our effort into this task without the unconditional support of our families, so that our most special thanks go to all of them.

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CONTENTS