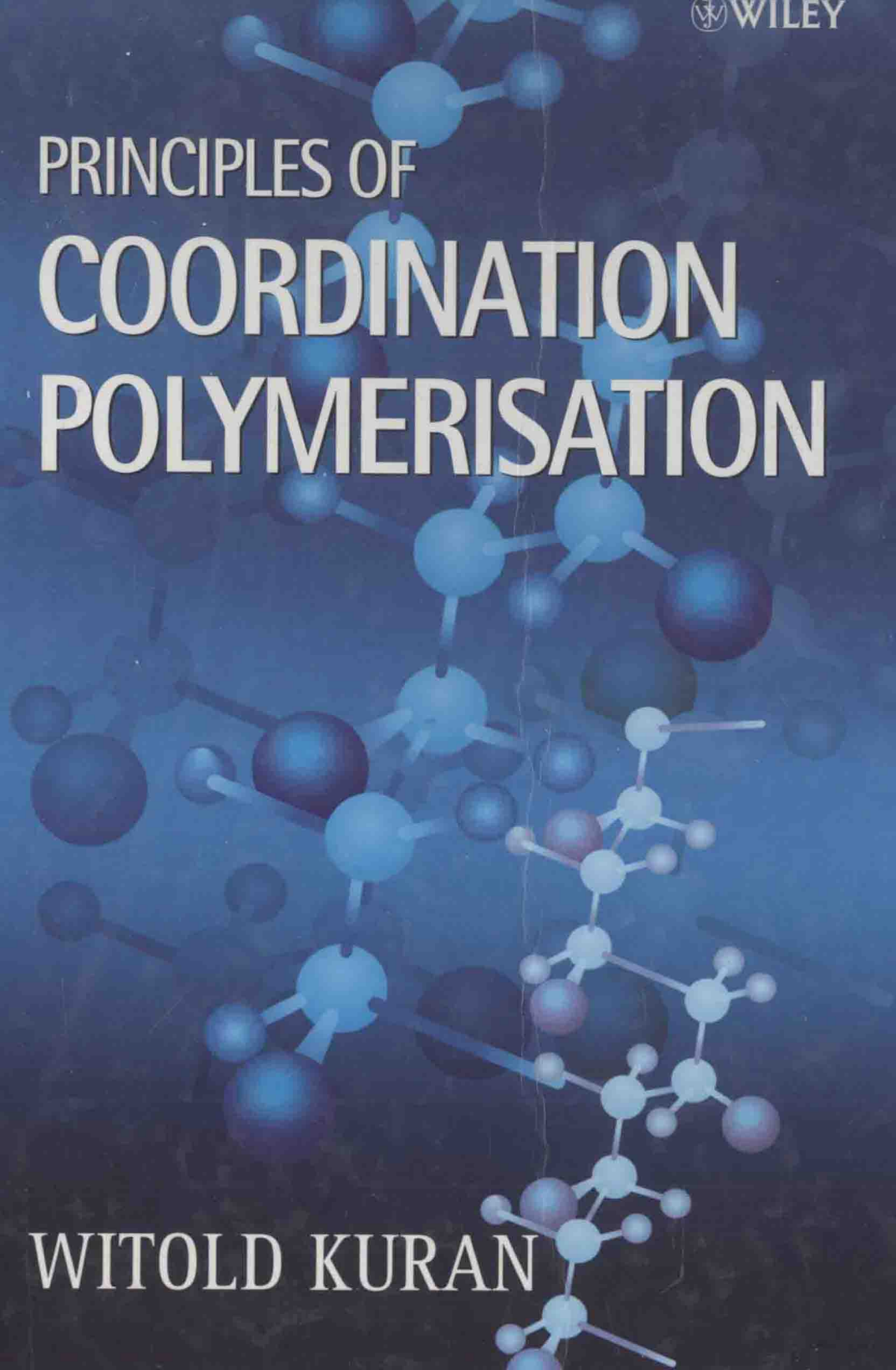
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PRINCIPLES OF
COORDINATION
POLYMERISATION
WITOLD KURAN

Principles of Coordination Polymerisation

Heterogeneous and homogeneous catalysis in polymer chemistry – polymerisation of hydrocarbon, heterocyclic and heterounsaturated monomers

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Principles of Coordination Polymerisation

Tribute to Witold Kuran

The author of this book, Witold Kuran, died on 19 November 1999 at the age of 58. For the last 25 years of his life he was a professor at the Faculty of Chemistry Warsaw University of Technology, where he chaired the Division of Polymer Synthesis and Processing. During his early studies he became fascinated with the discoveries of Karl Ziegler and Gulio Natta and the great opportunities provided by organometallic catalysts for the progress of the chemistry and technology of high polymers, and he concentrated on this subject throughout his professional life. Studies of the reactions of organoaluminium and organozinc compounds and the utilisation of these derivatives as catalysts in polymerisation processes of polar vinyl and heterocyclic monomers were the main focus of his work. At the end of the 1960s and beginning of the 1970s, he carried out pioneering studies of the alternating copolymerisation of acrylic monomers with vinyl chloride, olefins and dienes, catalysed by alkyaluminium chlorides, and found that these processes are initiated radically as a result of homolytic dissociation of metal–carbon bonds. In the mid-1970s he began to study the copolymerisation of carbon dioxide with heterocyclic monomers. In a short time, the team led by him developed a number of original and very active catalysts for these processes. During further studies it appeared that these catalysts could be successfully applied in the coordination polymerisation of oxiranes, cyclic carbonates and other heterocyclic monomers. His own broad experimental results and also extremely precise analysis of the results published by other researchers made it possible to form a general concept of organometallic catalysis in the polymerisation of heterocyclic monomers, which he presented in a number of monographic publications. Professor Kuran's output also includes a number of valuable publications dealing with other fields of organometallic chemistry and polymer chemistry. He is the coauthor of fundamental works on palladium(0) complexes, which appeared during his fellowship in the school of Gulio Natta in Milan, and also of many works devoted to the utilisation of cyclic carbonates in the synthesis of condensation polymers. Although he past away at the height of his creative powers at a mere 58, he left a very rich scientific output. He was the author or coauthor of two books and over 110 scientific papers and book chapters, and the holder of 30 patents.

In the Faculty of Chemistry of Warsaw University of Technology he conducted lectures on polymer chemistry and technology. In the mid-1980s, when it became apparent that catalytic polymerisation processes would have a decisive effect on the production of plastics, he made a decision to introduce a new lecture devoted to this field, entitled *Principles of Coordination Polymerisation*. This lecture gained great popularity among graduate and doctoral students, and its basic thesis was also presented in the form of a small monograph and a broad chapter in the Polish textbook 'Polymer Chemistry'. At the beginning of the 1990s, Professor Kuran made the decision to write a monograph, in which he intended comprehensively to present both basic notions and the latest achievements in the field of coordination polymerisation of various classes of monomers. The work on this book initially proceeded very quickly, and the publishing house John Wiley & Sons expressed an intention to publish it. Unfortunately, with time, deadlines for completing the work were postponed several times, since the development of new fields of studies on catalytic polymerisation processes was so rapid that, after nearly every visit to the library, corrections and supplements had to be introduced. The systematic deterioration in the health of Professor Kuran was also a key factor in slowing down the work on the book. The basic version of the manuscript was completed in May 1999 and, after it had been read by close coworkers, the decision was taken, together with Professor Kuran, to finalise the edition of the book. However, these plans could not be fulfilled. After Professor Kuran's death we undertook to complete his work, following as far as possible his instructions, as well as taking into account the comments of the reviewers. We hope that the small changes introduced by us do not disturb the original concept of the author, who was our teacher and friend, and that the great work of his life will prove to be useful both to students and to those professionally involved in polymer chemistry and technology.

Professor Zbigniew Florjańczyk

Preface

The book has been prepared on the basis of lectures dealing with polymer chemistry, coordination polymerisation, catalytic polymerisation processes, polymerisation stereochemistry and organic technology that I have been giving to students of various courses, mostly at the Faculty of Chemistry, Warsaw University of Technology, for more than 25 years. The lack of a single-volume book that would cover the entire area of the coordination polymerisation and collect the relevant literature in the field, with suitable comment, has induced me to do this work. Actually, only a few existing textbooks contain individual chapters connected with coordination polymerisation. However, these chapters omit the coordination polymerisation of some important classes of monomers and do not treat all important problems exhaustively and instructively enough, which makes it difficult to master this important subject. There is a great unfilled gap between the very great achievements and progress in the field of coordination polymerisation, in terms of both basic and industrial research after Ziegler's and Natta's discoveries, and respective textbooks that might deliver suitable data together with explanation and proper comment. The spectacular breakthrough made possible by these discoveries, honoured with the Nobel Prize in 1963, revolutionised polymer science and technology in the second half of the twentieth century. However, although the mentioned discoveries resulted in coordination polymerisation becoming one of the most active and exciting areas of research in academic and industrial laboratories, having a significant impact on progress in the plastics and rubber industries, Ziegler and Natta did not live to see a textbook dealing with coordination polymerisation that might be worthy of the name. Moreover, outstanding scientific achievements and innovations and process improvements in the mid-1980s revolutionised polyolefin technology for the second time. We are now witnessing the next phase of this revolution, which was initiated, in the mid-1980s, by the discoveries of metallocene single-site catalysts which could be tailored to produce polymers of virtually all feasible microstructures. These achievements offer attractive potential for the development of basic research in terms of mechanistic studies as well as for the introduction of new or improved industrial processes in various branches of the plastics and rubber industries. Thus, the lack of a suitable textbook lessens the chance of proper mastery of the important discipline of coordination polymerisation, and the training that most chemists receive seems to be inadequate, which is deplorable. The present

textbook represents an effort to overcome these barriers by offering a unified, possibly most complete, view of coordination polymerisation. This book aims to cover this field, addressing almost all the area of coordination polymerisation, i.e. polymerisation with a catalyst involved in the monomer coordination at each polymerisation step. It arose from the need for a text, devoted to coordination polymerisation, to accompany introductory courses as well as advanced courses in polymer science, catalysis and in polymerisation catalysis. It is thought to be useful for research students and research workers in industry, and will also be helpful as a reference book. The main inspiration that has enabled me, after many years, to prepare this book has been my constant interest in coordination polymerisation. This interest was kindled during my stay at the Istituto di Chimica Industriale at the Polytechnics of Milan as a post-doctoral fellow in the early 1970s and my visit to the Max Planck Institut für Kohlenforschung in Mülheim/Ruhr later on. Successively collected literature data, my own studies and the results of work carried out in the Institute of Organic Chemistry and Technology and the Division of Polymer Synthesis and Processing at the Faculty of Chemistry, Warsaw University of Technology, headed by me, were of assistance in the preparation of this work.

The textbook is focused on the polymerisation of monomers belonging to all the important classes of hydrocarbon as well as non-hydrocarbon monomers, in the presence of coordination catalysts of various kinds, and emphasises the growing importance of coordination polymerisation for basic research as well as for industrial processes. A vast amount of material, covering coordination polymerisation almost in its entirety and considering the whole range of monomers susceptible to polymerisation with coordination catalysts and the whole range of respective more important coordination catalysts, has been collected and selected conscientiously to suit readers with various levels and breadths of knowledge of the subject. Considering that several generations of catalysts and processes have been introduced on a commercial scale to produce a large variety of most widespread polymeric materials ranging from commodity thermoplastics to rubbers, to some extent the emphasis is laid on the coordination polymerisation of alkenes, particularly of 1,3-dialkenes, in the textbook. Chapters dealing with polymerisations of these monomers present the methods that have been applied for the implementation of industrial processes and show the evolution of these processes, since there are particularly strong interrelations between the basic and industrial research in this field.

The contents of the book are systematised, taking into account basic features of the mechanisms that operate in coordination polymerisations of various monomers and depend on the kind of monomer and catalyst. This is, essentially, consistent with the alignment of monomers according to their properties resulting from their structure. Thus, after introductory Chapter 1 and Chapter 2, dealing with the general characteristics of coordination polymerisation, subsequent chapters are devoted to the coordination polymerisation of unsaturated hydrocarbon monomers, such as olefins, considering primarily the

stereospecific polymerisation of α-olefins (Chapter 3), vinylaromatic monomers, especially styrene (Chapter 4), conjugated dienes (Chapter 5), cycloolefins (Chapter 6) and alkynes (Chapter 7), as well as the coordination polycondensation of divinyl monomers via the acyclic diene metathesis reaction and the coordination coupling polycondensation of functional aromatic compounds by Heck's reaction, including carbonylation coupling polycondensation (Chapter 8). Finally, Chapter 9 is concerned with the coordination polymerisation of non-hydrocarbon monomers, such as heterocyclic and heterounsaturated monomers. Although polymerisations and copolymerisations of these monomers in the presence of coordination catalysts do not represent high-mileage industrial processes (they have been restricted to the production of polyether elastomers on a larger scale), and have not influenced the progress in the plastics and rubber industries to such an extent as those processes involving hydrocarbon monomers, their importance for the development of new ideas in coordination polymerisation and the broad synthetic feasibilities are giving grounds for more detailed treatment of this subject, especially considering its instructive character. Taking the above into consideration, the individual chapters of the book are not equal, but differ in volume according to the importance and breadth of the problems presented as regards the chemistry rather than the technology.

Each chapter presents a unified view of monomers, catalysts and mechanisms, with a special emphasis on stereochemistry, the structures of polymers and the utility of coordination polymerisation, as well as attempts to delineate the current trends of research and actual or potential commercial applications. Problems are listed at the end of each chapter in order to enable students or other readers to absorb its contents more easily.

Taking into account one of the most important features of coordination catalysts, which is their capability of producing stereoregular polymers, when discussing the polymerisation of individual groups of monomers, special attention is paid to the structures of the catalyst active species and the stereocontrol mechanism of these polymerisations. These key questions for an understanding of the nature of coordination polymerisation are treated with special emphasis in the textbook, especially when considering that the utility of coordination polymerisation for producing stereoregular polymers is well established.

The rather difficult material covering the subject of coordination polymerisation has been presented in the book in a way that should be approachable and intelligible to undergraduate students who have mastered general subjects in chemistry. Introductory treatment of all questions, comprehensible for undergraduate students, is followed by more advanced considerations demanding deeper reflection that it is hoped will be rewarding to graduate students and others. The idea is for the text to be eminently teachable for instructors and easily comprehensible for students. By far the majority of colleges and universities have no courses in coordination polymerisation, no staff member conducting research in this area and only cursory mention of

polymers in other courses. There are, needless to say, many exceptions, ranging from the isolated effort of a single staff member to such major centres for polymer research as those where a dozen or more staff members constitute a formal or informal polymer research group. However, there are rather rare cases of such academic centres gathering more than a few specialists in the field of coordination polymerisation.

The approach to referencing the literature in the book is such that the most recent bibliography is cited as References, including most of the latest review articles and books; the most important original works are also listed, however. More general reviews and book chapters are also listed as Further Reading. Since this book is not a monograph, the references are by no means exhaustive, but the reader will easily find additional references by looking up those cited, since many citations, as mentioned, are of review articles and books. In order to avoid a long list of References and Further Reading at the end of the textbook, they are listed at the end of each individual chapter. The textbook, by condensing much of the latest knowledge in the field into a more convenient form, may therefore also enable specialists to benefit from the book.

The book is intended for MSc and PhD students in catalysis, and in polymerisation catalysis, for undergraduate and research students in polymer science in general, for college and university instructors and for industrial researchers.

List of Symbols and Abbreviations

A	activator for Ziegler–Natta catalyst precursor
Ac	acyl
Acac	acetylacetonyl
All	allyl
Ar	aryl
Bbn	9-borabicyclo[3.3.1]nonyl
Bu	butyl
Bz	benzyl
Bzo	benzo
CD	α-cyclodextrin
Chx	cyclohexyl
Cod	cycloocta-1,5-diene
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
Cp′	substituted or nonsubstituted Cp
Cp″	substituted or nonsubstituted Cp
C*	chiral carbon atom
C^*	total concentration of the active sites
C_p^*	concentration of the propagation active sites
Dmon	dimethanooctahydronaphthalene
Dmpe	1,2-bis(dimethylphosphine)ethane
DOX	1,4-dioxane
E	energy
EB	ethyl benzoate
Et	ethyl
Flu	9-fluorenyl
h	monomer head
Hx	hexyl
Ind	1-indenyl
k_a	rate constant of chain transfer with activator
k_{H_2}	rate constant of chain transfer with hydrogen
k_i	rate constant of chain initiation

k_m	rate constant of chain transfer with monomer
k_p	rate constant of chain propagation
k_s	rate constant of spontaneous chain transfer
k_t	average rate constant of chain transfer
k_{11}	monomer 1 homopropagation rate constant
k_{22}	monomer 2 homopropagation rate constant
k_{21}	monomer 1 heteropropagation rate constant
k_{12}	monomer 2 heteropropagation rate constant
K_p	propagation equilibrium constant
L	ligand
LA	Lewis acid
LB	Lewis base
Ln	lanthanide
M	monomer
M_1	comonomer 1
M_2	comonomer 2
m, *M*	mesogenic
Me	methyl
Mt	metal
$\bar{M}_n$	number-average molecular weight
$\bar{M}_w$	weight-average molecular weight
Nbd	2,5-norbornadiene
Np	neopentyl
Nph	naphthyl
Ph	phenyl
ppm	parts per million
Pr	propyl (or symbol of the element)
Py	pyridine
P_h	monomer head-linked propagating species
P_t	monomer tail-linked propagating species
P_n	polymer chain
P_x	polymer chain
P_m	conditional probability of forming *m* diad
P_r	conditional probability of forming *r* diad
$\bar{P}_n$	number-average degree of polymerisation
r_1	relative reactivity ratio of monomer 1
r_2	relative reactivity ratio of monomer 2
R	alkyl (hydrogen)
r, *R*	racemic
R	right-handed
R_p	overall polymerisation rate
S	left-handed
t	monomer tail
Tbp	2,2′-thiobis(4-methyl-6-*t*-butylphenolate)

THF	tetrahydrofuran
Thind	1-(4,5,6,7-tetrahydroindenyl)
Tmdn	trimethanododecahydronaphthalene
T_g	glass transition temperature
t	time
X	substituent
Z	substituent
Δ	right-handed
Λ	left-handed
Θ_A	fraction of centres complexed with activator
Θ_M	fraction of centres complexed with monomer
$\square$	coordination vacancy

Contents