HANDBOOK OF THERMAL ANALYSIS AND CALORIMETRY

SERIES EDITOR: PATRICK K. GALLAGHER

VOLUME 3

APPLICATIONS TO POLYMERS AND PLASTICS

EDITOR

STEPHEN Z.D. CHENG

ELSEVIER

HANDBOOK OF THERMAL ANALYSIS AND CALORIMETRY

VOLUME 3

APPLICATIONS TO POLYMERS AND PLASTICS

EDITED BY

STEPHEN Z.D. CHENG

DEPARTMENT OF POLYMER SCIENCE
UNIVERSITY OF AKRON
AKRON, OH 44325-3909
USA

2002

ELSEVIER

AMSTERDAM – BOSTON – LONDON – NEW YORK – OXFORD – PARIS
SAN DIEGO – SAN FRANCISCO – SINGAPORE – SYDNEY – TOKYO

ELSEVIER SCIENCE B.V.
Sara Burgerhartstraat 25
P.O. Box 211, 1000 AE Amsterdam, The Netherlands

First edition 2002

Library of Congress Cataloging in Publication Data
A catalog record from the Library of Congress has been applied for.

British Library Cataloguing in Publication Data
A catalogue record from the British Library has been applied for.

ISBN: 0-444-51286-1

⊗ The paper used in this publication meets the requirements of ANSI/NISO Z39.48-1992 (Permanence of Paper).
Printed in The Netherlands.

HANDBOOK OF THERMAL ANALYSIS AND CALORIMETRY

SERIES EDITOR

PATRICK K. GALLAGHER

DEPARTMENT OF CHEMISTRY
OHIO STATE UNVERSITY
USA

ELSEVIER

AMSTERDAM – BOSTON – LONDON – NEW YORK – OXFORD – PARIS
SAN DIEGO – SAN FRANCISCO – SINGAPORE – SYDNEY – TOKYO

FOREWORD

The applications and interest in thermal analysis and calorimetry have grown enormously during the last half of the 20th century and the beginning of the 21st. The renaissance in these methods has been fuelled by several influences. Certainly the revolution in instrumentation brought on by the computer and automation has been a key factor. Our imagination and outlooks have also expanded to recognize the tremendous versatility of these techniques. They have long been used to characterize materials, decompositions and transitions. We now appreciate the fact that these techniques have greatly expanded their utility to studying many processes such as catalysis, hazards evaluation, etc. or to measuring important physical properties quickly, conveniently, and with markedly improved accuracy over that in the past.

Consequently, thermal analysis and calorimetry have grown in stature and more scientist and engineers have become, at least part time, practitioners. It is very desirable that these people new to the field can have a source of information describing the basic principles and current state of the art. Examples of the current applications of these methods are also essential to spur recognition of the potential for further uses. The application of these methods is highly interdisciplinary and any adequate description must encompass a range of topics well beyond the interests and capabilities of any single investigator. To this end, we have produced a convenient four-volume compendium of such information (a handbook) prepared by recognized experts.

Volume 1 describes the basic background information common to the broad subject in general. Thermodynamic and kinetic principles are discussed along with the instrumentation and methodology associated with thermoanalytical and calorimetric techniques. The purpose is to collect the discussion of these general principles and minimize redundancies in the subsequent volumes that are concerned with the applications of these principles and methods. More unique methods which pertain to specific processes or materials are covered in later volumes.

The three subsequent volumes primarily describe applications and are divided on the basis of general categories of materials. Volume 2 concerns the wide range of inorganic materials, e.g., chemicals, metals, etc. It covers the synthesis, characterization, and reactivity of such materials. Similarly, Volume 3 pertains to polymers and describes applications to these materials in an appropriate manner. Lastly the many important biological applications are described in Volume 4.

Each of these 4 Volumes has an Editor, who has been active in the field for many years and is an established expert in the material covered by that specific volume. This team of Editors has chosen authors with great care in an effort to produce a readable, informative handbook on this broad topic. The chapters are not intended to be a comprehensive review of the specific subject. The intent is that they enable the reader to glean the essence of the subject and form the basis for further critical reading or actual involvement in the topic. Our goal is to spur your imagination to recognize the potential application of these methods to your specific goals and efforts. In addition, we hope to anticipate and answer your questions, to guide you in the selection of appropriate techniques, and to help you to apply them in a proper and meaningful manner.

P.K. GALLAGHER
Series Editor

PREFACE TO VOLUME 3

This volume focuses on the principles and techniques of thermal analysis and calorimetry of polymeric materials. Although there are several excellent reference books that I have cited, I find myself constantly checking each of them on my bookshelf. It is my intention that this volume will provide a unique addition to the literature in combining scientific concepts with technological aspects for a deeper understanding of their principles and practices.

Polymeric materials are the newest addition to the materials community. A very exciting new field of interdisciplinary macromolecular science and engineering is rapidly emerging: a field where materials science/polymer science, engineering disciplines, chemistry, physics and biology all intersect. This field will have a profound presence in 21^{st} century chemical, pharmaceutical, biomedical, manufacturing, infrastructure, electronic, optical and information technologies. The origin of this field derives from an area of polymer science and engineering encompassing plastic technologies. This field is rapidly expanding to new interdisciplinary research areas such as biomaterials, macromolecular biology, novel macromolecular structures, environmental macromolecular science and engineering, innovative and nano-fabrications of products, and it is translating discoveries into technologies.

This volume comprises sixteen chapters that cover principles of materials' thermodynamic and thermal behaviors such as heat capacity of polymer solids and liquids, relaxation processes, molecular dynamics, polymer crystallization and melting, liquid crystalline polymers, copolymer and polymer blends, polymer films, fibers, thermosets, elastomers, composites and polymer degradation. Various methodologies of thermal analysis and calorimetry appear in all of these chapters. In particular, the stimulating current method and modulated differential scanning calorimetry, which are the most practical and actively discussed topics, are introduced.

The contributors to this volume include three generations of scientists: some of the most well-known pioneering scientists in their own polymer research areas; currently active researchers in different topics of thermal analysis and calorimetry; some of a new generation of scientists who will make substantial progress in the future. These invited contributors reflect my most sincere hope and firm confidence for the future of this research area.

I am extremely grateful to my major Professor, Dr. Bernhard Wunderlich, for his mentorship and guidance. This volume I dedicate to him with my thanks and best wishes to him and his family. I would like to thank my wife, Susan, and my daughter, Wendy. Without their complete selfless support, care, and love, I would not be where I am today. My thanks also go to Dr. Edith Turi for her continuous encouragement and to my students for their valuable help in putting these chapters into the right computer format. Finally, I would like to acknowledge the various support I have received from the College of Polymer Science and Polymer Engineering at the University of Akron and the Division of Materials Research, and the National Science Foundation (DMR-9617030 and 0203994).

STEPHEN Z. D. CHENG
Volume Editor

Robert C. Musson & Trustees Professor
Chairman, Department of Polymer Science,
The University of Akron

CONTRIBUTORS

Altman, Mark B.	Goodyear Tire & Rubber Company, 142 Goodyear Blvd., Akron, OH 44305, USA
Avakian, Peter	E.I. du Pont de Nemours and Company, Central Research and Development, Experimental Station, P.O. Box 80356, Wilmington, DE 19880-0356, USA
Burlett, Donald J.	Goodyear Tire & Rubber Company, 142 Goodyear Blvd., Akron, OH 44305, USA
Cheng, Stephen Z. D.	Maurice Morton Institute and Department of Polymer Science, The University of Akron, Akron, OH 44325-3909, USA
Flynn, Joseph H.	Scientific Thermal Research & Data Analysis (STRDA), 5309 Iroquois Rd., Bathesda, MD 20816, USA
Hale, Arturo	AT&T Bell Laboratories, Room #7E-217, 600 Mountain Ave., Murray Hill, NJ 07974, USA
Huang, Jiang	Polymer Science Program, Department of Materials Science and Engineering, The Pennsylvania State University, 320 Steidle Building, University Park, PA 16802-5007, USA
Jin, Shi	Maurice Morton Institute and Department of Polymer Science, The University of Akron, Akron, OH 44325-3909, USA
Jing, Alexander J.	Maurice Morton Institute and Department of Polymer Science, The University of Akron, Akron, OH 44325-3909, USA
Kampert, William G.	E.I. du Pont de Nemours and Company, Central Research and Development, Experimental Station, P.O. Box 80356, Wilmington, DE 19880-0356, USA

Li, Christopher Y.	Department of Materials Engineering, Drexel University Philadelphia, PA 19104, USA
Lincoln, Jason E.	Polymer Matrix Composites Research Team, Materials and Manufacturing Directorate, Air Force Research Laboratory/MLBC, 2941 P Street, Room 136, Wright-Patterson Air Force Base, OH 45433, USA
Mathot, Vincent B. F.	DSM Research, P.O. Box 18, 6160 MD Geleen, The Netherlands
Matsuoka, Shiro	Polymer Research Institute, Polytechnic University, Six Metrotech Center, Brooklyn, NY 11201, USA
McKenna, Gregory B.	Department of Chemical Engineering, Texas Technology University, Lubbock, Texas 79409-3121, USA
Morgan, Roger J.	Department of Mechanical Engineering, Texas A&M University, College Station, Texas 77843-3123, USA
Reynaers, Harry	Katholieke Universiteit Leuven, Celestijnenlaan 200F, B-3001 Leuven-Heverlee, Belgium
Runt, James P.	Polymer Science Program, Department of Materials Science and Engineering, The Pennsylvania State University, 320 Steidle Building, University Park, PA 16802-5007, USA
Sauer, Bryan B.	E.I. du Pont de Nemours and Company, Central Research and Development, Experimental Station, Wilmington, DE 19880-0356, USA
Schick, Christoph E. G.	Department of Physics, University of Rostock, Universitätsplatz 3, 18051 Rostock, Germany
Shin, E. Eugene	NASA Glenn Research Center at Lewis Field, Mail Stop 49-1 21000 Brookpark Rd., Cleveland, OH 44135, USA

Simon, Sindee L. Department of Chemical Engineering, Texas Technology University, Lubbock, Texas 79409-3121, USA

Starkweather, Howard W. Jr. E.I. du Pont de Nemours and Company, Central Research and Development, Experimental Station, P.O. Box 80356, Wilmington, DE 19880-0356, USA

Wu, Zongquan Maurice Morton Institute of Polymer Science, The University of Akron, Akron, OH 44325-3909, USA

Wunderlich, Bernhard Department of Chemistry, University of Tennessee, Knoville, TN 37996-1600, USA

Zhu, Lei Institute of Materials Science and Department of Chemical Engineering, University of Connecticut, Storrs, CT 06269-3222, USA

Zhang, Anqiu Maurice Morton Institute of Polymer Science, The University of Akron, Akron, Ohio 44325-3909, USA

CONTENTS

CHAPTER 2. THE GLASS TRANSITION: ITS MEASUREMENT AND UNDERLYING PHYSICS
(Gregory B. McKenna and Sindee L. Simon)

CHAPTER 4. DIELECTRIC ANALYSIS OF POLYMERS
(Peter Avakian, Howard W. Starkweather, Jr. and William G. Kampert)

CHAPTER 5. CRYSTALLIZATION AND MELTING OF METASTABLE CRYSTALLINE POLYMERS
(Stephen Z. D. Cheng and Shi Jin)

CHAPTER 6. CRYSTALLIZATION, MELTING AND MORPHOLOGY OF HOMOGENEOUS ETHYLENE COPOLYMERS
(Vincent B. F. Mathot and Harry Reynaers)