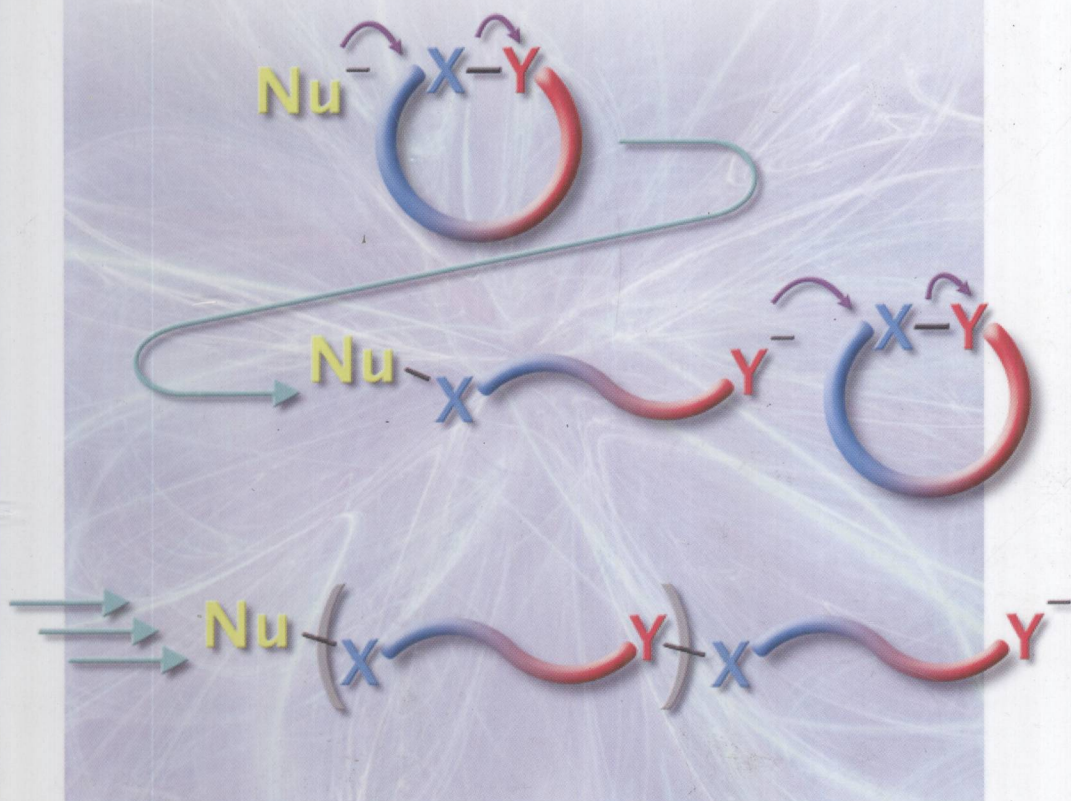


Philippe Dubois, Olivier Coulembier  
and Jean-Marie Raquez (Eds.)

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# Handbook of Ring-Opening Polymerization



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# Handbook of Ring-Opening Polymerization

*Edited by*  
*Philippe Dubois, Olivier Coulembier, and*  
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**Handbook of Ring-Opening  
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*Jean-Marie Raquez*

## ***Further Reading***

Soares, J. B. P., McKenna, T. F. L.

### **Polyolefin Reaction Engineering**

2008

ISBN: 978-3-527-31710-3

Matyjaszewski, K., Gnanou, Y., Leibler, L. (eds.)

### **Macromolecular Engineering**

**Precise Synthesis, Materials Properties, Applications**

2007

ISBN: 978-3-527-31446-1

Tadmor, Z

### **Principles of Polymer Processing 2e**

2006

ISBN: 978-0-471-79276-5

Shaw, M. T., MacKnight, W. J.

### **Introduction to Polymer Viscoelasticity**

2005

ISBN: 978-0-471-74045-2

Meyer, T., Keurentjes, J. (eds.)

### **Handbook of Polymer Reaction Engineering**

2005

ISBN: 978-3-527-31014-2

## Preface

Nowadays, polymeric materials—which we commonly refer to as ‘plastics’—form part of our daily life, finding applications in areas as diverse and versatile as automobiles, textiles, building construction and furniture, medicines, pharmacy, electric and electronic devices, and packaging. Among the vast worldwide production of synthetic ‘plastics’—which today is estimated at over 200 million metric tons per year—the so-called ‘commodity polymers’, including polyolefins such as polyethylene and polypropylene (and their derivatives), polyvinylchloride and styrene-based (co)polymers, undoubtedly share the major sector of the market in terms of volume production. All of these are cheap materials with physico-chemical and thermo-mechanical properties that allow their adaptation to a wide range of low-cost uses. For other, more demanding and specific applications, however, higher-performing synthetic polymeric materials are required, and this is where the ‘engineering plastics’ find their greatest use. Although produced in (relatively) smaller volumes, this family of polymeric materials today attracts interest over an enormous range of valuable applications.

Polymers and copolymers obtained by the ring-opening polymerization (ROP) process today constitute a significant portion of the ‘engineering plastics’ industry, where they are mainly used in the preparation of specialty materials. Among the many polymers produced by ROP, one example worthy of highlight is Nylon<sup>®</sup>-6, a polyamide produced via ring-opening of the  $\epsilon$ -caprolactam monomer. Although the first reports of the polymerization of lactams date back over 70 years, many of the fine details of the mechanism and kinetics involved still remain unanswered today. Consequently, in recent years many new reaction pathways have been investigated and a range of new catalytic processes developed that allow for the production of new copolymers, either between different lactams themselves, or between lactams and other (cyclic) monomers such as lactones. In the future, ROP will clearly pave the way to the creation of novel, high-performing materials, the properties of which may be tunable so that the (co)polymerization reaction can be controlled to a significant degree.

This *Handbook of Ring-Opening Polymerization* is intended as a single comprehensive reference covering all main classes of monomers, including heterocyclics, cyclic olefins and alkynes, and cycloalkanes, with special emphasis on the polymerization tools required for the precise control of macromolecular parameters,

structure and properties, and on the design of materials of practical interest. It is hoped that the Handbook will serve as a source of information for students, research teams, professors and technologists alike, as well as industrial managers. It thus aims to provide an integrated view of the various areas of research and to identify current trends in ROP.

All of the chapters in this *Handbook of Ring-Opening Polymerization* have been written by internationally recognized experts in their field and, for ease of reading, have been allocated to three parts.

Part 1 covers the theory and fundamentals of ROP, where Chapter 1 describes the thermodynamics and kinetics of the process, and Chapter 2 provides a description of the general mechanisms involved.

Part 2 includes chapters on specific classes of cyclic monomers and their polymerization mechanisms and kinetics, their main (co)polymer architectures and related products, as well as current and future applications. Hence, siloxane-containing and sulfur–nitrogen–phosphorus-containing polymers are described in Chapters 3 and 4, respectively, while the polymerization of cyclic depsipeptides, ureas and urethanes, of polyethers and polyoxazolines, and of polyamides are detailed in Chapters 5, 6 and 7, respectively. Chapters 9, 10, 11 and 12 include details of polyesters prepared from either  $\beta$ -lactones, from dilactones, from larger lactones and from polycarbonates, while the polymerization of cycloalkanes is described in Chapter 13. It should be noted that, slightly 'out of place', Chapter 8 covers the subject of ring-opening metathesis polymerization.

Part 3 is devoted more to the implementation of 'green chemistry' in ROP processes, where the latest advances in metal-free catalysis in ROP are described in Chapter 14, and of enzyme-mediated ROP in Chapter 15.

In preparing this Handbook, the efforts of all authors in providing up-to-date accounts of their research and development activities in the field of ROP are greatly appreciated. Grateful thanks are also extended to Dr Philippe Degée (who is now working at Cabot International, Belgium) for his extreme help not only in the initial launch of this Handbook but also for the valuable advice that he provided during its creation.

Mons, Belgium, November 2008

Philippe Dubois

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