POLYMER MODIFICATION

Principles, Techniques, and Applications

Acid Hydrolysis of Cellulose

edited by **JOHN J. MEISTER**

POLYMER Modification

Principles, Techniques, and Applications

edited by

JOHN J. MEISTER

Center for Forest Products Research, a Albuquerque, New Mexico





ISBN: 0-8247-0078-3

This book is printed on acid-free paper.

Headquarters

Marcel Dekker, Inc.

270 Madison Avenue, New York, NY 10016

tel: 212-696-9000; fax: 212-685-4540

Eastern Hemisphere Distribution

Marcel Dekker AG

Hutgasse 4, Postfach 812, CH-4001 Basel, Switzerland

tel: 41-61-261-8482; fax: 41-61-261-8896

World Wide Web

http://www.dekker.com

The publisher offers discounts on this book when ordered in bulk quantities. For more information, write to Special Sales/Professional Marketing at the headquarters address above.

Copyright © 2000 by Marcel Dekker, Inc. All Rights Reserved.

Neither this book nor any part may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, microfilming, and recording, or by any information storage and retrieval system, without permission in writing from the publisher.

Current printing (last digit): 10 9 8 7 6 5 4 3 2 1

PRINTED IN THE UNITED STATES OF AMERICA

POLYMER MODIFICATION

PLASTICS ENGINEERING

Founding Editor

Donald E. Hudgin

Professor Clemson University Clemson, South Carolina

- 1. Plastics Waste: Recovery of Economic Value, Jacob Leidner
- 2. Polyester Molding Compounds, Robert Burns
- 3. Carbon Black-Polymer Composites: The Physics of Electrically Conducting Composites, edited by Enid Keil Sichel
- 4. The Strength and Stiffness of Polymers, edited by Anagnostis E. Zachariades and Roger S. Porter
- Selecting Thermoplastics for Engineering Applications, Charles P. Mac-Dermott
- Engineering with Rigid PVC: Processability and Applications, edited by I. Luis Gomez
- 7. Computer-Aided Design of Polymers and Composites, D. H. Kaelble
- 8. Engineering Thermoplastics: Properties and Applications, edited by James M. Margolis
- 9. Structural Foam: A Purchasing and Design Guide, Bruce C. Wendle
- Plastics in Architecture: A Guide to Acrylic and Polycarbonate, Ralph Montella
- 11. Metal-Filled Polymers: Properties and Applications, edited by Swapan K. Bhattacharva
- 12. Plastics Technology Handbook, Manas Chanda and Salil K. Roy
- 13. Reaction Injection Molding Machinery and Processes, F. Melvin Sweeney
- 14. Practical Thermoforming: Principles and Applications, John Florian
- 15. Injection and Compression Molding Fundamentals, edited by Avraam I. Isayev
- 16. Polymer Mixing and Extrusion Technology, Nicholas P. Cheremisinoff
- 17. High Modulus Polymers: Approaches to Design and Development, edited by Anagnostis E. Zachariades and Roger S. Porter
- Corrosion-Resistant Plastic Composites in Chemical Plant Design, John H. Mallinson
- 19. Handbook of Elastomers: New Developments and Technology, edited by Anil K. Bhowmick and Howard L. Stephens
- Rubber Compounding: Principles, Materials, and Techniques, Fred W. Barlow

- Thermoplastic Polymer Additives: Theory and Practice, edited by John T. Lutz, Jr.
- 22. Emulsion Polymer Technology, Robert D. Athey, Jr.
- 23. Mixing in Polymer Processing, edited by Chris Rauwendaal
- 24. Handbook of Polymer Synthesis, Parts A and B, edited by Hans R. Kricheldorf
- 25. Computational Modeling of Polymers, edited by Jozef Bicerano
- Plastics Technology Handbook: Second Edition, Revised and Expanded, Manas Chanda and Salil K. Roy
- 27. Prediction of Polymer Properties, Jozef Bicerano
- Ferroelectric Polymers: Chemistry, Physics, and Applications, edited by Hari Singh Nalwa
- 29. Degradable Polymers, Recycling, and Plastics Waste Management, edited by Ann-Christine Albertsson and Samuel J. Huang
- 30. Polymer Toughening, edited by Charles B. Arends
- 31. Handbook of Applied Polymer Processing Technology, edited by Nicholas P. Cheremisinoff and Paul N. Cheremisinoff
- 32. Diffusion in Polymers, edited by P. Neogi
- 33. Polymer Devolatilization, edited by Ramon J. Albalak
- Anionic Polymerization: Principles and Practical Applications, Henry L. Hsieh and Roderic P. Quirk
- 35. Cationic Polymerizations: Mechanisms, Synthesis, and Applications, edited by Krzysztof Matyjaszewski
- 36. Polyimides: Fundamentals and Applications, edited by Malay K. Ghosh and K. L. Mittal
- 37. Thermoplastic Melt Rheology and Processing, A. V. Shenoy and D. R. Saini
- 38. Prediction of Polymer Properties: Second Edition, Revised and Expanded, Jozef Bicerano
- 39. Practical Thermoforming: Principles and Applications, Second Edition, Revised and Expanded, *John Florian*
- 40. Macromolecular Design of Polymeric Materials, edited by Koichi Hatada, Tatsuki Kitayama, and Otto Vogl
- 41. Handbook of Thermoplastics, edited by Olagoke Olabisi
- 42. Selecting Thermoplastics for Engineering Applications: Second Edition, Revised and Expanded, Charles P. MacDermott and Aroon V. Shenoy
- 43. Metallized Plastics: Fundamentals and Applications, edited by K. L. Mittal
- 44. Oligomer Technology and Applications, Constantin V. Uglea
- 45. Electrical and Optical Polymer Systems: Fundamentals, Methods, and Applications, edited by Donald L. Wise, Gary E. Wnek, Debra J. Trantolo, Thomas M. Cooper, and Joseph D. Gresser
- 46. Structure and Properties of Multiphase Polymeric Materials, edited by Takeo Araki, Qui Tran-Cong, and Mitsuhiro Shibayama
- 47. Plastics Technology Handbook: Third Edition, Revised and Expanded, Manas Chanda and Salil K. Roy
- 48. Handbook of Radical Vinyl Polymerization, *Munmaya K. Mishra and Yusuf Yagci*
- 49. Photonic Polymer Systems: Fundamentals, Methods, and Applications, edited by Donald L. Wise, Gary E. Wnek, Debra J. Trantolo, Thomas M. Cooper, and Joseph D. Gresser
- 50. Handbook of Polymer Testing: Physical Methods, edited by Roger Brown

- 51. Handbook of Polypropylene and Polypropylene Composites, edited by Harutun G. Karian
- Polymer Blends and Alloys, edited by Gabriel O. Shonaike and George P. Simon
- Star and Hyperbranched Polymers, edited by Munmaya K. Mishra and Shiro Kobayashi
- 54. Practical Extrusion Blow Molding, edited by Samuel L. Belcher
- Polymer Viscoelasticity: Stress and Strain in Practice, Evaristo Riande, Ricardo Díaz-Calleja, Margarita G. Prolongo, Rosa M. Masegosa, and Catalina Salom
- 56. Handbook of Polycarbonate Science and Technology, edited by Donald G. LeGrand and John T. Bendler
- 57. Handbook of Polyethylene: Structures, Properties, and Applications, *Andrew J. Peacock*
- Polymer and Composite Rheology: Second Edition, Revised and Expanded, Rakesh K. Gupta
- Handbook of Polyolefins: Second Edition, Revised and Expanded, edited by Cornelia Vasile
- Polymer Modification: Principles, Techniques, and Applications, edited by John J. Meister

Additional Volumes in Preparation

Handbook of Elastomers: Second Edition, Revised and Expanded, edited by Anil K. Bhowmick and Howard L. Stephens

Polymer Modifiers and Additives, edited by John T. Lutz, Jr., and Richard F. Grossman

To my wife, Mary Jean, and to R. Vincent Smith, retired manager at the Phillips Petroleum Company

Preface

This book was designed as both an advanced text for a course in polymer modification and a reference work for professionals in polymer science and engineering. In support of its use as a textbook, the work contains problems at the end of each chapter to allow students to verify their knowledge of the material in the chapter. At the end of the Introduction a series of questions are given that will allow students just starting the course to measure the expertise they possess against that which is needed to effectively utilize the materials of this book. Anyone who cannot correctly answer 80% of the questions at the end of the Introduction should read Appendix II before reading further chapters in the text. Anyone who cannot correctly answer 50% of the questions at the end of the Introduction should read Appendix II several times before reading further chapters in the text and may wish to take a good course in polymer science and engineering before utilizing this text.

The use of this book as a reference work is supported by its topical organization, the extensive references, the breadth of coverage of the chapters, and the copious index. The polymers discussed here cover the vast use of polymers today and virtually all current modification techniques.

My wife's help and support are gratefully acknowledged. I owe a great deal of my capacity to write technical material to Vince Smith and I hope that this text reflects well on his pedagogy.

Contributors

Witold Brostow Departments of Material Science and Chemistry, University of North Texas, Denton, Texas

William K. Cheung Consultant, New York, New York

Charles A. Daniels The Geon Company, Avon Lake, Ohio

Donal F. Day Audubon Sugar Institute, Louisiana Agricultural Experiment Station, Baton Rouge, Louisiana

Richard D. Gilbert Wood and Paper Science Department, North Carolina State University, Raleigh, North Carolina

Jeffrey W. Gilman National Institute of Standards and Technology, Gaithersburg, Maryland

Barbara F. Howell* Carderock Division, Naval Surface Warfare Center, Bethesda, Maryland

^{*}Retired Chemist, Melbourne Village, Florida.

x Contributors

John F. Kadla Wood and Paper Science Department, North Carolina State University, Raleigh, North Carolina

John M. Kelly Ticona, Houston, Texas

Byoung Chul Kim Division of Chemical Engineering, Hanyang University, Seoul, Korea

John J. Meister Center for Forest Products Research, Inc., Albuquerque, New Mexico

C. Mark Ott* Audubon Sugar Institute, Louisiana Agricultural Experiment Station, Baton Rouge, Louisiana

Bernd Strehmel Department of Physical and Theoretical Chemistry, Humboldt University of Berlin, Berlin, Germany

Veronika Strehmel† Institute of Technical and Macromolecular Chemistry, Martin-Luther-University Halle-Wittenberg, Merseburg, Germany

Current affiliation:

^{*}Wyle Laboratories, Houston, Texas.

[†]Institute of Thin Film Technology and Microsensorics, Berlin, Germany.

Contents

Preface v Contributors ix

- 1. Introduction to Polymer Modification 1 *John J. Meister*
- 2. Cellulose Modification 21
 Richard D. Gilbert and John F. Kadla
- 3. Modification of Lignin 67 John J. Meister
- 4. Modification of Starch 145

 C. Mark Ott and Donal F. Day
- 5. Modification of Natural Gums 185 C. Mark Ott and Donal F. Day
- 6. Modification of Polyethylene 229 Jeffrey W. Gilman

viii Contents

7. Ultra-High Molecular Weight Polyethylene 273 John M. Kelly

- 8. Modification of Polystyrene 293 William K. Cheung
- 9. Modification of Poly(Vinyl Chloride) 351 Charles A. Daniels
- Modification of Nylon 431 Byoung Chul Kim
- 11. Modification of Epoxy Resins 479 Barbara F. Howell
- 12. Modification of Phenol-Methanal Network Polymers 575

 Veronika Strehmel and Bernd Strehmel
- 13. Polymer Liquid Crystals and Their Blends 707 Witold Brostow

Appendix I: Answers to Problems and Exercises 733 Appendix II: Polymer Science, Engineering, and Technology Needed to Understand Polymer Modification 779 Index 849

1

Introduction to Polymer Modification

John J. Meister

Center for Forest Products Research, Inc., Albuquerque, New Mexico

Introduction	3
Exercises	12
References	15

Introduction 3

INTRODUCTION

Polymer modification has become a major route to better polymer properties and wider polymer applicability in the 1990's. The high cost of developing a completely new polymer and the many long-term performance objectives a new polymer must meet have pushed firms to innovate by modification and blending rather than synthesis of a new monomer and polymer.

This dependence on modification is not new. Indeed, while the use of stone and clay pottery is a use of polymeric silicates, cooked meat is denatured polymeric protein, and wool or cotton fabric are woven polymers, the first commercial polymer that was not just gathered and processed from nature was a modified cellulose, gun cotton.

Gun cotton was a serendipitous discovery in about 1846 of Christian Schonbein (1), a Swiss professor of chemistry. He mopped up a spill of nitric and sulfuric acids with his wife's apron and set the washed apron to dry in front of the stove. You might say that Schonbein's discovery occurred in a flash because the apron ignited as it dried. Dr. Schonbein had created cellulose nitrate, a modified form of cellulose. This polymer was first made by Braconnot (2) in 1832 but Schonbein's synthesis method (1) could be commercialized. It is shown in Figure 1. The European political environment in which Schonbein made his discovery was one of incessant military conflict and so was highly receptive to a new explosive. Schonbein patented his discovery and allowed it to be commercialized in Austria and England. Unfortunately, cellulose nitrate was so unstable that the last plant making Schonbein's product blew itself up in 1862.

4 Meister

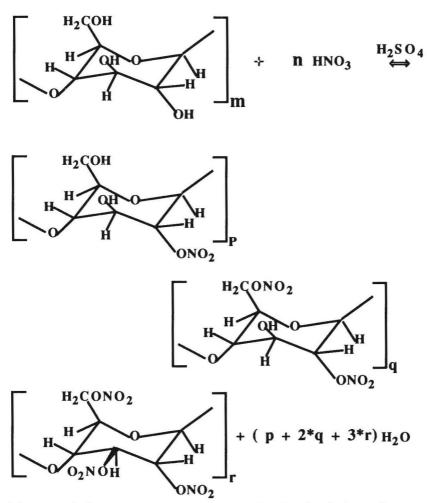


Figure 1. Sulfuric acid catalyzed synthesis of cellulose nitrate. The product will contain a mixture of mono (p subscript), di (q subscript), and tri (r subscript) substituted repeat units that will appear in the polymer backbone in random order. $p + q + r \le m$.