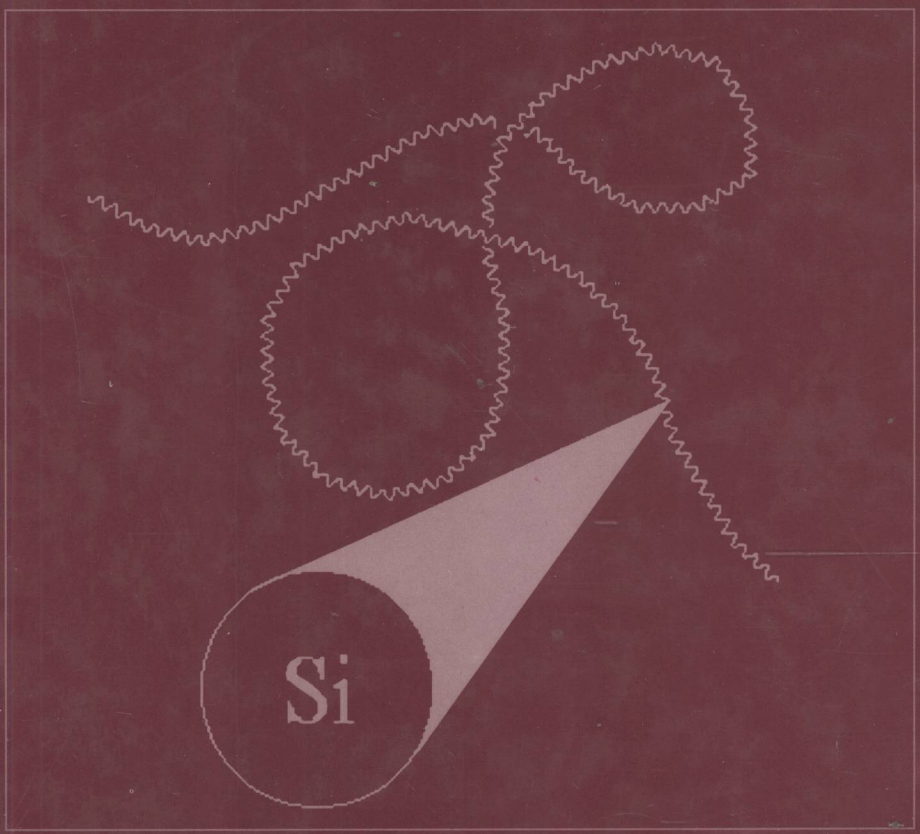
Silicon-Containing Polymers

The Science and Technology of Their Synthesis and Applications

Richard G. Jones, Wataru Ando and
Julian Chojnowski (Eds.)



Kluwer Academic Publishers

Silicon-Containing Polymers

The Science and Technology of Their Synthesis and Applications

Edited by

Richard G. Jones
University of Kent, Canterbury, U.K.

Wataru Ando
Dow Corning Asia Ltd., Kanagawa, Japan

and

Julian Chojnowski
Polish Academy of Sciences, Lódz, Poland

KLUWER ACADEMIC PUBLISHERS
DORDRECHT / BOSTON / LONDON

A C.I.P. Catalogue record for this book is available from the Library of Congress.

ISBN 0-412-83110-4

Published by Kluwer Academic Publishers,
P.O. Box 17, 3300 AA Dordrecht, The Netherlands.

Sold and distributed in North, Central and South America
by Kluwer Academic Publishers,
101 Philip Drive, Norwell, MA 02061, U.S.A.

In all other countries, sold and distributed
by Kluwer Academic Publishers,
P.O. Box 322, 3300 AH Dordrecht, The Netherlands.

Printed on acid-free paper

Printed in the Netherlands.

CONTRIBUTORS

RONALD H. BANEY
University of Florida,
Department of Materials Science and Engineering,
132 Rhines Hall, Gainesville, FL 32611-6400, USA

GEORGES BELORGEY
Laboratoire de Recherches sur les Macromolécules,
Institut Galilee, University Paris-XIII, Villetaneuse, France

SYLVIE BOILEAU
Laboratoire de Recherche sur les Polymères - UMR CNRS 7581,
2 rue Henri Dunant, 94320 Thiais, France

B. BOUTEVIN
Laboratoire de Chimie Appliquée - UMR CNRS 5076,
Ecole Nationale Supérieure de Chimie de Montpellier, 8, Rue de l' Ecole Normale, 34296 Montpellier Cedex 5, France

XINYU CAO
University of Florida,
Department of Materials Science and Engineering,
132 Rhines Hall, Gainesville, FL 32611-6400, USA

JULIAN CHOJNOWSKI
Centre of Molecular and Macromolecular Studies,
Polish Academy of Sciences,
Sienkiewicza 112, 90-363 Łódz, Poland

STEPHEN J. CLARSON
Department of Materials Science and Engineering and the Polymer Research Center,
College of Engineering, University of Cincinnati, Ohio 45221-0012USA

JOYCE Y. COREY
Department of Chemistry,
University of Missouri-St. Louis,
St. Louis, Missouri, 63121, USA

ROBERT J. P. CORRIU
Université Montpellier II,
Place Eugène Bataillon,
34095 Montpellier Cedex 05, France

M. CYPRYK
Centre of Molecular and Macromolecular Studies,
Polish Academy of Sciences,
Sienkiewicza 112, 90-363 Łódz, Poland

G. DABBAGH
Bell Laboratories,
Lucent Technologies, Murray Hill,
New Jersey 07974, USA

SOPHIE DEMOUSTIER-CHAMPAGNE
Unité de Physique et de Chimie des Hauts Polymères
Université Catholique de Louvain,
Croix du Sud , B-1348, Louvain-la-Neuve, Belgium

JACQUES DEVAUX
Unité de Physique et de Chimie des Hauts Polymères
Université Catholique de Louvain, Croix du Sud , B-1348, Louvain-la-Neuve, Belgium

PETAR R. DVORNIC
Michigan Molecular Institute, 1910 W. St. Andrews Road, Midland, Michigan 48640, USA

WILLIAM E. DOUGLAS
Université Montpellier II, Place Eugène Bataillon, 34095 Montpellier Cedex 05, France

GORDON FEARON
Dow Corning Corporation, Midland, Michigan 48686-0994, USA

MICHIYA FUJIKI
NTT Basic Research Laboratories 3-1 Morinosato Wakamiya, Atsugi, Kanagawa 243-0198, JAPAN

DANIEL GRAIVER
Dow Corning Corporation, Midland, Michigan 48686-0994, USA

GRAHAM M. GRAY
Centre for Materials Research, School of Physical Sciences, University of Kent, Canterbury, Kent CT2 7NR, UK

F. GUIDA-PIETRASANTA
Laboratoire de Chimie Appliquée - UMR CNRS 5076, Ecole Nationale Supérieure de Chimie de Montpellier, 8, Rue de l' Ecole Normale, 34296 Montpellier Cedex 5, France

YASUO HATANAKA
National Institute of Materials and Chemical Research 1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

SIMON J. HOLDER
Centre for Materials Research, School of Physical Sciences, University of Kent, Canterbury, Kent CT2 7NR, UK

LEONARD V. INTERRANTE
Department of Chemistry Rensselaer Polytechnic Institute, Troy, NY, 12180 USA

RICHARD G. JONES
Centre for Materials Research, School of Physical Sciences, University of Kent, Canterbury, Kent CT2 7NR, UK

JULIAN R. KOE
NTT Basic Research Laboratories 3-1 Morinosato Wakamiya, Atsugi, Kanagawa 243-0198, JAPAN

SHANE W. KRSKA
Department of Chemistry University of California, Berkeley, California 94720, USA

ANDRÉ MAS
Laboratoire de Chimie Macromoléculaire Université Montpellier II, Place Eugène Bataillon, 34095 Montpellier Cedex 05, France

NOBUO MATSUMOTO
Shonan Institute of Technology,
1-1-25, Nishi-kaigan,Tsujidou, 251-8511
Japan

MIECZYSŁAW MAZUREK
3M/ATC,
3M Centre, 201-4N-01,
St. Paul, Minnesota, 55144-1000, USA

JOSEF MICHL
Department of Chemistry and
Biochemistr,y
University of Colorado, Boulder,
Colorado 80309-0215, USA

HAJIME MIYAZAKI
Canon Inc.,
Fuji-Susono Research Park,
4202, Fukara, Susono-shi,410-1196
Japan

YUKIO NAGASAKI
Department of Materials Science,
Science University of Tokyo,
Noda 278-8510, Japan

O. NALAMASU
Bell Laboratories,
Lucent Technologies, Murray Hill,
New Jersey 07974, USA

ANTHONY E. NOVEMBRE
Bell Laboratories,
Lucent Technologies, Murray Hill,
New Jersey 07974, USA

MICHAEL J. OWEN
Dow Corning Corporation,
Midland, Michigan 48686-0994, USA

A. RATSIMIHETY
Laboratoire de Chimie Appliquée - UMR
CNRS 5076,
Ecole Nationale Supérieure de Chimie de
Montpellier, 8, Rue de l' Ecole Normale,
34296 Montpellier Cedex 5, France

ELSA REICHMANIS
Bell Laboratories,
Lucent Technologies, Murray Hill,
New Jersey 07974, USA

HIDEKI SAKURAI
Department of Industrial Chemistry,
Faculty of Science and Technology,
Science University of Tokyo,
Noda, Chiba 278, Japan

GEORGES SAUVET
Laboratoire de Recherches sur les
Macromolécules,
Institut Galilee, University Paris-XIII,
Villetaneuse, France

FRANÇOIS SCHUÉ
Laboratoire de Chimie
Macromoléculaire
Université Montpellier II,
Place Eugène Bataillon,
34095 Montpellier Cedex 05, France

DIETMAR SEYFERTH
Department of Chemistry,
Massachusetts Institute of Technology,
Cambridge, Massachusetts 02139, USA

Q. SHEN
Starfire Systems, Inc.
Watervliet, NY, 12189 USA

DAVID Y. SON
Department of Chemistry
Southern Methodist University,
Dallas, TX 75275-0314, USA

ALAIN SOUM
Laboratoire de Chimie des Polymères Organiques,
Unité Mixte de Recherche, CNRS – UNIVERSITE BORDEAUX 1,
Ecole Nationale Supérieure de Chimie et de Physique de Bordeaux,
Avenue Pey Berland - BP 108 – 33402,
Talence Cedex, France

HIROYUKI SUZUKI
NTT Basic Research Laboratories,
3-1 Morinosato-Wakamiya 243-0198,
Japan

KOHEI TAMAO
Institute for Chemical Research,
Kyoto Universit,y
Uji, Kyoto 611-0011, Japan

MASATO TANAKA
National Institute of Materials and Chemical Research
1-1 Higashi, Tsukuba, Ibaraki 305-8565,
Japan

DOMINIQUE TEYSSIÉ
Université de Cergy-Pontoise,
Neuville sur Oise, 5 Mail Gay-Lussac,
95031 Cergy-Pontoise Cedex, France

MICHAEL J. WENT
Centre for Materials Research,
School of Physical Sciences,
University of Kent,
Canterbury, Kent CT2 7NR, UK

TAKANOBU SANJI
Department of Industrial Chemistry, Faculty of Science and Technology,
Science University of Tokyo,
Noda, Chiba 278-8510, Japan

ROBERT WEST
Organosilicon Research Center,
Department of Chemistry,
University of Wisconsin, Madison,
Wisconsin 53706, USA

SHIGEHIRO YAMAGUCHI
Institute for Chemical Research,
Kyoto University,
Uji, Kyoto 611-0011, Japan

MASARU YOSHIDA
National Institute of Materials and Chemical Research,
1-1 Higashi, Tsukuba, Ibaraki 305-8565,
Japan

GREGG A. ZANK
Dow Corning Asia Ltd.,
603 Kishi, Yamakita,
Kanagawa 258-0112, Japan

PREFACE

BACKGROUND

Polysiloxanes have chains constructed of alternately arranged silicon and oxygen atoms with organic groups attached to the silicon atoms. This structure gives them a unique combination of properties that hold great interest for a host of practical applications. Although they have been known and manufactured for many years, their applications continue to expand rapidly and this boosts progress in the generation of new and modified polysiloxanes.

Polysiloxanes constitute the oldest known class of silicon-based polymers and the broadest one when viewed in terms of the variety of structures differing in topology and the constitution of organic substituents. There are also many and various types of siloxane copolymers, some of purely siloxane structure and others of siloxane-organic composition. There is no doubt that polysiloxanes are the most technologically important silicon-based polymers. The broad class of model materials known as silicones is based on polysiloxanes. They are also the best known, as most research in the area of silicon polymers has for many years been directed towards the synthesis of new polysiloxanes, to understanding their properties and to extending their applications.

It is, thus, obvious that polysiloxanes could not be missing from any book on silicon-based polymers. However, since the concept of the present monograph was to include all silicon polymer types in one melting pot it was decided that considerable attention should also be paid to the relatively new classes: polycarbosilanes, polysilazanes and polysilanes. To date, although they hold the interest of many silicon chemists, there has been relatively little review literature devoted to these polymers. They are nonetheless the subjects of a great number of scientific papers and considered to be materials of the future. In this latter context it was recognised that there are a number of topics of current importance, either from a technological point of view or because they relate closely to broader initiatives in polymer science, and these have also been singled out for particular consideration.

SCOPE

The concept of the book as presented above has confined polysiloxanes to fewer chapters than they might be perceived to deserve from their importance. However, taking account of the extensive review literature that is already available, the subjects selected for inclusion in the section devoted to polysiloxanes address important current trends in siloxane polymer science and technology. Thus, there is coverage of the modification of polysiloxane side groups to give the polymers new reactivity or new physical properties. The content on block copolymers and copolymer networks is directed to meeting the considerable interest of chemists and technologists in new siloxane-organic hybrids. Interest in polysiloxane networks is related to two important and still developing classes of silicone materials: silicone rubbers and silicone resins.

This is reflected in chapters devoted to silicone elastomers and to silsesquioxanes respectively. Among the important features of polysiloxanes that determine their wide-ranging applications are their unusual surface and thermal properties, so current developments in these areas have been included. Some important aspects of polysiloxanes are held over for consideration later in the book under special topics, but at the end of this section a perspective on future developments in polysiloxane science and technology is presented.

Polycarbosilanes and polysilazanes are covered in a special section. Because of their importance as preceramic materials, both established and potential, they have a technological significance second only to the polysiloxanes. The polysilazanes have nitrogen rather than carbon as the chain heteroatom and, in contrast to the polycarbosilanes, are relatively new materials. The editors believe that the two chapters of this special section lend the correct emphasis to these topics.

The next section is devoted to polysilanes and related polymers. The main difference between a polysilane and a polymer with a saturated carbon backbone is that there is significant electronic delocalisation within the σ-bonded framework of the former that, as a consequence of the smaller dimensions of the carbon atom, is not possible in the latter. This single feature plays a dominant role in determining the spectroscopic, electroactive, thermal and mechanical properties of polysilanes. The polysilylarylenes and polysilylalkylenes often share such properties. It is for this reason that this section groups all such polymers together in presentations of the current thinking surrounding their syntheses, and structural and property characterisations. A reliable strategy for the synthesis of polysilanes from accessible starting materials is still an unrealised objective. Accordingly, the different approaches to their synthesis and modification are covered. The characteristic spectroscopic, electronic and electrical properties of polysilanes are dealt with in two chapters, the thermal properties in another, and there are others that give appropriate consideration to the wealth of silicon chemistry directed to the synthesis of new silicon-backbone and main chain substituted polymer variants.

The challenge presented by silicon-based polymers is all the more intriguing because of the rapid growth over the past decade in the number of structural types available and our increasing understanding of the special and highly flexible role that silicon plays in these materials. The final section of this text explores such special topics. For instance, sol-gel technology has become a popular way to create organic/inorganic hybrid materials and nanocomposites. The silica-like structures formed around surfactant micelles afford solids of highly regular and controlled porosity. In recent years, the development of methods for the directed synthesis of macromolecules with precisely defined structures has also generated considerable excitement in the polymer science community, and one of the most widely studied is the class of hyperbranched polymers known as dendrimers. Organosilicon chemistry offers a number of high yield, selective reactions that are suitable for dendrimer construction. Chiral control is another such current area of chemical endeavour and optically active silicon-containing polymers are just beginning to be studied. Millennium old silicate ceramics have now been supplemented by the new ceramic materials derived from pyrolysis of formable preceramics polymers based on silicon. Progress has been made in the conversion of organofunctional silicon sol-gels and silicone resins to silicon oxycarbide ceramics. Polymeric materials have found widespread use in the electronics

industry both in the manufacturing processes used to generate today's microcircuitry and in other component structures of complete devices. The importance of polymers in such applications arises from our ability to design and synthesise versatile materials with the precise functionalities and process properties required. To a large degree, the progress enjoyed by the device industries has relied on parallel advances in polymeric materials technologies. Amongst silicon polymers, polysilanes have played a notable role as lithographic imaging materials and as dielectric, effective luminescence and large carrier mobility materials.

As a consequence of the overlap of the subject matter of different contributors, some repetition has proved to be unavoidable. In addition, we realise that this monograph does not cover what others may deem to be important aspects of silicon-based polymer science and technology. In the light of our present experience, and given the benefit of hindsight, we hope that the subjects that might be viewed as serious omissions can be included in subsequent editions of the book.

Wataru Ando, Julian Chojnowski and *Dick Jones*

Wataru Ando received his Ph.D. degree from Osaka City University in 1963. This was followed by post-doctoral research at the University of California, Los Angles with Professor C. S. Foote and then at Princeton with Professor Maitland Jones Jr. On his return to Japan in 1967 he was appointed an associate professor at Gunma University and in 1975 to a full professorship at the University of Tsukuba. He is now an Emeritus Professor of the University of Tsukuba and since 1998 a consultant of Dow Corning. He received the DAAD Fellowship in 1987, Alexander Humboldt-Forschungsceprise in 1992, the Chemical Society of Japan Award in 1994, the American Chemical Society Kipping Award in 1996, and a Purple Ribbon Medal in 1997. His research interests embrace high-energy molecules, and especially synthesis and reactive intermediates in carbon, organosilicon, organogermanium and heteroatom chemistry.

Julian Chojnowski graduated from Lodz Technical University, Poland, from where in 1963 he also received his Ph.D. degree after researching under the supervision of Professor Stanislaw Chrzczonowicz. His post-doctoral research was carried out at the University of Wisconsin-Milwaukee, USA, with Professor Werner W. Brandt. He achieved his habilitation in 1971. Since 1972 he has been a research group leader at the Centre of Molecular and Molecular Studies of the Polish Academy of Sciences at Łodz in Poland where he was nominated Professor in 1983. He has been a visiting professor at the Universities Montpellier II and Paris XIII in France, and consultant to Dow Corning. His research interests have focussed on reaction mechanisms in silicon chemistry and silicon polymer formation.

Dick Jones graduated from Victoria University of Wellington in New Zealand before studying for his Ph.D. degree under the direction of the late Professor Lord Dainton FRS at the University of Leeds in Britain. His first appointment, in 1966, was to a Lectureship in Applied Chemistry at the former Lanchester Polytechnic in Coventry. In 1970 he moved to a lectureship at the University of Kent at Canterbury where he is now

Professor of Polymer Science and presently the Head of the School of Physical Sciences. In 1980 he was a visiting professor at the University of Southern California. His research interests include mechanisms of polymerisation and the synthesis, modification and characterisation of polymers for application as microlithographic resists, and in recent years polysilanes have held a particular fascination.

ACKNOWLEDGEMENTS

Underpinning the culture of science is the notion of open collaboration in the pursuit of understanding, and it knows no national boundaries. This book is an excellent example of the fruit born from such collaboration. It could not have been brought to print without the patience and forbearance of the many contributors from different countries as my co-editors and I have painstakingly sought a balanced structure and as consistent a style as is possible. We sincerely thank them.

I should also like to thank my co-editors who, from the day in Montpellier in 1996 when we first agreed to pursue this task, have maintained close contact with me and sought to resolve the many problems that we have met along the way.

The full text was eventually assembled in Canterbury, UK, where the overall editing was carried out. I was ably assisted in this task by one of my research students, Alkay Mustafa, who I thank for undertaking a substantial amount of the standardisation of the layout in readiness for camera-ready formatting. I also thank my colleague, 'JJ' James, for his skill in drawing diagrams. It still took many weekends and a lot of the time that I would otherwise have shared with the people around me. It is impossible to measure the support that I got from the person closest to me and any expression of appreciation seems almost inadequate when compared to the sacrifice but my gratitude could not be tendered with more sincerity.

Dick Jones

Photograph of the Editors taken in May 1999 during the 12th International Symposium of Organosilicon Chemistry, Sendai, Japan (from left to right: Wataru Ando, Richard G. Jones, Julian Chojnowski).

TABLE OF CONTENTS

LIST OF CONTRIBUTORS xiii
PREFACE xvii
ACKNOWLEDGEMENTS xx

SECTION 1 : POLYSILOXANES
Editor: J. Chojnowski 1

1 - SYNTHESIS OF LINEAR POLYSILOXANES 3
J. Chojnowski and M. Cypryk
1. Introduction 3
2. The Siloxane Bond - Structural Considerations 3
3. Precursors of Polysiloxanes 4
4. Industrial Synthesis of Polysiloxanes from Chlorosilanes 5
5. Polysiloxanes by Polycondensation Routes 6
6. Ring-Opening Polymerisation of Cyclic Siloxanes 17

2 - ORGANOSILOXANE BLOCK AND GRAFT COPOLYMERS 43
G. Belorgey and G. Sauvet
1. Introduction 43
2. Synthesis of Siloxane-Organic Copolymers 43
3. Phase Separation 63
4. Mechanical Properties 68
5. Surface Properties 70
6. End-use Properties and Applications 72
7. Conclusion 74

3 - SIDE GROUP MODIFIED POLYSILOXANES 79
B. Boutevin, F. Guida-Pietrasanta and A. Ratsimihety
1. Introduction 79
2. Synthesis of Polysiloxanes Modified in Side Groups 80
3. Applications 105
4. Conclusion and Perspectives 107

4 - SILICONE COPOLYMER NETWORKS AND INTERPENETRATING POLYMER NETWORKS **113**
M. Mazurek
1. Introduction 113
2. Interpenetrating Polymer Networks and Copolymer Networks 115
3. Silicone Interpenetrating Polymer Networks 117
4. Silicone Copolymer Networks 126
5. Other Network Structures 131
6. Applications 131
7. Future Trends 133

5 - PREPARATION AND PROPERTIES OF SILICONE ELASTOMERS **139**
S. J. Clarson
1. Introduction 139
2. Preparation of Silicone Elastomers 140
3. Elasticity Theories 141
4. The Flory-Erman Model 142
5. Equilibrium Stress-Strain Behaviour of Silicone Elastomers 142
6. Stress-Strain Behaviour of Silicone Elastomers in the Swollen State 145
7. Equilibrium Swelling of Silicone Elastomers 146
8. Tear Strength of Silicone Elastomers 147
9. Adhesion of Silicone Elastomers to Substrates 149
10. Networks with Bimodal Distributions of Chain Lengths between Junctions 149
11. Stereoregular Siloxane Elastomers 151

6 - POLYSILSESQUIOXANES **157**
R. H. Baney and X. Cao
1. Introduction 157
2. General Considerations in the Preparation of Polysilsesquioxanes 159
3. Poly(phenylsilsesquioxane)s 160
4. Poly(methylsilsesquioxane)s 164
5. Other Polysilsequioxanes 166
6. Bridged Polysilsesquioxanes 166
7. Cage Silsesquioxanes 167
8 Structure of polysilsesquioxanes 175
9. Applications 178

7 - THERMAL PROPERTIES OF POLYSILOXANES **185**
P. R. Dvornic
1. Introduction 185
2. Structural Characteristics of Polysiloxanes that Determine their Thermal Behaviour 186
3. Thermal Properties of Polysiloxanes at Low Temperatures 194
4. High Temperature Degradation and Stability 200

8 - SURFACE PROPERTIES AND APPLICATIONS **213**
M. J. Owen
1. Introduction 213
2. Fundamental Physical Characteristics 215
3. PDMS Surface Data Survey 218
4. Fluorosilicones 221
5. Surface Applications 222
6. Future Applications 229

9 - POLYSILOXANES: DIRECTION OF APPLICATIONS AND PERSPECTIVES **233**
D. Graiver and G. Fearon

SECTION 2 : POLYCARBOSILANES AND POLYSILAZANES
Editor: R. G. Jones **245**

10 - POLYCARBOSILANES **247**
L. V. Interrante and **Q. Shen**
1. Introduction 247
2. Recent Advances in the Methodology for Preparing Carbosilanes 249
3. Polycarbosilanes as SiC Precursors 266
4. Linear Polycarbosilanes 274

11 - POLYSILAZANES **323**
A. Soum
1. Introduction 323
2. Polymerisation of Organosilazanes 325
3. Structure and Thermal Properties of Polysilazanes 342
4. Properties of Polysilazanes 345
5. Potential Applications of Polysilazanes 347

SECTION 3 : POLYSILANES AND RELATED POLYMERS 351
Editor: R. G. Jones

12 - SYNTHESIS OF POLYSILANES BY THE WURTZ REDUCTIVE-COUPLING REACTION 353
R. G. Jones and S. J. Holder
1. Introduction 353
2. Alkali Metals Dispersions and Addition Procedures 354
3. Solvents and Additives 357
4. Temperature Effects 358
5. Reagent Distribution 360
6. Mechanistic Considerations and a Unifying Model 361

13 - SYNTHESIS OF POLYSILANES BY NEW PROCEDURES: PART 1 RING-OPENING POLYMERISATIONS AND THE POLYMERISATION OF MASKED DISILENES 375
H. Sakurai and M. Yoshida
1. Introduction 375
2. Catalytic Disproportionation of Functionalised Disilanes 377
3. Ring-Opening Polymerisation of Small Rings 377
4. Anionic Polymerisation of Masked Disilenes 384

14 - SYNTHESIS OF POLYSILANES BY NEW PROCEDURES: PART 2 CATALYTIC DEHYDRO-POLYMERISATION OF HYDROSILANES 401
G. M. Gray and J. Y. Corey
1. Introduction 401
2. Catalytic Dehydrocoupling of Silanes 402
3. Mechanistic Studies 410
4. Properties and Reactions of Poly(hydrosilane)s 414
5. Conclusion 416

15 - MODIFICATION AND FUNCTIONALISATION OF POLYSILANES 419
M. J. Went, H. Sakurai and T. Sanji
1. Introduction 419
2. Incorporation of Organic Substituents 420
3. Incorporation of Metallic Functional Groups 427
4. Incorporation of Polymeric Substituents 429

16 - HYDROSILYLATION AND SILYLATION IN ORGANOSILICON POLYMER SYNTHESIS **439**
M. Tanaka and Y. Hatanaka
1. Introduction 439
2. Hydrosilylation in Organosilicon Polymer Synthesis 439
3. Synthesis of Polysilanes by Transiton-Metal-Catalysed Dehydrocoupling Reaction of Hydrosilanes 444
4. Electrochemical Routes to Organosilicon Polymers 449
5. Other Metal-Complex-Catalysed Synthesis of Organosilicon Polymers 454

17 - SIGMA- AND PI-CONJUGATED ORGANOSILICON POLYMERS **461**
S. Yamaguchi and K. Tamao
1. Introduction 461
2. Polymer Consisting of Oligosilylene Units and π-Electron Systems 461
3. π-Conjugated Polymers Based on Silicon-Containing Cycles 485
4. Silole-Based σ- and π-Conjugated Oligomers and Polymers 487
5. Conclusion 494

18 - ELECTRONIC STRUCTURE AND SPECTROSCOPY OF POLYSILANES **499**
J. Michl and R. West
1. Introduction 499
2. Oligomers 499
3. Polysilane High Polymers 509
4. A Note on the Photochemistry of Polysilanes 524

19 - ELECTRONIC AND OPTICAL PROPERTIES IN DEVICE APPLICATIONS OF POLYSILANES **531**
N. Matsumoto, H. Suzuki and H. Miyazaki
1. Introduction 531
2. Electronic Structures of Polysilanes 531
3. Electroluminescent Properties and an Application to Electroluminescent Devices 535
4. Photo-conductive Properties and Application to Photoreceptors 545
5. Conclusions 550

20 - THERMAL PROPERTIES AND PHASE BEHAVIOUR OF POLYSILANES **553**
S. Demoustier-Champagne and J. Devaux
1. Introduction 553
2. Thermal Characterisation of Poly(methyl-*n*-propylsilane) 555
3. Crystalline Structure of Poly(methyl-*n*-propylsilane) 557
4. Microstructural Characterisation of Poly(methyl-*n*-propylsilane) 559
5. WAXS Measured Crystallisation Kinetics of Poly(methyl-*n*-propylsilane) 560
6. Thermal Characterisation of Poly(methylphenylsilane 563
7. Structural analysis of Poly(methylphenylsilane) 566
8. Conclusions 571

SECTION 4 : SPECIAL TOPICS
Editor: W. Ando **575**

21 - SILICON-CONTAINING VINYL MONOMERS AND POLYMERS **577**
Y. Nagasaki
1. Introduction 577
2. Monomer Synthesis 577
3. Polymerisations 581

22 - LIQUID CRYSTALLINE SILICON-CONTAINING POLYMERS **593**
D. Teyssié and S. Boileau
1. Introduction 593
2. Synthesis 594
3. Poly(di-*n*-alkylsiloxane)s 597
4. Cyclic Siloxanes 599
5. Silsesquioxanes 600
6. Ferroelectric Liquid Crystalline Polysiloxanes 602
7. Elastomeric Networks 606
8. Characterisation 608
9. Conclusion 610