

## “Handbook of Metathesis” 2nd Edition

**Edited by Robert H. Grubbs (California Institute of Technology, USA), Anna G. Wenzel (W. M. Keck Science Center, USA), Daniel J. O’Leary (Pomona College, USA) and Ezat Khosravi (University of Durham, UK), Volumes 1–3, ISBN: 978-3-527-33424-7, 1608 pages, Wiley-VCH, Weinheim, Germany, 2015, £365.00, €492.80, US\$605.00**

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Published more than ten years after the first edition of “Handbook of Metathesis” (1) which enjoyed tremendous success, the new edition is a milestone in the development of metathesis chemistry. The three volumes are edited by the Nobel laureate Professor Robert H. Grubbs (California Institute of Technology, USA) in collaboration with an impressive panel of co-editors, all famous experts in the field. 41 comprehensive chapters, superbly written by 86 internationally well-recognised contributors, cover to date the most significant advances in metathesis chemistry and its industrial applications based on more than 2200 literature references. Since the first edition several books, thematic issues and extensive reviews on metathesis reactions have appeared (2–8) and this new edition enormously adds to the present knowledge, representing the most important compendium of the

state-of-the-art of alkene, alkane and alkyne metathesis and metathesis polymerisation, with a strong focus on the present research in this fascinating field of chemistry. Metathesis has real potential for large scale valorisation in many industrial areas in the near future.

### **Volume 1: “Catalyst Development and Mechanism”**

The first volume, “Catalyst Development and Mechanism” (423 pp.), edited by Robert Grubbs and Anna Wenzel covers the most recent developments in metathesis catalysts and reaction mechanism.

### **High Oxidation State Molybdenum and Tungsten Catalysts**

In Chapter 1 the Nobel laureate Professor Richard R. Schrock (Massachusetts Institute of Technology, USA) authoritatively and attractively surveys high oxidation state molybdenum and tungsten complexes relevant to olefin metathesis. Special attention is paid to the synthesis of novel imido ligands, bispyrrolide and related complexes, and to the appealing applications of monoalkoxide pyrrolide (MAP) complexes which are highly efficient in *Z*-selective olefin metathesis reactions (homocoupling, cross-coupling, ethenolysis and ring-opening metathesis polymerisation (ROMP)). The

rich information offers deep insights into the mechanism and stereochemistry of metathesis reactions initiated by high oxidation state Mo and W complexes that have played a crucial role in the development of olefin metathesis chemistry.

## Progress in Alkane Metathesis

Jean-Marie Basset, Emmanuel Callens and Nassima Riache (King Abdullah University of Science and Technology, Saudi Arabia) discuss in the next chapter a very interesting topic of metathesis chemistry which has recently experienced a rapid upsurge i.e. alkane metathesis promoted either by single-catalyst systems or tandem, dual catalytic systems. Herein, using the refined concept of 'surface organometallic chemistry', the authors unveil in various alkane metatheses the substantial activity and selectivity of the new Basset heterogeneous catalysts consisting of highly coordinatively unsaturated  $d$ -block transition metals (zirconium, tantalum, tungsten), supported on metal oxides or metals. The potential for producing supported metal-alkylidene catalysts (of Mo, Ta, W) and their applications in alkane metathesis is fully illustrated. Alkane metathesis based on the 'tandem concept' in the Chevron process (tungsten oxide on silica and platinum-lithium on alumina) or in the Goldman and Brookhart procedure (a combination of an iridium-pincer-based catalyst with Schrock-type, Mo- or W-alkylidene complexes), is properly dealt with.

## Challenges on Ruthenium Catalysts

The third chapter by Benjamin K. Keitz (California Institute of Technology) gives an interesting account of diastereocontrol in olefin metathesis when using  $Z$ -selective ruthenium catalysts. This chapter concentrates on the fulminant development of Ru-based  $Z$ -selective metathesis catalysts as well as on a fresh mechanistic grasp specifically concerning the effects of  $N$ -heterocyclic carbenes (NHC) and of their substituents on reaction stereoselectivity and catalyst decomposition. Remarkable applications of  $Z$ -selective Ru catalysts in cross-metathesis (CM), ring-closing metathesis (RCM) and ROMP are showcased. David S. Weinberger and Vincent Lavallo (University of California, Riverside, USA) introduce, in Chapter 4, the recently developed Ru olefin metathesis catalysts ligating cyclic alkyl amino carbenes (CAAC)

which possess a quaternary  $sp^3$  carbon in place of one N atom in the standard NHC. Catalyst preparation, characterisation and utilisation in RCM, CM, ethenolysis and degenerate metathesis are discussed. A particular challenge for the evolution of this type of catalysts is evidenced, namely the implementation of CAAC ligands for stereospecific control in asymmetric olefin metathesis and regioselectivity in ring expansion metathesis polymerisation. Chapter 5 by Daryl P. Allen (Materia Inc, USA) is dedicated to supported catalysts and non-traditional reaction media, both issues of intense contemporary research. Some of the strategies are aimed principally at well-defined, supported catalyst systems, such as immobilised Grubbs' Ru catalysts and Schrock's Mo- and W-based catalysts, and are presented in the first section with a special emphasis on the efficiency, sustainability and recyclability of these catalytic systems. In the second part modern concepts of using non-traditional reaction media (for example water, ionic liquids, fluorinated systems) are introduced.

Chapter 6 by Xavier Solans-Monfort (Universitat Autònoma de Barcelona, Spain), Christophe Copéret (ETH Zürich, Switzerland) and Odile Eisenstein (Université Montpellier 2, France) provides new mechanistic insights from computational studies on  $d^0$  metal-catalysed alkene, alkyne and alkane metathesis. The assets of computational chemistry in terms of understanding at a molecular level and the recent advances in structure-reactivity relationships (catalytic performance) are revealed. From another perspective Peng Liu, Buck L. H. Taylor, Jesus Garcia-Lopez and Kendall N. Houk (University of California, Los Angeles, USA) provide, in Chapter 7, compelling computational studies on Ru-catalysed olefin metathesis. They first focus on the general mechanisms assigned to Ru complexes coordinating phosphine and NHC, then explain the effects of spectator and ancillary ligands (phosphine, NHC and anionic ligands), and evaluate the intriguing topic of  $E/Z$ -selectivity tackling the mechanism, selectivity and decomposition pathways in  $Z$ -selective metathesis. Intermediates in the early and late transition metal-catalysed olefin metathesis, as investigated by X-ray crystallography and nuclear magnetic resonance (NMR) spectroscopy, are examined by Anna G. Wenzel in Chapter 8. Herein care is given to the direct observation of the metathesis-active metallacyclobutane intermediates and to the stability and orientation of the metal

alkylidene/olefin complexes arising in metathesis reactions as considered in the context of Z-selective catalysts, catalyst degeneracy and the prevention of catalyst decomposition.

## New Insights on Olefin Metatheses

How initiation rates play an essential role in olefin metatheses induced by Grubbs, Hoveyda-Grubbs, Piers and Herrmann catalysts or by indenylidene-Ru precatalysts is enticingly portrayed in Chapter 9 by Justin R. Griffiths and Steven T. Diver (University of Buffalo, USA). A detailed analysis of the main factors affecting the initial rates such as ligand dissociation and exchange, alkene coordination, and the nature of the catalyst and solvent is given. In the next chapter, the intriguing topic of degenerate metathesis reactions as promoted by heterogeneous and homogeneous, early- and late-transition metal catalytic systems, is reviewed by Ian C. Stewart (ExxonMobil Chemical Company, USA). In order to obtain conclusive evidence on the mechanism of methylene exchange process, some selected metathesis reactions are screened using various isotopic-labelling experiments, in addition to pertinent stereochemical studies.

In Chapter 11, Yann Schrodi (California State University, Northridge, USA) considers the most significant aspects of the mechanism of catalyst decomposition in olefin metathesis as well as specific methods for catalyst reactivation. Along these lines, the decomposition mechanisms of very active and stereoselective Mo- and W-imido alkylidene complexes are elaborated followed by a report on the decomposition pathways of numerous classes of Ru-alkylidene complexes. The information provided indicates different behaviour in the thermal decomposition for the first and second generation catalysts, particularly for Ru-alkylidene complexes. Critical observations on catalyst stability, nature of intermediates and products of catalyst decomposition are advanced. The decomposition mechanism in the presence of functional groups or small molecules is also discussed. Strategies for preventing catalyst decomposition and for extending catalyst life i.e. ligand choice, immobilisation on solid support, catalyst loading and adequate reaction conditions are viewed as having major importance for industrial applications.

The crucial role played by the solvent and additives on catalyst activity and selectivity is thoroughly documented by Shawn K. Collins (University of Montreal, Canada)

in Chapter 12. Examples include the effects of perfluoroaromatic solvents or additives such as alcohols that increase the initiation rates of metathesis reactions induced by Ru-based catalysts. In enyne metathesis promoted by Ru catalysts, the author convincingly shows that both activity and selectivity are strongly influenced when changing the reaction atmosphere from nitrogen to ethylene. In numerous asymmetric metathesis reactions the reactivity and enantioselectivity can be strongly determined by halide salts in numerous asymmetric metathesis reactions. Additives of the Lewis-acid type frequently promote macrocyclisations whereas other types of acid or base additives suppress olefin isomerisation favouring metathesis.

Chapter 13 by David W. Knight (Cardiff University, UK) focuses on a critical issue for olefin metathesis – the purification of reaction products. Removal of catalyst traces is key for the ensemble of the metathesis processes at a larger scale, especially for production of pharmaceuticals, foods, cosmetics, domestic devices and appliances. Moreover, catalyst traces in the metathesis product could lead to unwanted side reactions like isomerisation, rearrangements, cyclisations and condensations that drastically affect the yield and composition of the product. In separate sections the author shows that good efficiency in Ru removal from metathesis products is possible by adequate chromatographic techniques and chemical protocols, by specific complexation reactions or selective immobilisation on solid supports, all of which could be successfully applied either on a small scale or employed on a pilot and an industrial scale.

In the last chapter of Volume 1 by Pierre H. Dixneuf and Christian Bruneau (Université de Rennes 1, France) who are true pioneers in the field of metathesis chemistry, the authors cover recent developments of Ru indenylidene catalysts for alkene metathesis. Details for accessing a range of catalysts with monodentate ligands such as phosphines, phosphites, NHC, pyridines or bidentate ligands based on NHC-phosphine and indenylidene-ethers are given. After a tutorial on Ru-indenylidene complexes, the reader will find an authoritative presentation of one of the most important issues in Ru-allenylidene/indenylidene chemistry i.e. the intramolecular allenylidene into indenylidene rearrangement, an area in which the authors published remarkable contributions. Furthermore, the synthesis of binuclear Ru catalysts from (arene)Ru(II) complexes is followed by an excellent overview of the preparation

methods of the first, second and third generation Ru indenylidene catalysts. Finally, a summary of Ru catalysts bearing a chelating indenylidene ligand is given.

## Volume 2: “Applications in Organic Synthesis”

In the second volume “Applications in Organic Synthesis” (743 pp.), Robert Grubbs and Daniel O’Leary, the editors, debate the current synthetic use of various types of olefin metatheses with an emphasis on commercial valorisation. Application of metathesis chemistry in organic synthesis has greatly expanded following the discovery of new, highly active and stereoselective metathesis catalysts able to efficiently promote the reaction of a broad range of olefinic and acetylenic substrates. The rich literature published on this subject during the last decade gives this volume a special utility for many experimentalists. The first chapter by Paul R. Hanson, Soma Maitra, Rambabu Chegondi, and Jana L. Markley (University of Kansas, USA) extensively explores RCM as a very efficient approach for synthesising a diversity of cyclic compounds, concentrating on the synthesis of carbocycles, heterocycles and macrocycles starting from adequate dienes. The extension of metathesis to alkyne substrates is tackled separately taking into account the assets of intramolecular enyne metathesis and dienyne metathesis. Furthermore the advantage of combining RCM in tandem processes and the efficiency of relay RCM (RRCM) are highlighted. The debate over *Z*-selective and enantioselective RCM is of great interest for the stereoselective synthesis of cyclic compounds. Chapter 2 by Daniel J. O’Leary and Gregory W. O’Neil (Western Washington University, USA) extensively examines CM, a different type of metathesis which is almost as versatile as RCM due to the diversity of available substrates. After briefly introducing some early applications using well-defined Mo and Ru catalysts, they showcase the value of the selectivity model published by Grubbs that was fruitfully valorised in designing CM reactions. This chapter pinpoints alkane functionalisation by CM, and gives examples of their applications to common olefinic substrates as well as to vinyl boronates, N-containing compounds (amines, nitriles), allylic and homoallylic alcohols, unsaturated ethers, aldehydes, acids, halides and P- and S-containing derivatives. Productive access to bioactive compounds and polyenes by CM is further illustrated.

## The Diversity of Metathesis Processes

Chapter 3 by Yuya A. Lin and Benjamin G. Davis (University of Oxford, UK) extends metathesis applications to chemical biology by presenting site-selective peptide and protein modification protocols such as CM of sulfur- and selenium-containing substrates, incorporation of allyl chalcogenides into proteins and specific olefin metathesis reactions on proteins. Ru catalysed tandem metathesis processes and non-metathesis transformations for various syntheses are scrutinised by Youn H. Nam and Marc L. Snapper (Boston College, USA) in Chapter 4, focusing on RCM, CM and enyne metathesis along with various other chemical transformations (i.e. isomerisation, hydrogenation, oxidation, hydroxylation, cyclisation, atom transfer radical polymerisation (ATRP), atom transfer radical addition (ATRA), cyclopropanation, rearrangement, olefination and carboxylation) that together allow intricate molecules to be built in a straightforward and efficient way. The authors state that further research is needed to elucidate catalytic species and mechanistic aspects of these complex processes, posing a great challenge for future work.

Enyne metathesis is closely looked at by Jingwei Li and Daesung Lee (University of Illinois at Chicago, USA) in Chapter 5. The authors first discuss the most important aspects of reaction mechanism, regioselectivity in metal-carbene induced enyne metathesis and metal-salt induced skeletal reorganisation. Enyne RCM and enyne CM are both considered. Particular attention is paid to the relationship between enyne metathesis and metallotropic shift. In the second part of the chapter, the reader will find interesting applications of enyne metathesis in organic synthesis and especially for accessing natural products. The success of tandem concepts including RCM, CM, ring-rearrangement metathesis (RRM), Diels-Alder and other traditional reactions in sequence with enyne metathesis is fully described. Chapter 6 by Alois Fürstner (Max-Planck-Institut für Kohlenforschung, Germany) offers a comprehensive report on recent advances in alkyne metathesis. After introducing novel generations of Mo- and W-alkylidyne catalysts endowed with good reactivity and functional group tolerance, applications of alkyne metathesis in the synthesis of a broad palette of complex molecular frameworks including bioactive natural compounds, are exemplified. Catalyst-controlled stereoselective olefin metathesis

is further elaborated by Amir H. Hoveyda, R. Kashif, M. Khan, Sebastian Torker and Steven J. Malcolmson (Boston College) in Chapter 7. Progress in the design and development of catalyst-controlled enantio- and Z-selective olefin metathesis reactions in particular their utility in chemical synthesis are reviewed. Both chiral Ru and Mo catalysts are largely considered and the stereoselective abilities of both are comparatively defined. Selected applications of enantioselective metatheses in the synthesis of natural compounds are also included.

Two stimulating vignettes in Chapter 8 study the high potential for implementing RCM in the total synthesis of natural products. Along this line, in the first vignette Christopher D. Vanderwal (University of California, Irvine, USA) shows how RCM of allylsilane combined with electrophilic desilylation is a convenient way to access rings with exocyclic alkenes whereas in the second vignette, Maciej A. Walczak and Samuel J. Danishefsky (Columbia University, USA) feature a concise entry into the synthesis of antimetastatic agents using RCM as exemplified by the 14-membered macrolide migrastatin and analogues. In Chapter 9 Cezary Pietraszuk, Piotr Pawluć and Bogdan Marciniak (Adam Mickiewicz University in Poznań, Poland), well-known authorities in the field of silicon chemistry, successfully combine olefin metathesis with silicon chemistry to construct a broad array of silicon compounds which are difficult to synthesise using more conventional methods. Thus, CM is a productive way of obtaining different classes of vinylsilanes. RCM affords cyclic scaffolds bearing silicon functionalities, while acyclic diene metathesis (ADMET) and ROMP of Si-containing monomers effectively lead to polymers incorporating Si.

Using RCM to synthesise pharmaceuticals or produce active pharmaceutical ingredients (API) on a pilot or a large scale, is illustrated by Vittorio Farina and András Horváth (Janssen Pharmaceutica NV, Belgium) in Chapter 10. Examples include the use of Ru metathesis catalysts to synthesise by RCM Ciluprevir (BILN-2061) and its analogues, Vaniprevir (MK-7009), Simeprevir (TMC435) and SB-462795. Of practical significance, the influence of catalyst, solvent, additives, impurities, air and moisture on productivity of RCM in large scale synthesis of pharmaceuticals is underlined. Involvement of metathesis strategies in diversity-oriented synthesis (DOS) is nicely documented in the next chapter by Alan Rolfe and Lisa A. Marcaurelle

(H3 Biomedicine Inc, USA). These authors point out that CM, RCM, ring-closing enyne metathesis and metathesis cascade reactions applied in solid-phase and in parallel solution phase procedures are most beneficial in DOS approaches. Various techniques for preparing small to medium size rings and macrocycles are considered.

The last chapter of Volume 2 by Diana Stoianova, Adam Johns and Richard Pederson (Materia Inc) concentrates on commercial applications and future opportunities of olefin metathesis reactions. The renewable feedstock-based processes using seed oil, soybean oil, fatty acids, amino acids as well as those employing hydrogenated nitrile butadiene rubber (HNBR), diverse pharmaceutical candidates and ROMP-derived functionalised oligomers are of particular relevance for industry. It is shown that Lanxess' Therban<sup>®</sup>, a high performance HNBR product which is successful in many key industries requiring high resistance to aggressive fluids, oil and grease, is more easily processed and therefore offers a competitive advantage over traditional HNBR. A significant commercial application for Grubbs' metathesis catalyst which is also an eloquent example of a renewable feedstock process is the start-up of the Elevance-Wilmar biorefinery plant in Gresik, Indonesia. Pharmaceutical candidates of practical importance are highlighted for example constrained peptides such as Aileron's ALRN-5281, a stapled peptide, and Janssen's and Medivir AB's Simeprevir (TMC435), a NS3/4A protease inhibitor for treating hepatitis C. The emergence of hydrogenated metathesised soybean oil wax, of  $\alpha,\omega$ -diacids, amino acids, ROMP-derived oligomer reagents and ethylene from renewable feedstocks, offer further commercial opportunities for valorising olefin metathesis-based protocols.

### Volume 3: "Polymer Synthesis"

The third volume "Polymer Synthesis" (403 pp.), edited by Robert Grubbs and Ezat Khosravi assembles fast-growing developments in metathesis polymerisation highly pertinent for commercial utilisation. The first chapter by Christian Slugovc (Graz University of Technology, Austria) gives an inspiring overview on the synthesis by ROMP of homopolymers and copolymers. By evaluating the main catalysts and introducing nonconventional monomers, novel structures and complex architectures

of polymers are presented. Additional information on reaction mechanism, stereochemistry and sequence-controlled ROMP is expertly introduced. In the second chapter, Valérie Héroguez (Laboratoire de Chimie des Polymères Organiques, France), Abraham Chemtob (Université de Haute Alsace, France) and Damien Quemener (Institut Européen des Membranes, France) deal with polymerisation in dispersed media. Here, the reader will find abundant data on emulsion, dispersion and suspension polymerisation techniques with useful points on emulsion ROMP (mini-emulsion, micro-emulsion, non-aqueous) and micellar or dispersion ROMP. Original aspects on biomedical applications and nanoparticle formation are furnished. The next chapter by Nils Hanik and Andreas F. M. Kilbinger (University of Fribourg, Switzerland) looks at telechelic polymers of considerable industrial importance. Various functionalisation methods involving metathesis in constructing the targeted homo- and hetero-telechelic polymers are described with emphasis on their valorisation.

### **The Versatility of Ring-opening Metathesis Polymerisation**

Elizabeth Elacqua, Niels ten Brummelhuis and Marcus Weck (New York University, USA) provide, in Chapter 4, excellent information on main-chain- and side-chain-functionalised supramolecular polymers as accessed by ROMP and ADMET. Particular features on polymer assembling through directional supramolecular interactions (for example hydrogen bonding, metal-ligand coordination and inclusion complexation) are discussed. In a very attractive and stimulating chapter, Garret M. Miyake, Raymond A. Weitekamp and Robert H. Grubbs (California Institute of Technology) focus on the synthesis of materials with nanostructured periodicity. Progress in valorising Ru-mediated ROMP to yield block-copolymers for the assembly of bulk periodic nanostructures is reported. ABA triblock copolymers, organic/inorganic composite materials or nanostructures with domain sizes exceeding 100 nm are valuable models for practical applications. The synthesis of nanoparticles *via* ROMP is further elaborated by Anthony M. Rush, Carrie R. James and Nathan C. Gianneschi (University of California, San Diego, USA) in Chapter 6. Present day nanoparticles have a strong impact on a range of technologies including advanced materials production,

microelectronics, biosensing or bio-diagnostics, drug and gene delivery. Due to their unique behaviour, amphiphilic block copolymers which generate polymeric micellar nanoparticles are of particular note. The most efficient techniques for obtaining ROMP-based micellar nanoparticles i.e. the grafting-through, grafting-to and grafting-from approaches are distinctively described.

Chapter 7 by Izabela Czelusniak (University of Wroclaw, Poland) and Ezat Khosravi (University of Durham) provides a front-row view of biodegradable products from the classes of polyester-, peptide- and carbohydrate-functionalised polymers, and antimicrobial and polymeric betaines. Appealing applications such as drug carriers and tissue scaffolds are included. Rewardingly, it is shown that ROMP has the capability to control the structure of biodegradable and biocompatible polymers so as to compete with enzyme specificity encountered in degradation processes. A variety of biologically active polymers is advanced by Laura L. Kiessling and Joshua M. Fishman (University of Wisconsin, USA) in Chapter 8. In this context, although benefitting from the advantages that ROMP catalysts offer, the authors outline the multiple difficulties posed by the biologically active sites of the monomers. An attractive presentation of the bulk properties of polymers including hydrogels and coatings as well as of the main probes for biological detection and drug delivery is also included. The fruitful combination of olefin metathesis polymerisation with click chemistry to prepare different polymeric architectures or to functionalise polymeric structures at the chain end, side chain or in the backbone is discussed in Chapter 9 by Steffen Kurzhals and Wolfgang H. Binder (Martin-Luther University, Germany). In this brief account the generation of polymeric structures based on block copolymers, star-shaped polymers, cyclic polymers, graft copolymers and polymeric networks is clearly evidenced.

Chapter 10 by Timothy C. Mauldin and Dylan J. Boday (IBM Materials Engineering, USA) is devoted to relevant aspects of polymer self-healing in conjunction with ROMP and CM. The delicate role of the monomer and catalyst in self-healing as well as second-generation self-healing materials with intrinsic mechanisms in which metathesis catalysts are directly incorporated into the polymer structure are outlined. Remarkable improvements in metathesis catalysis by using various functional monolithic supports and materials in association with up-to-date metathesis catalysts are brought to the forefront by Emily B. Anderson and Michael R.

Buchmeiser (Universität Stuttgart, Germany) in Chapter 11. Herein novel techniques used in the preparation of selected functional monolithic supports and applications in metathesis catalysis, biocatalysis, separation science and tissue engineering are described in depth. Latent Ru catalysts for ROMP, of great consequence for industrial valorisation, are highlighted by Eyal Tzur and Gabriel Lemcoff (Ben-Gurion University, Israel) in the next chapter. There is extensive coverage of the various activation techniques for achieving latent Ru catalysis such as thermal (for example for *cis*-dianion type catalysts and for those bearing electron-rich carbenes or chelating ligands), light-induced, chemical and mechanical activation methods.

### Related Metathesis Polymerisation Protocols

ADMET polymerisation, a step-growth polymerisation process differing from ROMP, is proficiently overviewed by Michael D. Schulz and Kenneth B. Wagener (University of Florida, USA) in Chapter 13. Key aspects on the reaction mechanism, monomers, catalysts, solvents and a variety of applications using a broad range of simple or functionalised dienes as substrates are unveiled. As a fine addition, the superior attributes of the ADMET protocol in production of copolymers and functional materials like biologically oriented polymers, electroactive polymers, liquid crystalline polymers, conjugated polymers, and biorenewable, hyperbranched and interlocked polymers are portrayed. Solid-state polymerisation and ADMET depolymerisation are other important issues to be considered.

Recent developments in synthesising biorenewable polymers by metathesis processes including ADMET polymerisation, acyclic triene metathesis (ATMET) polymerisation and ROMP are discussed by John H. Phillips (Materia Inc) in Chapter 14. An important bonus for practical valorisation is provided by metathesis procedures using biorenewable resources including plant oils, castor oil, fatty acids and terpenes. The last chapter of Volume 3 by Toshio Masuda and Afang Zhang (Shanghai University, China) is dedicated to polymerisation of substituted acetylenes. The reader will find useful information on monomers and catalysts employed, controlled polymerisation processes and data on polymer structure and properties. These specialty polymers are endowed with unique mechanical, electrical and optoelectronic properties such as gas permeability, semiconductivity, photoconductivity, insulating capacity, nonlinear optical

properties or photo- and electroluminescence. These polymers encompass an important class of advanced materials suitable for unprecedented commercial applications.

### Conclusion

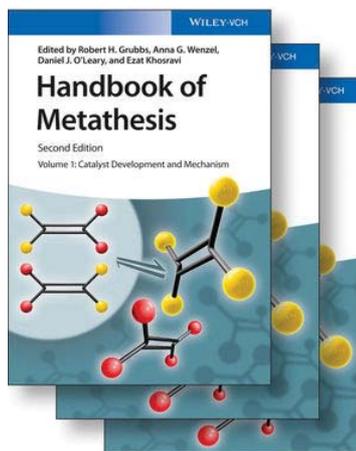
By successfully compiling and interpreting a vast amount of cutting-edge information on metathesis chemistry, the three-volume “Handbook of Metathesis” represents an outstanding compendium of the current knowledge in this field that features multiple applications in organic and polymer synthesis, in petrochemical, pharmaceutical, biomedical and materials sciences. Each volume starts with a detailed table of contents, followed by the editors’ concise preface outlining the scope of this second edition and by a complete list of contributors to the respective volumes, while at the end a very informative subject index is provided. The high quality debating text from each chapter, accompanied by excellent graphical work, is pleasant to read. The list of references is relevant and quite helpful.

This new, exquisite edition will undoubtedly be of great value and very useful for all synthetic chemists working in the area of organic, organometallic, coordination and polymer chemistry. It will serve as a leading information source, indispensable for scientists and practitioners using multifarious alkene and alkyne metathesis reactions in their research and teaching programmes. The three-volume set is a precious acquisition for all those interested in the field and an asset for libraries of universities and academic or industrial research institutions. The vast knowledge offered by this admirable new edition will certainly stimulate further research on metathesis chemistry and related areas and will effectively promote metathesis-based industrial application and diversification.

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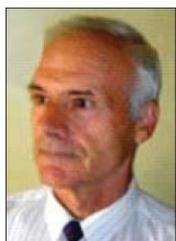
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## The Reviewers



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Ileana Dragutan is a Senior Researcher at the Institute of Organic Chemistry of the Romanian Academy. Her interests are in syntheses of olefinic monomers *via* olefin metathesis, metathesis-based protocols for biologically active compounds and natural products, sterically hindered amines. She is also interested in transition metal complexes with free radical ligands.