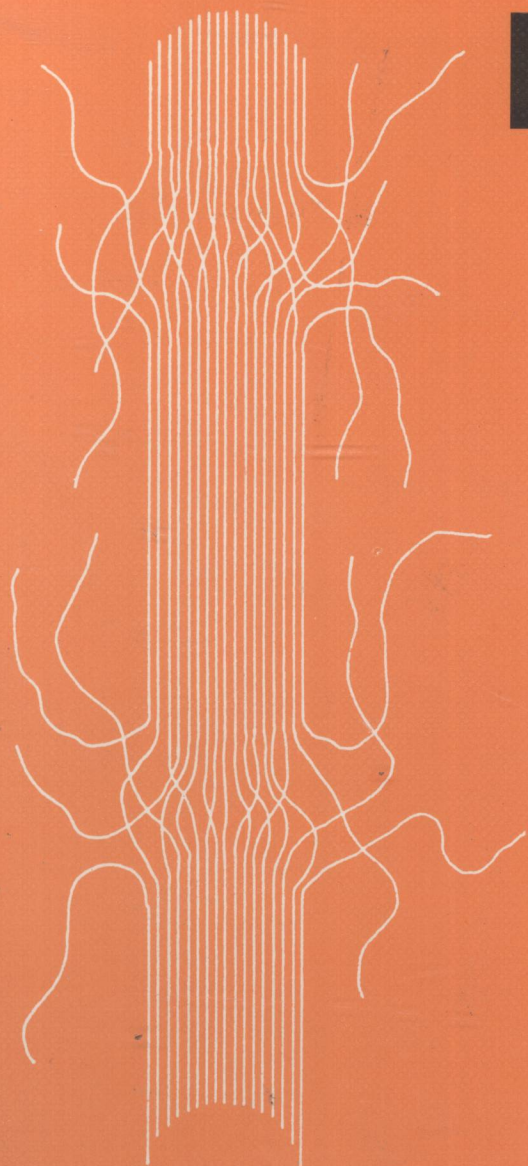


Stoyko Fakirov (Ed.)

Oriented Polymer Materials



Hüthig & Wepf

TB 324
069

9960917

Oriented Polymer Materials

Edited by Stoyko Fakirov



With 337 Figures and 42 Tables



E9960917

Hüthig & Wepf Verlag Zug · Heidelberg · Oxford CT/USA

Editor's Addresses

Prof. Dr. Stoyko Fakirov
Bogazici University, Polymer Research Center,
School of Engineering, and TUBITAK Advanced
Polymereic Materials Research Center
Bebek 80815
Istanbul
Turkey

Permanent Address:
Sofia University
Laboratory on Structure and Properties of Polymers
Bld. A. Ivanov 1
1126 Sofia
Bulgaria

Die Deutsche Bibliothek – CIP-Einheitsaufnahme
Oriented polymer materials : with 42 tables / ed. by Stoyko Fakirov. – Basel ; Heidelberg ;
New York : Hüthig und Wepf, 1996
ISBN 3-85739-123-5
NE: Fakirov, Stojko [Hrsg.]

Stoyko Fakirov
Oriented Polymer Materials

Contributors

Argon, A. S.

Massachusetts Institute of Technology,
Cambridge, MA 02139, USA

Bahar, I.

Bogazici University, Polymer Research Center,
School of Engineering, and TUBITAK Advanced
Polymeric Materials Research Center,
Bebek 80815, Istanbul, Turkey

Bartczak, Z.

Massachusetts Institute of Technology,
Cambridge, MA 02139, USA

Present address: Center of Molecular and
Macromolecular Studies,
Polish Academy of Sciences,
99-368 Lodz, Poland

Bonart, R.

Universität Regensburg,
Institut für Angewandte Physik,
Postfach 10 10 42, 8401 Regensburg, Germany

Cohen, R. E.

Massachusetts Institute of Technology,
Cambridge, MA 02139, USA

Erman, B.

Bogazici University, Polymer Research Center,
School of Engineering and TUBITAK Advanced
Polymeric Materials Research Center,
Bebek 80815, Istanbul, Turkey

Fakirov, S.

Bogazici University, Polymer Research Center,
School of Engineering, and TUBITAK Advanced
Polymeric Materials Research Center,
Bebek 80815, Istanbul, Turkey

Permanent address: Sofia University, Laboratory
on Structure and Properties of Polymers,
1126 Sofia, Bulgaria

Frenkel, S.

Institute of Macromolecular Compounds,
Russian Academy of Sciences,
199004 St. Petersburg, Russia

Friedrich, K.

Institut für Verbundwerkstoffe GmbH,
University of Kaiserslautern,
D-67663 Kaiserslautern, Germany

Galeski, A.

Massachusetts Institute of Technology,
Cambridge, MA 02139, USA

Present address: Center of Molecular and
Macromolecular Studies,
Polish Academy of Sciences,
99-368 Lodz, Poland

Godovsky, Y. K.

Karpov Institute of Physical Chemistry,
103064 Moscow K-64, Russia

Gupta, V. B.

Indian Institute of Technology,
Textile Technology Department,
New Delhi 110016, India

Kunugi, T.

Yamanashi University,
Faculty of Engineering,
Takeda-4, Kofu, 400 Japan

Prevorsek, D. C.

Allied-Signal Inc., Research & Technology
P.O.Box 1021, Morristown, NJ 07962, USA

Schledjewski, R.

Institut für Verbundwerkstoffe GmbH,
University of Kaiserslautern,
D-67663 Kaiserslautern, Germany

Schultz, J. M.

University of Delaware,
Materials Science Program,
Newark, DE 19716, USA

Sheiko, S. S.

Faculteit der Chemische Technologie,
Universiteit Twente,
P.O.Box 217, 7500 AE Enschede, The Netherlands

Present address: Universität Ulm,
Abteilung Organische Chemie III,
89069 Ulm, Germany

Siesler, H. W.

Universität GH Essen,
Abteilung Physikalische Chemie,
45117 Essen, Germany

Lee, B. J.

Massachusetts Institute of Technology,
Cambridge, MA 02139, USA

Present address: University of California,
Department of Applied Mechanics and Engineering Sciences,
San Diego, LaJolla, CA 92093, USA

Marikhin, V. A.

Ioffe Physico-Technical Institute,
194021 St. Petersburg, Russia

Matsuo, M.

Department of Clothing Science,
Nara Women's University,
Nara 630, Japan

Möller, M.

Faculteit der Chemische Technologie,
Universiteit Twente, P.O.Box 217,
7500 AE Enschede, The Netherlands

Present address: Universität Ulm,
Abteilung Organische Chemie III
89069 Ulm, Germany

Moneva, I. T.

Institute of Polymers,
Bulgarian Academy of Sciences,
1113 Sofia, Bulgaria

Myasnikova, L. P.

Ioffe Physico-Technical Institute,
194021 St. Petersburg, Russia

Parks, D. M.

Massachusetts Institute of Technology,
Cambridge, MA 02139, USA

Petermann, J.

Universität Dortmund, Fachbereich Chemietechnik,
44227 Dortmund 50, Germany

Preface

The orientation phenomenon is a basic inherent peculiarity of polymers, arising from the chain character of macromolecules and their ability to adopt different conformations — from a coil to an extended chain. The realization of these two extreme conformations or some intermediate ones determines to the greatest extent the mechanical properties of polymers as materials. In addition to the synthesis of new polymers, orientation is a basic approach to the obtaining of polymeric materials with superior properties. Incidentally, the outstanding mechanical properties of liquid crystalline polymers do not stem directly from their chemical composition, but are related to their unique ability of perfect orientation due to the peculiarities of their chemical composition.

The driving forces for the preparation of this book were the clear understanding of the importance of orientation itself and of the oriented polymeric materials, I met everywhere, as well as the fact that the last book related to this important topic appeared more than ten years ago. This situation was recognized somewhat earlier by other polymer scientists, too, and I am pleased to note here that this project was started, although in another form, by Dr. I. Moneva and some colleagues of ours from St. Petersburg, but the turbulent changes in the former Soviet Union and in the contries of Central and Eastern Europe affected it badly. Owing to the generous encouragement and support of Dr. R. E. Bareiss from *Die Makromolekulare Chemie*, the project was modified and could be materialized.

Although the chapters are not formally organized in larger units, an attempt is made to start the book with an overview of the orientation phenomenon, followed by chapters dealing with basic techniques for the study and characterization of orientation and oriented polymers. Another goal was to include as much as possible different representatives of oriented polymer materials, as well as approaches to the improvement of their mechanical properties. These two fields are by far not completely covered and many more contributions are required for doing so.

Like many books of this type, the present one suffers from the diversity of styles and ways of presentation of the chapters, but we hope that this disadvantage is compensated by the high professionalism of the co-authors and by the updated results they have offered. Here it should be mentioned that the chapters differ also in their volume, the contributions from the

Russian co-authors being the longest. The reason is that for many decades there were no equal opportunities for worldwide exchange of information, therefore research in the former Soviet Union did not have access to Western scientists. The review character of the two introductory chapters is an attempt to overcome partially this situation.

As editor, I wish to express my sincere gratitude to the individual contributors, because this type of publication requires perseverance and a great deal of patience. I am greatly indebted to my co-worker Mrs. S. Petrovich — without her everyday help this project could not have been undertaken. A special note of thanks to Dr. Z. Denchev for preparing the Author and Subject Indices as well as appreciation to the Bosphorus University in Istanbul for the hospitality offered to me during my sabbatical year when the book was finalized.

Sofia 1991 — Istanbul 1994

S. Fakirov
Editor

The book is dedicated to

Professor Anton Peterlin in recognition of his essential contribution to the understanding of orientation phenomena and oriented polymers.

Professor Peterlin was one of the most enthusiastic co-authors at the beginning of this project but, to our deep sorrow, he passed away before completing the chapter he had started on the influence of amorphous layers.

CONTENTS

Chapter 1 Problems of the physics of the oriented state of polymers

S. Frenkel

1. Introductory considerations	1
1.1. Interplay of fundamental and applied problems. Molecular cybernetics	1
1.2. Principal routes to the formation of uniaxially oriented structures in polymers	8
2. Configurational information and orientation phenomena in synthetic polymers	10
2.1. Direct generation of orientational order from solutions and melts. Orientational hardening, orientational crystallization, and orientational catastrophes	10
2.2. Assemblage; liquid crystalline polymers	22
2.3. Reconstruction	25
3. Failure under load	26
4. Some specific properties of superoriented polymers	30
5. Technological implications	31
6. General conclusions and summary	32
6.1. What is clear?	32
6.2. What is incomprehensible?	33
6.3. What needs better understanding?	34
References	36

Chapter 2 Structural basis of high-strength high-modulus polymers

V. A. Marikhin, L. P. Myasnikova

1. Introduction	38
2. Structural transformation in semicrystalline polymers on stretching	39
2.1. Deformation mechanisms at small strain	39
2.2. Folded-extended chain solid phase transition in the neck region	42
2.3. Micro- and macrofibrillar structure in oriented polymers and its plastic deformation	47
2.4. Drawing arrest and fracture of oriented polymers	57
2.5. Alternative mechanisms of drawing	59
3. Deformation-induced strengthening of semicrystalline polymers	62
3.1. Structural kinetic approach to the enhancement of polymer characteristics by deformation	62
3.2. Physical criteria for the optimization of the drawing process	67
3.3. Optimal molecular weight and molecular weight distribution	72
4. Mechanical properties of highly oriented polymers	76
5. Thermal properties of superstrong high-modulus polymers	80
6. Structural peculiarities of highly oriented polymers	85
References	92

Chapter 3 X-ray diffraction by quasiperiodic polymer structures

R. Bonart

1. Introduction	99
2. Qualitative phenomenological aspects	102
2.1. Fibre diagrams	102
2.2. Crystal density, chain cross section and chain conformation	107
2.3. Anisotropy perpendicular to the chain direction, planes of plates	108
2.4. Position sphere	109
2.5. Lattice distortions of the first and second kind. Distortion parameter	111

2.6. Special lattice types	115
2.7. Small-angle scattering, fibrils, layer lattices	117
3. Basics of experiments	120
3.1. X-ray spectrum and absorption	120
4. Theoretical relationships	122
4.1. Structure factor	122
4.2. The Ewald sphere	125
4.3. Pair distribution	126
4.4. A special application example	128
5. Simple lattice models	129
5.1. Ideal periodic lattices	129
5.2. Distortions of the first kind	130
5.3. Distortions of the second kind	132
5.4. Inhomogeneous coordination statistics	133
References	136

Chapter 4 Characterization of polymer deformation by vibrational spectroscopy

H. W. Siesler

1. Introduction	138
2. Experimental and instrumentation	139
3. Orientational measurements by infrared dichroism	143
4. Segmental mobility in liquid crystalline side-chain polymers	145
5. Rheo-optical FT-IR studies of the poly(ethylene terephthalate) film forming process	148
5.1. Drawing of PET in the machine direction	153
5.2. Drawing of PET in the transverse direction	154
5.3. Rheo-optical FT-NIR spectroscopic light-fiber investigations of the PET film process	157
6. Rheo-optical FT-Raman spectroscopy of the stress-induced conformational changes in poly(vinylidene fluoride)	160
7. Conclusions	163
References	164

Chapter 5 Morphology in oriented semicrystalline polymers

J. Petermann

1. General considerations	167
2. Morphologies in oriented polymers	168
3. Formation of morphologies in oriented polymers	171
3.1. Morphologies obtained by crystallization of oriented melts	171
3.2. Orientation at interfaces	172
3.3. Orientation in thermal gradients	174
3.4. Orientation by plastic deformation	174
3.5. Polymerization induced orientations	175
4. Morphological changes during thermal treatments	177
5. Outlook to morphology-property relationships	181
References	182

Chapter 6 Deformation calorimetry of oriented polymers

Y. K. Godovsky

1. Introduction	184
2. Deformation calorimetry	185
2.1. Gas calorimeters	185
2.2. Heat-conducted deformation calorimeters	187
3. Thermodynamics of the stretching of oriented polymers	189
4. Thermophysical behaviour of oriented polymers during deformation	193
4.1. Oriented amorphous polymers	193
4.2. Oriented crystalline polymers	194
4.3. Superioriented crystalline polymers	199
5. Anisotropy of thermophysical behaviour of oriented polymers	200
6. Mechanisms of deformation of oriented polymers as revealed by deformation calorimetry and their relation to morphology	202

7. Thermophysical behaviour of oriented polymers under fracture	204
References	208

Chapter 7 Scanning force microscopy on the orientation of gel-crystallized ultrahigh molecular weight polyethylene

S. S. Sheiko, M. Möller

1. Introduction	210
2. On the structure of dried and solvent containing gels	211
3. Gel necking	215
4. Fibrillar structure	223
5. Gel blending	232
References	237

Chapter 8 Polarized light scattering from polymer textures

I. T. Moneva

1. Introduction	241
2. Polarized light scattering: theory and instrumentation	243
2.1. Fluctuations in density and fluctuations in optical anisotropy and orientation	243
2.2. Scattering considerations	244
2.3. Polarized light scattering technique	250
3. Applications of the scattering analysis	251
3.1. Formation of shear bands during zone drawing	252
3.2. Formation of macrofibrils in shear crystallization	253
3.3. Determination of Poisson's ratio by double exposure speckle photography	255
4. Polarized light scattering from textures of liquid crystalline polymers	257
4.1. Polarized light scattering from schlieren textures	257

4.2. Polarized light scattering from banded and other nematic textures	259
5. Concluding remarks	260
References	261

Chapter 9 **Deformation induced texture development in polyethylene: computer simulation and experiments**

A. S. Argon, Z. Bartczak, R. E. Cohen, A. Galeski,
B. J. Lee, D. M. Parks

1. Introduction	265
2. Model description	269
2.1. Basic assumptions	269
2.2. Constitutive relations	270
2.3. Composite inclusion	275
2.4. Interaction law and solution procedure	276
2.5. Parameter selection	278
3. Predicted results and comparison with experiments	279
3.1. Modes of straining	279
3.2. Uniaxial compression	280
3.3. Plane strain compression	289
4. Discussion	298
5. Conclusions	299
References	300

Chapter 10 **Intrinsic anisotropy of highly oriented polymeric systems in relation to molecular orientation and crystallinity**

M. Matsuo

1. Introduction	302
2. Crystal lattice moduli of crystalline polymers	303
3. Theoretical approach to the estimation of the crystal lattice modulus as measured by X-ray diffraction	307