
HANDBOOK OF THERMAL ANALYSIS AND CALORIMETRY

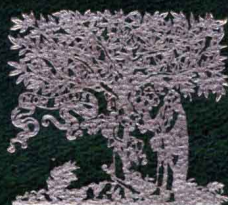
SERIES EDITOR: PATRICK K. GALLAGHER

VOLUME 3

**APPLICATIONS
TO POLYMERS AND PLASTICS**

EDITOR

STEPHEN Z.D. CHENG



ELSEVIER

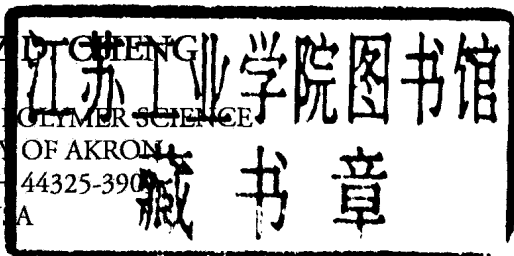
HANDBOOK OF THERMAL ANALYSIS AND CALORIMETRY

VOLUME 3
APPLICATIONS TO POLYMERS AND PLASTICS

EDITED BY

STEPHEN Z. D'GONG

DEPARTMENT OF POLYMER SCIENCE
UNIVERSITY OF AKRON
AKRON, OH 44325-3901
U.S.A.



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

© 2002 Elsevier Science B.V. All rights reserved.

This work is protected under copyright by Elsevier Science, and the following terms and conditions apply to its use:

Photocopying

Single photocopies of single chapters may be made for personal use as allowed by national copyright laws. Permission of the Publisher and payment of a fee is required for all other photocopying, including multiple or systematic copying, copying for advertising or promotional purposes, resale, and all forms of document delivery. Special rates are available for educational institutions that wish to make photocopies for non-profit educational classroom use.

Permissions may be sought directly from Elsevier Science via their homepage (<http://www.elsevier.com>) by selecting 'Customer support' and then 'Permissions'. Alternatively you can send an e-mail to: permissions@elsevier.co.uk, or fax to: (+44) 1865 853333.

In the USA, users may clear permissions and make payments through the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, USA; phone: (+1) 978 7508400, fax: (+1) 978 7504744, and in the UK through the Copyright Licensing Agency Rapid Clearance Service (CLARCS), 90 Tottenham Court Road, London W1P 0LP, UK; phone: (+44) 207 631 5555, fax: (+44) 207 631 5500. Other countries may have a local reprographic rights agency for payments.

Derivative Works

Tables of contents may be reproduced for internal circulation, but permission of Elsevier Science is required for resale or distribution of such material.

Permission of the Publisher is required for all other derivative works, including compilations and translations.

Electronic Storage or Usage

Permission of the Publisher is required to store or use electronically any material contained in this work, including any chapter or part of a chapter.

Except as outlined above, no part of this work may be reproduced, stored in a retrieval system or transmitted in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, without prior written permission of the Publisher.

Address permissions requests to: Elsevier Science Global Rights Department, at the fax and e-mail addresses noted above.

Notice

No responsibility is assumed by the Publisher for any injury and/or damage to persons or property as a matter of products liability, negligence or otherwise, or from any use or operation of any methods, products, instructions or ideas contained in the material herein. Because of rapid advances in the medical sciences, in particular, independent verification of diagnoses and drugs dosages should be made.

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 UNIVERSITY
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 21st 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,
Knoxville, 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

Foreword - P.K. Gallagher.....	v
Preface - S.Z.D. Cheng.....	vii
Contributors	xxvii

CHAPTER 1. HEAT CAPACITY OF POLYMERS

(B. Wunderlich)

1. MEASUREMENT OF HEAT CAPACITY.....	1
2. THERMODYNAMIC THEORY.....	5
3. QUANTUM MECHANICAL DESCRIPTION.....	5
4. THE HEAT CAPACITY OF SOLIDS.....	10
5. COMPLEX HEAT CAPACITY.....	14
6. THE ADVANCED THERMAL ANALYSIS SYSTEM, ATHAS	16
6.1. The crystallinity dependence of heat capacity.....	16
6.2. Heat capacities of solids	18
6.3. Polyoxide heat capacities	25
6.4. Heat capacities of liquids	27
7. EXAMPLES OF THE APPLICATION OF ATHAS.....	28
7.1. Poly(tetrafluoroethylene)	28
7.2. Poly(oxybenzoate- <i>co</i> -oxynaphthoate)	29
7.3. Large-amplitude motion of polyethylene	30
7.4. Polymethionine	31
7.5. MBPE-9	31
7.6. Liquid selenium	32
7.7. Poly(styrene- <i>co</i> -butadiene)	33
8. TEMPERATURE-MODULATED CALORIMETRY.....	34
8.1. Heat capacity and glass transition	36
8.2. First-order transitions and chemical reactions	40
9. CONCLUDING REMARKS.....	45
ACKNOWLEDGMENTS	46
REFERENCES.....	46

CHAPTER 2. THE GLASS TRANSITION: ITS MEASUREMENT AND UNDERLYING PHYSICS

(Gregory B. McKenna and Sindee L. Simon)

1. INTRODUCTION	49
2. THE APPARENT THERMODYNAMIC BEHAVIOR.....	50
2.1. Some thermodynamic definitions	50
2.2. Time or rate effects	52
2.3. Path dependence of the PVT surface	54
2.4. Isobaric (constant pressure) glass formation vs isochoric (constant volume) glass formation	55
3. KINETICS OF GLASS FORMATION.....	58
3.1. Preliminary comments	58
3.2. Phenomenology of structural recovery	59
3.2.1. The asymmetry of approach experiment	60
3.2.2. The memory or cross-over experiment	61
3.3. The Tool-Narayanaswamy-Moynihan-Kovacs-Aklonis-Hutchinson Ramos (TNM-KAHR) description of structural recovery	62
3.3.1. Strengths and weaknesses of the models	65
3.4. The thermoviscoelastic model	67
3.4.1. Model predictions for volume recovery: comparison with Kovacs' data.....	70
3.4.2. Strengths and weaknesses of the thermoviscoelastic model	72
3.5. Viscosity and segmental relaxation behavior above the glass transition temperature.....	73
4. MICROSCOPIC THEORIES RELATED TO THE GLASS TRANSITION.....	76
4.1. General comments	76
4.2. Free volume models	76
4.3. The Gibbs-DiMarzio configurational entropy model	78
4.4. Comparison of the free volume and configurational entropy models with experiments.....	81
5. MEASUREMENT OF T_g	81
5.1. General comments	81
5.2. Dilatometric methods	82
5.2.1. Fluid confinement dilatometry	82
5.2.2. Length change dilatometry.....	84
5.3. Calorimetric techniques	85

5.3.1. Differential scanning calorimetry (DSC)	86
5.3.2. Temperature-modulated differential scanning calorimetry (TMDSC).....	92
5.3.3. Dynamic heat spectroscopy (DHS)	94
6. PHYSICAL AGING EFFECTS	95
6.1. Linear viscoelastic regime	96
6.2. Nonlinear viscoelastic regime	99
6.3. Engineering properties	100
6.3.1. Yield strength	101
6.3.2. Failure related properties	101
6.3.3. Residual stresses	103
7. CONCLUDING REMARKS	104
ACKNOWLEDGMENTS	104
REFERENCES	104
CHAPTER 3. MECHANICAL RELAXATION PROCESSES IN POLYMERS (S. Matsuoka)	
1. WHAT DO WE MEAN BY THE RELAXATION PROCESS	111
1.1. On the experimental scale	111
1.2. On the molecular scale	116
2. INTERMOLECULAR COOPERATIVITY.....	119
2.1. Free volume and excess enthalpy in the condensed state	121
2.2. Excess enthalpy that drops faster than the conformational entropy	123
3. CHEMICAL STRUCTURE AND T_g	124
4. VISCOELASTICITY DATA ANALYSIS	127
4.1. Viscoelasticity data analysis near but above T_g	127
4.2. Viscoelasticity data analysis of polymer melt	131
4.2.1. Polymers in solution	131
4.2.2. Polymers in bulks	137
5. BEYOND LINEAR VISCOELASTICITY	143
REFERENCES	145

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

1. INTRODUCTION 147

2. POLAR AMORPHOUS POLYMERS 150

2.1. Polymethyl methacrylate (PMMA) 150

2.2. Polycarbonate 152

2.3. Polyamides 154

3. NONPOLAR POLYMERS 157

3.1. Hydrocarbon polymers 157

3.2. Fluoropolymers 158

4. MISCIBILITY OF POLYMER BLENDS 159

5. COLD CRYSTALLIZATION OF AMORPHOUS POLYMERS
ABOVE T_g 161

6. FREQUENCY-TEMPERATURE RELATIONSHIPS 163

ACKNOWLEDGMENTS 164

REFERENCES 164

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

1. INTRODUCTION 167

2. THERMODYNAMIC DEFINITIONS OF THE PHASE AND PHASE
TRANSITIONS 167

2.1. Description of phases 167

2.2. Definitions of phase transitions 169

2.3. Phase equilibrium and stability 172

2.4. Concepts of classical metastable states 173

2.5. Metastable states in polymers 174

3. POLYMER CRYSTALLIZATION AND MORPHOLOGY 175

3.1. Isothermal crystallization 176

3.2. Overall crystallization rates 178

3.3. Linear crystal growth rates 180

3.4. Non-isothermal crystallization	181
3.5. Crystalline morphology	182
4. POLYMER CRYSTAL MELTING	183
4.1. Extrapolations to obtain equilibrium melting properties	184
4.2. Metastability changes in polymer crystal melting	187
4.3. Interfaces between crystalline and amorphous regions	189
5. CONCLUDING REMARKS	191
ACKNOWLEDGMENTS	192
REFERENCES	192
CHAPTER 6. CRYSTALLIZATION, MELTING AND MORPHOLOGY OF HOMOGENEOUS ETHYLENE COPOLYMERS (Vincent B. F. Mathot and Harry Reynaers)	
1. INTRODUCTION	197
2. ETHYLENE-PROPYLENE COPOLYMERS	200
2.1. Influence of comonomer content on crystallization and melting	200
2.2. Heat capacity, enthalpy, crystallinity, baseline and excess heat capacity	204
2.3. Illustrating the use of the 'extrapolation method' for calculating crystallinities as applied to 'pseudo heat capacity' measurements on characteristic samples.....	212
2.4. Remarks on the use of the extrapolation method for crystallinity determination	212
2.5. Morphology	213
3. ETHYLENE-1-BUTENE COPOLYMERS	219
3.1. Influence of comonomer content	219
3.2. Metastability: influence of cooling rate	221
3.3. Morphology	222
3.3.1. Metastability: measurements as in temperature modulated calorimetry	224
4. ETHYLENE-1-OCTENE COPOLYMERS	225
4.1. Influence of comonomer content for copolymers with densities above about 870 kg/m ³	225
4.2. Copolymers having a density of about 870 kg/m ³	228
4.2.1. Micro chain structure	228

4.2.2. Crystallization and melting	229
4.2.3. Morphology	233
4.3. Characteristic copolymers with densities below about 870 kg/m ³	236
5. OVERVIEW	239
ACKNOWLEDGMENTS	240
REFERENCES	240
CHAPTER 7. RECENT ADVANCES IN THERMAL ANALYSIS OF THERMOTROPIC MAIN-CHAIN LIQUID CRYSTALLINE POLYMERS (Christopher Y. Li)	
1. INTRODUCTION	245
2. LIQUID CRYSTALS AND LIQUID CRYSTALLINE POLYMERS .	247
3. THERMODYNAMIC TRANSITION BEHAVIORS	253
4. ENANTIOTROPIC AND MONOTROPIC BEHAVIORS	259
5. EFFECTS OF MESOGENIC GROUPS AND SPACERS ON THE LIQUID CRYSTALLINE ORDERS AND STABILITY	263
6. CONCLUDING REMARKS	268
REFERENCES	268
CHAPTER 8. POLYMER BLENDS AND COPOLYMERS (James Runt and Jiang Huang)	
1. INTRODUCTION	273
2. BACKGROUND	273
2.1. Copolymers	273
2.2. Polymer blends	274
3. POLYMER BLENDS	274
3.1. Phase behavior – transitional analysis	274
3.1.1. Background	274