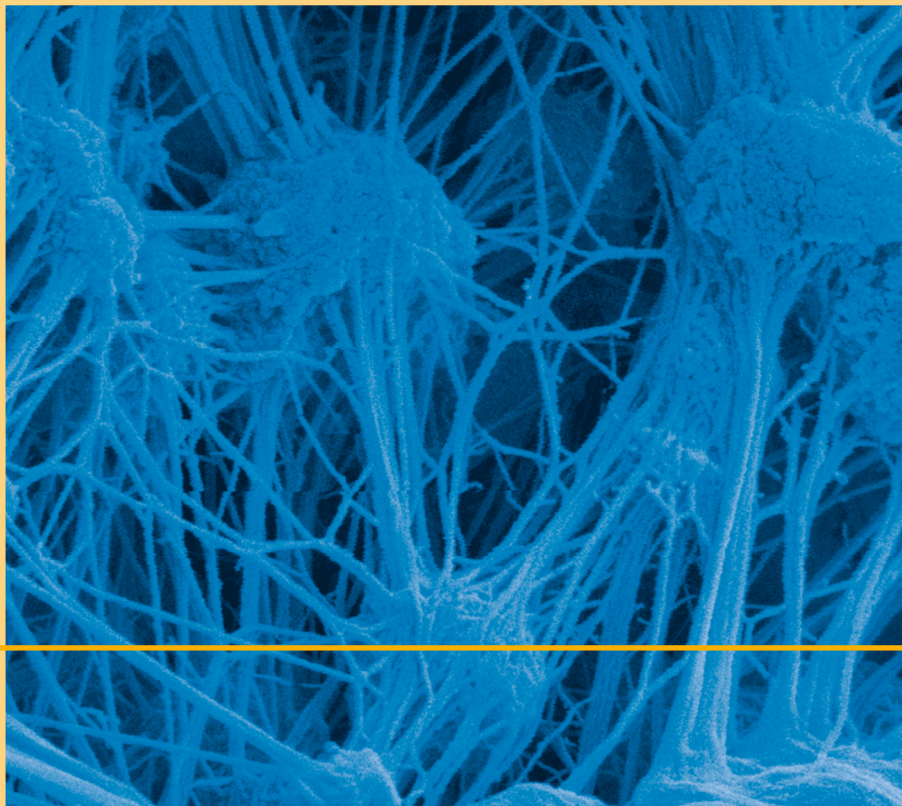


Goerg H. Michler

# Atlas of Polymer Structures

Morphology, Deformation and Fracture Structures



HANSER







Goerg H. Michler

# **Atlas of Polymer Structures**

Morphology, Deformation and Fracture Structures

Hanser Publishers, Munich

**HANSER**  
Hanser Publications, Cincinnati

**The Author:**

*Prof. Dr. habil. Goerg H. Michler*, Martin-Luther-Universität Halle-Wittenberg, Institut für Physik, 06099 Halle (Saale), Germany

Distributed in North and South America by:  
Hanser Publications  
6915 Valley Avenue, Cincinnati, Ohio 45244-3029, USA  
Fax: (513) 527-8801  
Phone: (513) 527-8977  
[www.hanserpublications.com](http://www.hanserpublications.com)

Distributed in all other countries by  
Carl Hanser Verlag  
Postfach 86 04 20, 81631 München, Germany  
Fax: +49 (89) 98 48 09  
[www.hanser-fachbuch.de](http://www.hanser-fachbuch.de)

The use of general descriptive names, trademarks, etc., in this publication, even if the former are not especially identified, is not to be taken as a sign that such names, as understood by the Trade Marks and Merchandise Marks Act, may accordingly be used freely by anyone. While the advice and information in this book are believed to be true and accurate at the date of going to press, neither the authors nor the editors nor the publisher can accept any legal responsibility for any errors or omissions that may be made. The publisher makes no warranty, express or implied, with respect to the material contained herein.

The final determination of the suitability of any information for the use contemplated for a given application remains the sole responsibility of the user.

Cataloging-in-Publication Data is on file with the Library of Congress

Bibliografische Information Der Deutschen Bibliothek  
Die Deutsche Bibliothek verzeichnet diese Publikation in der Deutschen Nationalbibliografie;  
detaillierte bibliografische Daten sind im Internet über <http://dnb.d-nb.de> abrufbar.

All rights reserved. No part of this book may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying or by any information storage and retrieval system, without permission in writing from the publisher.

© Carl Hanser Verlag, Munich 2016  
Editor: Cheryl Hamilton  
Production Management: Jörg Strohbach  
Coverconcept: Marc Müller-Bremer, [www.rebranding.de](http://www.rebranding.de), München  
Coverdesign: Stephan Rönigk  
Layout: Manuela Treindl, Fürth  
Printed and bound by Kösel, Krugzell  
Printed in Germany

ISBN: 978-1-56990-557-9  
E-Book ISBN: 978-1-56990-558-6

# Preface

Polymers are important materials in many fields of daily life, from household, medicine, agriculture, and automotive industry products, up to microelectronics and space research. The morphology of polymers provides and controls the physical, chemical, and other properties of technical relevance. Therefore, analysis and control of the morphology of polymers is a crucial precondition to material development, to improve properties in general and to better fit specific properties to defined applications.

In the last few decades, the amount of interest in polymeric systems has gradually shifted from the micron-scale to the nanometer-scale region. As a consequence of the trend toward producing more nanostructured polymers and miniaturizing components (microsystems), a better understanding of the hierarchical structure of polymers is needed. In general, knowledge of the property-determining structures and microprocesses or mechanisms is a necessary precondition for exploiting the full potential of polymeric materials and is key in successfully developing new polymers and improving the properties of polymers already in use. This Atlas will help scientists and engineers to understand the morphology of polymers and, therefore, to understand their properties better.

The detailed investigation of the complex hierarchical structures of many polymers requires the use of specialized techniques. Electron microscopy and atomic force microscopy have both developed into powerful tools in the field of polymer science. By using different techniques, morphological details can be detected at length scales from the visible (0.1 mm) down to the atomic level (about 0.1 nm). Additionally, the influence of several parameters, such as temperature, environment, and mechanical stresses, can be investigated together with the morphology of the material. In particular, under mechanical loading, the influence of the local morphology on the mechanical effects that occur at the nano- and microscopic level can be examined. Therefore, electron microscopy and atomic force microscopy directly contribute to a better understanding of structure-property correlations in polymers.

This book reviews the research results of academia and industry with a comprehensive overview of the morphology of all groups of polymers. The different levels of morphology, that is, the hierarchical structure of polymers, are illustrated with micrographs from all of the different microscopic techniques with magnifications from the millimeter down to the subnanometer scale. In addition, changes in morphology during and after mechanical loading up to fracture structures are presented together with illustrations of the nano/micromechanical and failure mechanisms. The reader will find a compact and understandable description and illustration of the structural or morphological variety of polymers with a focus on the morphological details, which are relevant for the application properties of the polymers. The micrographs and explanations allow correlations between the morphology and properties of the polymers and help readers to better understand the ultimate properties. The aim of this book is to give guidelines for polymer researchers, chemists, chemical engineers, and material scientists in institutions and industry for understanding the principles of morphology formation and for improving

properties, in particular mechanical properties. Finally, the book will also be helpful for students of polymer physics, chemistry, and engineering, as well as for those researchers interested in the microscopic and nanoscopic world of polymers.

After an introductory chapter in Part I of the Atlas, with an overview of the molecular and supermolecular structures (morphology) and the mechanical behavior of polymers, Chapter 2 offers a summary of the main techniques and methods used to investigate the nanostructure and morphology as well as the nano- and micro-mechanical processes and mechanisms. It describes briefly the wide variety of preparation methods and the different microscopic techniques of electron microscopy and atomic force microscopy used in morphological investigations, accompanied by representative micrographs. In particular, contrast formation in the different microscopes is discussed to help the reader to interpret the micrographs of the many polymers. Chapter 3 discusses several factors of sample preparation as well as investigation technique that can influence the appearance of micrographs or lead to false interpretations.

The subsequent nine chapters of Part II form the main part of the Atlas, with the presentation of micrographs of the different groups of polymers, including amorphous and crystalline polymers, block copolymers, blends and rubber-toughened polymers, particle- and fiber-reinforced composites, biopolymers and biomedical polymers, nanofibers, and special polymer forms. Each of these chapters starts in the first section with a general overview of the particular polymer group; the following sections show in detail representative micrographs from different microscopic techniques with short descriptions, illustrating the characteristic features and also the variety of structures and morphologies of the polymers and showing the influence of the preparation method. In addition to the legend for each micrograph, in some cases micrographs are grouped and compared in one figure with extended information. In all cases, a clear identification of magnification with a scale bar and, if necessary, the direction of mechanical loading are indicated. Next to the typical morphologies, examples of deformation and fracture structures together with the relevant deformation mechanisms and the most commonly occurring defects and failures are highlighted as well. Each chapter closes with a list of relevant references.

In Part III are some tables to help the reader quickly find the figures of the different polymers illustrated in Part II and find micrographs with characteristic morphological details and characteristic deformation and fracture structures. In addition, some morphological terms have a culinary or natural background.

This book presents lots of illustrating micrographs that result from all of the direct imaging methods of optical, electron, and atomic force microscopy. It contains knowledge and experiences developed over more than four decades in different working groups in academia, universities, applied research institutes, and the polymer industry. For many of the microscopic investigations and micrographs I thank my former coworkers in Halle, Schkopau, and Merseburg, Germany, in particular DI (FH) Irene Naumann, DI (FH) Helga Steinbach, Dr. Katerina Morawietz, Ingeburg Schülke, DI (FH) Sylvia Goerlitz, Cornelia Becker (†), Dipl.-Phys. Werner Lebek, Dipl.-Phys. Volker Seydewitz, DI Stefanie Scholtyssek, Dr. Reinhold Godehardt, Dr. Ashraf Sh. Asran, Dr. Sven Henning (now Fraunhofer Institute of Materials Mechanics in Halle), Dr. Rameshwar Adhikari (now Kathmandu, Nepal),



Prof. Dr. Gyeong-Man Kim (now South Korea), Prof. Dr. Roland Weidisch (†), and many diploma and Ph.D. students. Valuable contributions with micrographs of several polymers came from Dr. František Lednicky, Institute of Macromolecular Chemistry of the Czech Academy of Sciences in Prague. For special micrographs I want to thank many friends and colleagues, including Prof. Dr. Volker Abetz, Geesthacht, Prof. Dr. Andrzej Bledzi, Kassel, Prof. Dr. Stoyko Fakirov, Auckland, New Zealand, Prof. Dr. Hans-Peter Fink, Potsdam-Golm, Prof. Dr. Klaus Friedrich, Kaiserslautern, Prof. Dr. Andrzej Galeski, Lodz, Poland, Prof. Dr. Jozsef Karger-Kocsis, Budapest, Ungarn, Prof. Dr. Lacayo Pineda, Hannover, Dr. Arthur Bobovitch, Beer-Sheva, Israel, Dr. Ralf Lach, Merseburg, Ing. Claudia Mayrhofer, Graz, Austria, Dr. Christopher Plummer, Lausanne, Switzerland, and Dr. Helge Steininger, Ludwigshafen. In particular I have to thank DI Wolfgang Schurz and DI Sven Borreck (†) for transforming many of the micrographs into a digital form, for image processing, and for technical editing of figures.

Many examples of polymers with representative micrographs together with a description of the nano- and micromechanical properties are from the first publication in this field by G. H. Michler, “Kunststoff-Mikromechanik: Morphology, Deformations- und Bruchmechanismen,” Hanser, 1992, and from the book “Nano- and Micromechanics of Polymers: Structure Modification and Improvement of Properties,” Hanser, 2012, together with my friend Francisco Jose Baltá-Calleja, Madrid, whom I also thank for improvements of the manuscript. For helpful discussions over many years, I thank Prof. Dr. Dr. h.c. Hans-Henning Kausch, Lausanne, Switzerland, and Prof. Dr. Wolfgang Grellmann, Merseburg, Germany.

Finally, I thank the Carl Hanser Verlag for the cooperation and the careful realization of the book project.

Halle (Saale), September 2015

*Goerg Hannes Michler*



# Contents

<b>Part I – Introduction</b> .....	<b>1</b>
<b>CHAPTER 1</b>	
<b>Overview</b> .....	<b>3</b>
1.1 Aim of the Atlas .....	3
1.2 Molecular Structures .....	7
1.2.1 Constitution .....	7
1.2.2 Configuration .....	7
1.2.3 Conformation .....	9
1.3 Supramolecular Structures and Morphology .....	11
1.3.1 Homopolymers .....	11
1.3.2 Copolymers .....	13
1.3.3 Polymer Blends .....	14
1.3.4 Composites .....	15
1.3.5 Additional Morphologies .....	18
1.4 Mechanical Behavior .....	18
1.4.1 Types of Deformation .....	18
1.4.2 Deformation Mechanisms .....	20
1.4.3 Fracture .....	22
<b>CHAPTER 2</b>	
<b>Techniques and Methods</b> .....	<b>27</b>
2.1 Microscopic Techniques .....	27
2.1.1 Overview .....	27
2.1.2 Optical Microscopy .....	28
2.1.3 Scanning Electron Microscopy .....	28
2.1.4 Transmission Electron Microscopy .....	31
2.1.5 Atomic Force Microscopy .....	33
2.1.6 Image Processing and Image Analysis .....	33
2.2 Sample Preparation Methods .....	35
2.2.1 Overview .....	35
2.2.2 Preparation of Surfaces .....	39
2.2.3 Preparation of Thin Sections .....	43
2.2.4 Contrast Enhancement .....	47
2.2.5 Stereoscopic Imaging and 3D Analysis .....	51
2.3 Deformation and Fracture Tests .....	52
<b>CHAPTER 3</b>	
<b>Influences of Techniques and Methods on Micrographs</b> .....	<b>57</b>
3.1 Influence of Sample Preparation .....	57
3.1.1 Influence of Fracture Processes .....	57
3.1.2 Influence of Section Thickness .....	57

3.2	Influence of Investigation Parameters in TEM .....	61
3.2.1	Influence of Electron Beam Intensity .....	61
3.2.2	High-Resolution Micrographs.....	65
3.2.3	Tilting of the Specimen in TEM.....	66

**Part II – Groups of Polymers ..... 69**

**CHAPTER 1**

**Amorphous Polymers ..... 71**

1.1	Main Characteristics .....	71
1.1.1	Structure and Morphology.....	71
1.1.2	Deformation Mechanisms .....	75
1.2	Homopolymers.....	82
1.2.1	Polystyrene (PS) .....	82
1.2.2	Poly(methyl methacrylate) (PMMA) .....	95
1.2.3	Poly(vinyl chloride) (PVC) .....	99
1.2.4	Polycarbonate (PC).....	104
1.3	Copolymers .....	110
1.3.1	Styrene Acrylonitrile Copolymers (SAN) .....	110
1.3.2	Cyclic Olefin Copolymers (COC) .....	115

**CHAPTER 2**

**Semicrystalline Polymers ..... 121**

2.1	Overview .....	121
2.1.1	Lamellar Structure.....	123
2.1.2	Structural Hierarchy.....	127
2.1.3	Parameters Influencing Morphology .....	130
2.1.4	Deformation and Fracture Mechanisms .....	132
2.2	Polyethylenes .....	139
2.2.1	High-Density Polyethylene (Linear PE, HDPE).....	139
2.2.2	Ultrahigh Molecular Weight Polyethylene (UHMWPE) .....	156
2.2.3	Low-Density Polyethylene (Branched PE, LDPE).....	166
2.2.4	Linear-Low Density Polyethylenes (LLDPE, VLDPE) .....	181
2.3	Polypropylene ( $\alpha$ -, $\beta$ -iPP, sPP); .....	191
2.3.1	PP Morphology .....	191
2.3.2	PP Deformation and Fracture Structures .....	198
2.4	Additional Polymers (PA, PVDF, PBT, PEN, PEEK, POM, PEO, sPS) .....	208
2.4.1	Morphology .....	208
2.4.2	Deformation and Fracture .....	217

**CHAPTER 3**

**Block Copolymers ..... 223**

3.1	Overview .....	223
3.1.1	Morphology of Block Copolymers.....	224
3.1.1.1	Nanostructures via Self-Assembly.....	224
3.1.1.2	Influence of Chain Architecture .....	225
3.1.1.3	Block Copolymer/Homopolymer Blends.....	226

3.1.1.4	Processing-Induced Nonequilibrium Morphologies .....	227
3.1.1.5	Block Copolymer Nanocomposites.....	229
3.1.2	Deformation Mechanisms in Block Copolymers .....	229
3.2	Block Copolymers – Morphology.....	237
3.2.1	Morphology of Diblock and Triblock Copolymers .....	237
3.2.2	Morphology of Block Copolymer / Polymer Blends .....	246
3.3	Deformation and Fracture Structures .....	254
<b>CHAPTER 4</b>		
<b>Polymer Blends..... 269</b>		
4.1	Overview .....	269
4.1.1	Morphology .....	270
4.1.2	Deformation Mechanisms .....	274
4.2	Blends of Amorphous Polymer Components .....	278
4.2.1	Morphology of the Blends .....	278
4.2.2	Deformation and Fracture Structures.....	282
4.3	Blends of Amorphous and Semicrystalline Polymers .....	287
4.3.1	PE/PS Blends, Morphology, and Deformation Structures.....	287
4.3.2	PP Blends with PS and PEO.....	291
4.3.3	Blends of TPU with SAN and ABS .....	293
4.3.4	Blends of PBT/PET with PC.....	296
4.3.5	Blends of PA with ABS, HIPS, and sPS.....	299
4.3.6	PE Multiphase Blends .....	303
4.4	Blends of Semicrystalline Polymers.....	305
4.4.1	Blends of HDPE, LDPE, and VLDPE.....	305
4.4.2	PE/PP Blends .....	310
4.4.3	PP/PA Blends .....	313
4.4.4	PBT, PET Blends (with EVA, PE, PP, PA) .....	315
4.5	Rubbers and Elastomers .....	317
4.5.1	NR and SBR Blends .....	317
4.5.2	EVA Copolymer .....	323
4.5.3	Polyurethanes (PU, TPU).....	323
4.5.4	Further Elastomers .....	327
<b>CHAPTER 5</b>		
<b>Rubber-Toughened Polymers..... 331</b>		
5.1	Overview .....	331
5.1.1	Morphology .....	331
5.1.2	Basic Micromechanical Mechanisms .....	334
5.2	Systems with an Amorphous Matrix.....	342
5.2.1	High-Impact Polystyrene (HIPS) .....	342
5.2.1.1	Morphology.....	342
5.2.1.2	Deformation Mechanisms .....	348
5.2.2	Acrylonitrile-Butadiene-Styrene .....	358
5.2.2.1	Morphology.....	358
5.2.2.2	ABS Deformation Mechanisms .....	364
5.2.3	Rubber-Modified SAN: SAN/EVA, SAN/CPE (ACS), SAN/PBA (ASA) .....	378
5.2.4	Rubber-Toughened PMMA (RTPMMA) .....	385

5.2.5	Additional Amorphous Rubber-Toughened Polymers (Rubber-Toughened PC, COC, Epoxy) .....	392
5.2.6	Rubber-Toughened PVC.....	398
5.2.6.1	Toughened PVC with Disperse Structure.....	398
5.2.6.2	Toughened PVC with Network Structure .....	405
5.3	Systems with Semicrystalline Matrix.....	412
5.3.1	Rubber-Modified Polypropylene .....	412
5.3.2	Rubber-Modified Polyamide .....	424

**CHAPTER 6**

**Composites .....** 427

6.1	Main Characteristics.....	427
6.1.1	Particle-Filled Polymer Composites.....	427
6.1.2	Nanoparticle Polymer Composites.....	432
6.2	Particle-Filled Polymer Composites .....	438
6.2.1	Morphology.....	438
6.2.2	Deformation Structures.....	445
6.3	Nanoparticle-Filled Polymers (Nanocomposites).....	449
6.3.1	Morphology.....	449
6.3.2	Deformation Structures.....	458

**CHAPTER 7**

**Fiber-Reinforced Polymer Composites .....** 463

7.1	Overview.....	463
7.2	Inorganic and Carbon Fiber Polymer Composites.....	469
7.3	Polymer-Polymer Composites and Natural Fiber Composites .....	475

**CHAPTER 8**

**Biopolymers and Polymers for Medical Applications.....** 485

8.1	Overview.....	485
8.1.1	Biobased and Biodegradable Polymers .....	486
8.1.2	Biomedical Polymers .....	487
8.2	Biobased Polymers .....	497
8.3	Medical Applications.....	506

**CHAPTER 9**

**Special Processing Forms .....** 527

9.1	Overview.....	527
9.2	Hot-Compacted Fibers and Films.....	539
9.3	Coextruded Multilayered Polymers .....	541
9.3.1	Morphology.....	541
9.3.2	Deformation Structures.....	552
9.4	Nanofibers .....	558
9.5	Polymeric Foams and Membranes .....	567

**Part III – Tables** ..... **577**

Table 1 Connection of Polymers with Morphological Details and Deformation Structures ..... 579

Table 2 Appearance of Morphological Details in Polymers ..... 586

Table 3 Deformation and Fracture Structures in Polymers ..... 590

Table 4 Structural/Morphological Details with Culinary or Natural Backgrounds ..... 592

List of Abbreviations..... 593

**Subject Index**..... **599**