Catalytic Polymerisation of Cycloolefins

CATALYTIC POLYMERIZATION OF CYCLOOLEFINS. IONIC, ZIEGLER-NATTA AND RING-OPENING METATHESIS POLYMERIZATION

BY V. DRAGUTAN AND R. STRECK, Elsevier, Amsterdam, 2000, 1272 pages, ISBN 0-444-89519-1, €351.68, U.S.$406

This book represents a comprehensive survey of the polymerisation of cycloolefins by, as the subtitle indicates, all pertinent polymerisation methods. By any standards the discussion of such a broad field is a monumental task, and this is reflected in the size of the book which has 18 chapters and covers 1247 pages plus index. It is Volume 131 of "Studies in Surface Science and Catalysis" and one of the longest in this well-known series.

The purpose of the book is to survey the available literature including patent publications on polymers derived from cyclic olefins, with emphasis on the monomers and their chemistry, rather than on catalysts and reaction mechanisms. One of the authors (R. Streck) is an industrial chemist, which helps to emphasise the applications angle. The abundance of material covered leads to a fairly dense text in the style of a review article. Literature up to 1999 is covered, although most references date from the 1960s through to the 1980s. The inclusion of older material is certainly very useful and helps to put more recent research into context.

Chapter 1 introduces some general principles of Ziegler-Natta and ring-opening metathesis polymerisation (ROMP) chemistry and introduces the main polymer types that can be produced. However, there is no information on reaction mechanisms and catalysts here – the discussion of this fundamental aspect is delayed until Chapter 15. Chapter 2 is a detailed discussion (98 pages) of the monomers and their synthesis.

Catalytic Systems

Chapter 3 deals with catalytic polymerisation systems and is subdivided into: (1) cationic, (2) anionic, (3) Ziegler-Natta, and (4) ROMP catalysts. The term 'catalyst' is used rather widely, and no distinction is made here between a true catalyst, that is a metal centre involved in every reaction step, and initiators like those present in cationic and anionic polymerisations. The emphasis is clearly on ROMP catalysts, which are quite extensively covered, and includes 'classical' platinum metal catalysts such as ruthenium, osmium and iridium chlorides, as well as Grubbs-type ruthenium catalysts. By comparison, the description of the commercially much more important Ziegler-Natta systems is rather limited. Section (5) of Chapter 3 deals with some catalyst synthesis.

Chapter 4 discusses reaction conditions, such as the effect of monomer concentration on ROMP catalysts, of catalyst concentration (mainly of metathesis catalysts), of the reactant ratio, and of the reaction temperature. Chapter 5 describes the cationic polymerisation of cycloolefins, followed in Chapter 6 by a brief discussion of anionic, lithium alkyl-initiated polymerisations.

The discussion of Ziegler-Natta polymerisations (Chapter 7) is ordered according to ring size, from 4- to 9-membered cycloolefins. This section deals mostly with classical Ziegler-Natta catalysts based on early transition metal halides activated with aluminium alkyls, although on occasions molybdenum or rhenium metathesis systems make an appearance. There is extensive coverage of the polymerisation of norbornene, norbornadiene and functionalised cyclic olefins with a variety of soluble palladium catalysts, including aqueous emulsion polymerisations catalysed by palladium chloride or acetate.

ROMP Reactions

Chapter 8 deals with ROMP of cycloolefins and with 356 citations is the most extensively referenced chapter in the book, compared to 50 references on Ziegler-Natta catalysis. Again the monomers are treated in order of ring size. Most catalyst systems discussed are based on vanadium, molybdenum, tungsten and rhenium, with some mention of ruthenium and other noble metal catalysts. This is

followed in Chapter 9 by a discussion of ROMP of functionalised monomers, catalysed by ruthenium as well as molybdenum and tungsten complexes, and in Chapter 10 with the description of ROMP of heterocyclic olefins by tungsten and, mainly, ruthenium catalysts.

Copolymerisations of Cycloolefins

Chapter 11 deals with the large area of copolymerisations involving cycloolefins. Not surprisingly in view of the extensive literature, it is the longest in the book (187 pages). Structure and properties of poly(cycloolefins) are discussed in Chapter 12, thermodynamic aspects in Chapter 13, and reaction kinetics in Chapter 14. Aspects of polymerisation mechanisms are the topic of Chapter 15. It is subdivided into sections on cationic, anionic, Ziegler-Natta and ROMP. While the Ziegler-Natta discussion is rather rudimentary and deals mainly with the 1,2- to 1,3-isomerisation during the polymerisation of cyclopentene, the ROMP section is quite comprehensive. Chapter 16 is concerned with the stereochemistry of cycloolefin polymerisations.

While up to this point the authors have followed strictly the title of the book and focused exclusively on cyclic olefins, Chapter 17, entitled 'Related Processes' is, somewhat surprisingly, concerned with the cationic, anionic and Ziegler-Natta polymerisation of non-cyclic monomers: isobutene, styrene, butadiene and 1-alkenes. Even *alkane* metathesis, olefin isomerisation, atom transfer radical polymerisation of vinyl monomers (including ruthenium catalysed reactions) and the metathesis of olefins and acetylenes are covered. The section on ring-closing metathesis with Grubbs-type ruthenium catalysts is a useful demonstration of the versatility of this method in synthetic applications.

Applications and Outlook

Finally, Chapter 18 deals with practical applications and commercial products. Some of these are discussed in relative detail, although overall one might wish for more precise information on actually commercialised products and their market sizes. In view of recent mergers and acquisitions the list of manufacturers grouped by country is now of limited use. Few production figures seem up-to-date.

The book is fairly free of errors, although some of them are rather glaring. This starts with Chapter 1: Equation (1.2) refers to vinyl polymerisation, the label 'ROMP' is misplaced. Equation (1.15) shows *cis/trans* ROMP isomers and not the iso/syndiotacticity claimed in the text. In Chapter 3, structures 6–9 of *ansa*-zirconocenes (and their copies in subsequent chapters) show the undesirable *meso*- rather than the correct *rac*-isomers.

The text is densely written, and space is limited. This being so, one wonders, for example, whether it is really necessary in the section on catalyst synthesis to include equations for the preparation of compounds such as $AlCl_3$, HF and $ZnCl_2$. In the section on *ansa*-zirconocene syntheses, the repetition of very similar reaction schemes for closely related ligands hardly seems justified. The index, by contrast, is rather sparse. For example, the entry 'ruthenium catalysts' refers only to Chapter 3 but gives no hint to the extensive coverage of these compounds in Chapters 8 and 9. One will search in vain for keywords such as 'iridium', 'osmium' and even 'palladium'.

This book is addressed to the specialist with detailed knowledge of the underlying catalytic chemistry. It provides a wealth of references to the primary literature, and the authors are to be congratulated on undertaking such a large task so comprehensively. There is, however, little discussion and evaluation, which is regrettable since more overviews, summaries and informed re-evaluations of earlier results would have been helpful to the less experienced reader. Anyone already concerned with cycloolefin polymerisation and especially ROMP chemistry, as well as those wishing to familiarise themselves with this area, for example, at the start of a new research project, will find this book a most valuable source.

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TITLE: Synthesis of New Polymer Ionomers via Ring-Opening Metathesis Polymerization. AUTHORS: A. A. Santiago, J. Vargas, Jorge A. Cruz-Morales, M. A. Tlenkopatchev, R. GaviÃ±o, Yu. A. Malkanduev, N. A. Sivov. KEYWORDS: Polynorbornene Dicarboximide, Ring-Opening Metathesis Polymerization, Ionomers. JOURNAL NAME: Open Journal of Organic Polymer Materials, Vol.4 No.4, October 28, 2014. Stereochemistry of Cycloolefin Polymerization. Steric efffects in cationic polymerization. Steric configuration of vinyl polymers. Stereoselectivity in Ziegler-Natta polymerization. Steric configuration of polyalkenamers. Stereoselectivity in ring-opening metathesis polymerization. Tacticity of polyalkenamers. The nature of steric interactions in ROMP. Related Processes. Catalytic polymerization of olefins and dienes. Atom transfer radical polymerization of vinyl compounds. Metathesis reactions of olefins and acetylenes. Acyclic diene methatesis (ADMET) and acyclic diyne methatesis (ADIMET) po... Ring-opening metathesis polymerisation (ROMP) of a series of cycloolefins (cyclopentene, cyclooctene, cyclododecene, dicyclopentadiene) in the presence of different WCl6-based catalysts exhibited a wide range of polymer stereoselectivity depending mainly on the nature of the catalytic system employed. It is of interest that in the reaction of cyclopentene catalysts derived from WCl6 and organoaluminium compounds lead preferentially to trans-polypentenamer while catalysts obtained from WCl6 and organotin compounds form mainly cis-polypentenamer. The role of organometallic cocatalyst showed to b In 2005 there were "several types of commercial cyclic olefin copolymers based on different types of cyclic monomers and polymerization methods. Cyclic olefin copolymers are produced by chain copolymerization of cyclic monomers such as 8,9,10-trinorborn-2-ene (norbornene) or 1,2,3,4,4a,5,8,8a-octahydro-1,4:5,8-dimethanonaphthalene (tetracyclododecene) with ethene (such as TOPAS Advanced Polymer's TOPAS, Mitsui Chemical's APEL), or by ring-opening metathesis polymerization of various cyclic monomers. followed by hydrogenation (Japan Synthetic Rubber's ARTON, Zeon Chemical's Zeonex and Zeonor)."