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Polymer Science and Technology Series

Siloxane Polymers

Stephen J. Clarson
J. Anthony Semlyen

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Stephen J. Clarson
University of Cincinnati

J. Anthony Semlyen
University of York

PTR PRENTICE HALL
Englewood Cliffs, New Jersey 07632

Library of Congress Cataloging-in-Publication Data
Clarson, Steven J.
Siloxane polymers / Steven J. Clarson, J. Anthony Semlyen.
p. cm.
Includes index.
ISBN 0-13-816315-4
1. Silicones. I. Semlyen, J. A. II. Title.
QD383.S54C53 1993 92-46170
688.4'227--dc20 CIP

British Library Cataloguing-in-Publication Data
Siloxane Polymers
S. J. Clarson and J. A. Semlyen
CIP catalogue record for this book is available from the British Library.
ISBN 0-13-816315-4

Acquisitions editor: Betty Sun
Supplements editor: Alicia Aurichio
Production: Fred Dahl
Buyer: Mary McCartney

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

ISBN 0-13-816315-4

Prentice-Hall International (UK) Limited, *London*
Prentice-Hall of Australia Pty. Limited, *Sydney*
Prentice-Hall Canada Inc., *Toronto*
Prentice-Hall Hispanoamericana, S.A., *Mexico*
Prentice-Hall of India Private Limited, *New Delhi*
Prentice-Hall of Japan, Inc., *Tokyo*
Prentice-Hall of Southeast Asia Pte. Ltd., *Singapore*
Editora Prentice-Hall do Brasil, Ltda., *Rio de Janeiro*

Siloxane Polymers

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Series Foreword

Polymer Science and Technology Series

J. E. MARK
University of Cincinnati, Series Editor

One of the most exciting areas in chemistry, chemical engineering, and materials science is the preparation, characterization, and utilization of polymers. The growing importance of polymers has been truly astounding, to the point that it is difficult to imagine our lives without them. They are under development in virtually every industrialized country in the world with activities accelerating rather than abating.

Not surprisingly, the amount of information relevant to polymer science and engineering is increasing correspondingly, making it more and more difficult to enter new fields in this area or even to remain abreast of developments in one's current field. There is thus a real need for authoritatively written, easily accessible books on polymer science and engineering, both for the relatively uninitiated and for the better-informed professional.

The present series of books was inaugurated to help meet this need. It will cover the organic chemistry of polymers, the relevant physical chemistry and chemical physics, polymer processing and other engineering aspects, and the applications of polymers as materials. The level will range from highly introductory treatments that are tutorial and therefore particularly

useful for self-study, to rather advanced treatments of more specialized subjects. Many of these books will be exceedingly useful as textbooks in formal courses at colleges and universities.

Considerable attention will be paid to polymers as "high-tech" materials. This is in response to the fact that the most exciting applications of polymers no longer involve huge tonnage amounts of materials. Rather, they involve situations in which polymers generally are not present in large amounts, but are absolutely critical for the functioning of the system. Examples are polymer matrices and encapsulants for the controlled release of drugs and agricultural chemicals, biopolymers and synthetic polymers for biomedical applications, conducting polymers for batteries and their electrical devices, polymers having non-linear optical properties for optoelectronic applications, high-temperature polymers for use in outer space and in other hostile environments, ultra-oriented polymers for high strength materials, new types of polymer-based composites, photosensitive polymers for microlithography, and inorganic and organometallic polymers for use as ceramic precursors. These are all rapidly developing fields, and there is particularly a great need for authoritative, comprehensive treatments of these subject areas.

It is hoped that this series of volumes will meet these needs, and be of lasting value to the polymer community.

Editors' Foreword

During our early discussions on the preparation of a book on siloxane polymers, or silicones, it became quickly apparent that a comprehensive review of the scientific and patent literature of these important materials would be a monumental task. The format that we therefore considered to be most appropriate was a collection of commissioned monographs covering the areas that we considered to be pertinent. The book then represents the combined efforts of our colleagues from various academic and industrial laboratories in both Europe and America. We would like to extend our sincere thanks to each of them for their dedication, perseverance and good humor throughout this endeavor. We would also like to thank Mr. Thomas C. Kendrick, of Dow Corning Ltd., for his help and advice during the planning of this volume. Finally, we are privileged to have a preface to this book contributed by Professor Eugene G. Rochow, a pioneering leader of the field of organosiloxane chemistry.

The 1980s saw something of a renaissance in the overall area of organosilicon chemistry—with significant developments in silicon-mediated reactions, polysilane chemistry and silicon-based ceramic precursors, to name a just few. We have also seen advances in instrumentation and

increasingly powerful computers, both of which have been widely applied to investigations of the properties of siloxane polymers. It was our decision to keep the focus of this volume on the chemistry and properties of materials where a silicon-oxygen backbone was of central importance. It is our hope, then, that both students and fellow scientists and engineers will find this to be a useful overview of a very important class of polymeric materials.

STEPHEN J. CLARSON
University of Cincinnati

J. ANTHONY SEMLYEN
University of York

Preface

E. G. ROCHOW

Fifty years ago a new material, methyl silicone, appeared on the scene. It did not *burst* upon the scene with a fanfare; in fact, it was scarcely noticed at all. People did not know what to make of it, either actually or figuratively. It had been created because a few people thought it might provide better electrical insulation at high temperatures than the natural products and the organic polymers then in use. It did.

Methyl silicone was so different in composition, in structure, and in physical and chemical properties that it was outside the ordinary day-to-day thinking of chemists and engineers fifty years ago. Organometallic chemistry had scarcely entered into their training, and, anyway, silicon was not considered a metal—it was a singularly unreactive metalloid not yet even recognized as a semiconductor. Hence a slow period of education and investigation began, with practically no aid from the textbooks of the day, or even from the chemical literature on organosilicon compounds. However, the properties of the first methyl silicone resins and oils (and soon elastomers too) were so different from those of the established materials that the silicone polymers were bound to find a place just because they could do some things the ordinary polymers could not do. For this simple reason

methyl silicone and the related siloxane polymers gradually found uses. Eventually they became accepted as new and valuable engineering materials. In fact, they became essential to many new products and processes developed around them.

Today the world production of silicone materials (almost entirely methyl silicone) is about 475,000 metric tons, worth about $3,500,000,000. Silicone rubber, in its several forms, represents about half of this dollar value; silicone fluids represent about 40%, and silicone resins the rest. This is indeed a remarkable growth, having started at zero in 1940! All this material is consumed in thousands of ways, chiefly in the electrical, textile, plastics, rubber, paper, paint, automobile, and construction industries, with minor amounts going into food and medical products and into office machines. I think no one today goes through a day without touching or using some product that contains (or once contained) methyl silicone.

All this growth means that the siloxane polymers are now a big business, and a sharply competitive business. From the very beginning, research and development have played a very important part, and the result has been an enormous scientific and technical literature in the open journals. I remember when articles dealing with organometallic chemistry were scattered all throughout the sections on organic, inorganic, and physical chemistry in *Chemical Abstracts,* their number being far too few to justify a separate heading. Now the field of siloxane polymers is so active as to require a full-time perusal of the journals and patents every day just to keep up! And that is where this book comes in: It summarizes a tremendous amount of information on siloxane polymers, all neatly presented by sixteen experts from the many university and commercial laboratories active in such research in Europe and the United States. All this has great value to the reader in time saved and improved understanding.

It is not my place to assess the various contributions, or to attempt a summary of their contents. I wish only to express my heartfelt thanks to the editors and authors of this volume for furnishing so much interesting and useful information within a compact space, and for making it pleasant to read. They have made life simpler and more enjoyable.

EUGENE G. ROCHOW
Prof. Emeritus
Harvard University

List of Contributors

Dr. Martin Beevers is a lecturer in Chemical Engineering and Applied Chemistry at the University of Aston in Birmingham, UK. His research interests include dielectric and electro-optic relaxation in polymers and liquid-crystal materials.

Julian Chojnowski is leader of a research group and professor in the Centre of Molecular and Macromolecular Studies of the Polish Academy of Sciences. He graduated from the Department of Chemistry of Politechnika Lodzka in 1957, where he received his Ph.D. in 1963 and habilitation in 1971.

Stephen J. Clarson is a Yorkshireman by birth but now resides in the Cincinnati area with his wife and their four Himalayan Persians. He obtained his D.Phil. in Chemistry from the University of York in 1985, where he studied with Dr. Tony Semlyen. He then spent the summer at the Institute of Macromolecular Chemistry, Prague before taking up a post-doctoral appointment with Dr. James E. Mark in Cincinnati. In the spring of 1988 he joined the faculty of the Department of Materials Science and Engineering at the University of Cincinnati. He is a member of the American Chemical Society, member of the Royal Society of Chemistry and

Chartered Chemist and is on the editorial board of *Trends in Polymer Science*. His current research interests include polymer synthesis, organosilicon chemistry, the physical properties of siloxane based polymers and plasma polymerization.

Jean Pierre Cohen-Addad is a native of France and holds a faculty position at the University of Grenoble, Laboratoire de Spetrometrie Physique (CNRS). He received his D.Sc. (1966) in Physics from the University of Grenoble. From 1966–67 he was at the Laboratory of Solid State Physics, Orsay and from 1967–69 was at Bell Laboratories, Murray Hill. He is a member of the European Physical Society and of the American Physical Society. His research interests include NMR in polymer gels, molten polymers and filled polymers.

H. L. Frisch obtained an A.B. from Williams College and a Ph.D. from the Polytechnic Institute of Brooklyn. For eleven years he was a member of the technical staff at Bell Telephone Laboratories at Murray Hill, New Jersey. He has been a Professor of Chemistry at the State University of New York at Albany since 1967, where he was also the Dean of Mathematics. Since 1978 he has been named a distinguished Professor of Chemistry. He is a member of the editorial board of the *Journal of Polymer Science* (*Polymer Physics*). His polymer research interests include the synthesis and characterization of macromolecular topological isomers, template copolymerization and transport in polymers.

Misty W. Huang received her B.S. in Chemical Engineering from Dalian Institute of Light Industry in 1982. She obtained a Ph.D. degree in Physical/Polymer Chemistry with Professor H. L. Frisch at the State University of New York at Albany in 1989. She then spent three years as a research associate at the Polytechnic University, Brooklyn, New York, before joining the Chemistry Department at Millersville University, Pennsylvania, in August, 1992. Her research interests include miscibility of polymer blends, modification of engineering plastics and polymer materials for biomedical applications.

Dr. John J. Kennan received his Ph.D. in Chemistry from The Pennsylvania State University in 1984. He has been with Dow Corning since 1984 and is currently a Research Specialist in their Central Research Department, Midland, Michigan. His research interests have included Direct Process chemistry for the manufacture of chlorosilanes, siloxane polymerization, polymer characterization and the preparation and properties of silicone elastomers.

James E. Mark received his Ph.D. in Physical Chemistry from the University of Pennsylania in 1962. From 1962 to 1964 he was a Postdoctoral Fellow with Professor Paul J. Flory at Stanford University. Prior to joining the faculty of the Chemistry Department at the University of Cincinnati, he held faculty positions at the Polytechnic Institute of Brooklyn (1964–67) and the University of Michigan (1967–1977). Dr. Mark has lectured extensively

in polymer chemistry, has published approximately 350 papers and is a Fellow of the New York Academy of Sciences, the American Physical Society and the American Association for the Advancement of Science. His research interests pertain to the physical chemistry of polymers, conformational properties of polymer chains and the elasticity of polymer networks. He is currently Distinguished Research Professor of Chemistry at the University of Cincinnati and is Editor of *Computational Polymer Science.*

Mike Owen is a native of Wales. He received his B.Sc. (1962), Ph.D. (1965) and D.Sc. (1991) from the University of Bristol in England. He is a Fellow of the Royal Society of Chemistry and Chartered Chemist. He joined Dow Corning Corporation in the UK and transferred to the USA in 1975. He has worked on a variety of aspects of surface science and published over fifty articles and ten patents in this field. He is currently a Research Scientist in the Dow Corning Central Science and Technology Department, Midland, USA and is head of the Analytical Research Surface Characterization Group.

R. A. Pethrick has a Chair in the Physical Chemistry Section of the Department of Pure & Applied Chemistry at the University of Strathclyde. His research activities over the last 20 years have involved investigations of various aspects of molecular motion in small and high polymeric materials using the techniques of ultrasonics, viscoelastics, and dielectrics. His current interests are in the investigation of the kinetics of cure in thermoset polymers and the characterization of glass phenomena in polymeric solids and viscoelastic fluids.

J. Anthony Semlyen obtained his M.A., B.Sc. and D.Ph. degrees at the University of Oxford from 1958 to 1964. He carried out research with Professor Paul Flory at Stanford University as a Fulbright Scholar between 1964 and 1966. Since 1967 he has been at the University of York. His research interest is polymers with particular reference to cyclic polymers.

R. F. T. Stepto is Professor of Polymer Science at the University of Manchester Institute of Science and Technology. He has published widely in the fields of polymerization statistics, polymer networks, and the conformation behavior of polymer chains.

Dr. D. R. (Dave) Thomas is a Development Scientist with Dow Corning, with thirty years experience in the silicone industry. During this period he has worked in the areas of siloxane polymerization, cross-linking, and catalysis.

Richard C. Treadgold was born in Wales and educated at University College, Swansea. He obtained a first class honors degree in Chemistry and a Ph.D. in peptide chemistry. Winner of the E. E. Ayling prize in 1977. Having joined Dow Corning Ltd., Barry in 1980 and initially in Technical Service and Development, his current position is as European Graduate Recruitment Programme Manager.

James W. White, born in Cornwall, was educated at Launceston College and graduated in 1976 from the University of Bath with Honours (class 1) in Chemistry and continued for a Ph.D. in Organometallic Chemistry (1979). He did postdoctoral research in metal cluster chemistry with Dr. M. Mingos at Oxford University before joining Dow Corning Limited, Barry in 1980. He has held several Research and Development, Technical Service and Management positions in the Science and Technology function at Dow Corning and is currently Manager of a Global Commercialization Program within the Sealants Business located in Midland, Michigan, USA.

Dr. Michael White, after studying for his B.Sc. and D.Phil. at the University of York, did four years postdoctoral research on side chain liquid crystal polymers with Professor G. W. Gray and Dr. D. Lacey at Hull University. Following this, he joined Unilever Research in 1988. He is a member of the editorial board of *Trends in Polymer Science.*

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