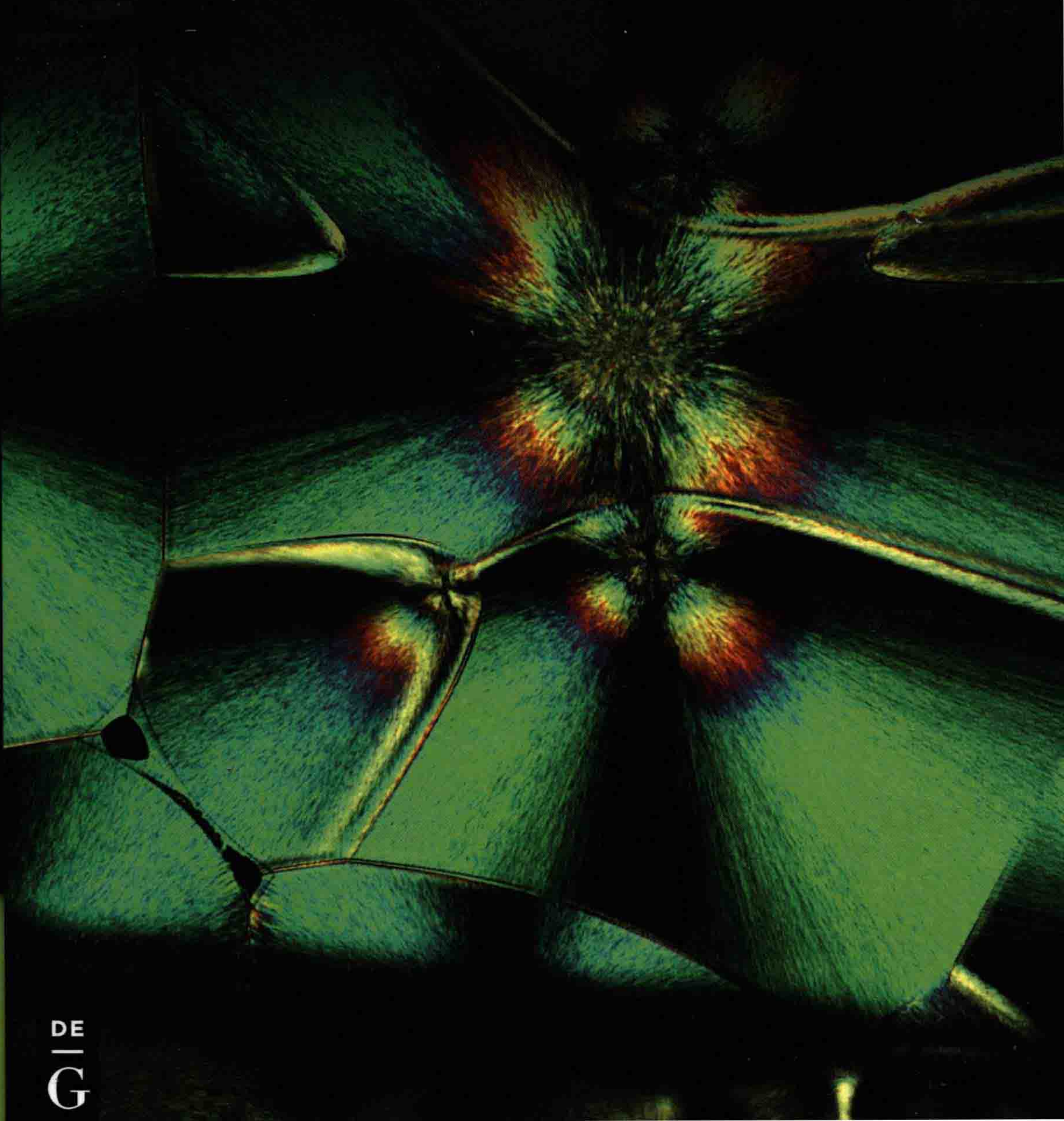
DE GRUYTER

GRADUATE

Luigia Sabbatini (Ed.)

POLYMER SURFACE CHARACTERIZATION



DE
G

Polymer Surface Characterization

Edited by Luigia Sabbatini

DE GRUYTER

Editor
Prof. Dr. Luigia Sabbatini
University of Bari Aldo Moro
Chemistry Department
Via Orabona 4
70125 Bari
Italy
e-mail: luigia.sabbatini@uniba.it

ISBN 978-3-11-027508-7
e-ISBN 978-3-11-028811-7

Library of Congress Cataloging-in-Publication data
A CIP catalog record for this book has been applied for at the Library of Congress.

Bibliographic information published by the Deutsche Nationalbibliothek
The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available in the Internet at http://www.dnb.de.

Typesetting: Compuscript Ltd.
Printing and Binding: Hubert & Co. GmbH & Co. KG, Göttingen
Cover image: “Green with Envy” by Waiken Wong. Permission granted by Materials Research Science and Engineering Center, University of Massachusetts, Amherst, MA, visual program supported by National Science Foundation.

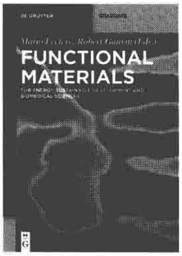
∞ Printed on acid-free paper
Printed in Germany
www.degruyter.com

FSC www.fsc.org MIX Papier aus verantwortungsvollen Quellen FSC® C016439

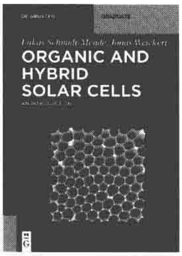
De Gruyter Graduate

Sabbatini • Polymer Surface Characterization

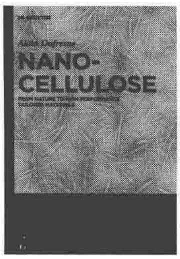
Also of Interest



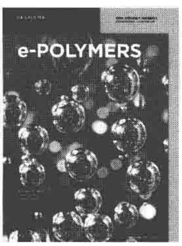
Functional Materials – For Energy, Sustainable Development, and Biomedical Sciences, 2014
Mario Leclerc, Robert Gauvin (Eds.)
ISBN 978-3-11-030781-8, e-ISBN 978-3-11-030782-5



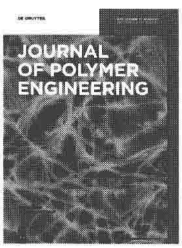
Organic and Hybrid Solar Cells – An Introduction, 2015
Lukas Schmidt-Mende, Jonas Weickert
ISBN 978-3-11-028318-1, e-ISBN 978-3-11-028320-4



Nanocellulose – From Nature to High Performance Tailored Materials, 2012
Alain Dufresne
ISBN 978-3-11-025456-3, e-ISBN 978-3-11-025460-0,
Set-ISBN 978-3-11-219133-0



e-Polymers
Seema Agarwal, Andreas Greiner (Editor-in-Chief)
ISSN 1618-7229



Journal of Polymer Engineering
Ica Manas-Zloczower (Editor-in-Chief)
ISSN 2191-0340

Preface

Polymers permeate our everyday life more than any other materials. It is difficult to think of another material as versatile and irreplaceable as polymers in terms of applications both in consolidated and in emerging technological areas. Their use spans from the most trivial consumer goods to the most advanced microelectronics packaging, miniaturized pieces for artificial organs, high-performance coating in aerospace industry, etc.

Technological demand, moreover, requires materials not only with peculiar bulk properties but also with specific surface chemistry and structure, both generally different from the bulk one. The combination of these two requisites makes a polymeric material suitable and unique for the job it is called to do.

In this respect, surfaces in polymers, more than any other class of materials, can be quite easily handled and engineered to a high level of sophistication by fully exploiting their chemical reactivity. Furthermore, apart from the changes intentionally promoted on polymer surfaces to tailor new application-oriented properties, the importance of polymer dynamics occurring on surfaces whenever they are exposed to the environment (real world) or put in contact with another material (interface) is self-evident: dramatic changes of structural and thermodynamic properties in the confinement area can occur, and these dramatically reflect on properties such as bonding, friction, adsorption, wettability, inertness, etc. Moreover, aging modifies the surface chemistry of polymers (as well as of any other material), thus provoking a remarkable deterioration of their properties.

In all the above cases, knowledge of both the surface chemistry and the structure is mandatory to understand the behavior of polymeric materials, monitor the surface processing, and tailor and develop new surface modification strategies. A wealth of analytical techniques is available for the purpose; they are surface specific, and the analyst/researcher needs a basic knowledge of their principles and procedures in order to choose the most appropriate way to solve the specific problem. In this book, techniques have been selected that are well suited for characterization of surfaces/interfaces of thin polymer-based films but also of more general applicability in materials science. Basic principles, operative conditions, applications, performance, and limiting features are supplied, together with current advances in instrumental apparatus. Each chapter is devoted to one technique and is self-consistent; the end-of-chapter references would allow the reader a quick access to more detailed information.

After an introductory chapter, techniques that can interrogate the very shallow depth of a polymer surface, spanning from the top few angstroms in secondary ions mass spectrometry to 2–10 nm in X-ray photoelectron spectroscopy are discussed in Chapters 2 and 3, respectively. Their potential in the definition of surface chemical composition of polymers is highlighted and documented by selected application examples. Chapter 4 is dedicated to attenuated total reflection Fourier transform infrared spectroscopy, which provides information on polymer chemical structure with varying surface thicknesses, of the order of tenths of a micrometer. Chapter 5 deals with atomic force microscopy, a technique endowed with high-resolution capability to map a variety of material properties on the nanoscale. Evidence is supplied of how probing mechanical properties leads to the identification of important polymer surface processes such as phase segregation, continuity of phases, and dispersion, which play a major role in determining macroscopic properties. Characterization of surface morphology is also addressed in Chapter 6, which is focused on electron microscopy. Scanning electron microscopy is described in detail, and some general information on transmission electron microscopy is given. The point of strength of electron microscopy characterization, well highlighted in this chapter, is that the surface morphology of a polymer system is always closely connected with its chemical composition and processing conditions. Chapter 7 addresses the issue of wettability and its measurements; contact angle measurements and its relationships with surface energy and wetting behavior are clearly described as well as advanced technological processes to develop polymer surfaces with tunable hydrophobic/hydrophilic character. Chapter 8 ends the book with an insight on spectroscopic ellipsometry: after the description of the basics of the method, an investigation of optical, structural, and thermodynamic properties of polymers in the whole spectral range (UV-VIS-IR) is discussed. Some interesting industrial applications such as those in the quality control of roll-to-roll fabrication process or heterogeneity control of micropatterned films are also reported.

The editor gratefully acknowledges the invaluable contributions of the authors and, as it is behind every edited book, the kind invitation and precious support of the publisher, in particular, the enthusiasm of Karin Sora, Senior Editorial Director, Science and Technology, and the continuous, qualified, and friendly cooperation of Julia Lauterbach, Project Editor, Science, Technology & Medicine (STM), at De Gruyter.

Contributing authors

Eva Bittrich
Leibniz-Institut für Polymerforschung
Dresden e.V.
Hohe Strasse 6
01069 Dresden
Germany
e-mail: bittrich-eva@ipfdd.de

Stefania Cometa
Jaber Innovation s.r.l.
Via Calcutta 8
00144 Rome
Italy
e-mail: stefania.cometa@virgilio.it

Elvira De Giglio
Chemistry Department
University of Bari Aldo Moro
Via Orabona 4
70126 Bari
Italy
e-mail: elvira.degiglio@uniba.it

Rosa Di Mundo
Department of Mechanics Mathematics
and Management
Polytechnic University of Bari
V.le Japigia 182
70126 Bari
Italy
e-mail: rosa.dimundo@poliba.it

Nicoletta Ditaranto
Chemistry Department
University of Bari Aldo Moro
Via Orabona 4
70126 Bari
Italy
e-mail: nicoletta.ditaranto@uniba.it

Klaus-Jochen Eichhorn
Leibniz-Institut für Polymerforschung
Dresden e.V.
Hohe Strasse 6
01069 Dresden
Germany
e-mail: kjeich@ipfdd.de

Beat A. Keller
Swiss Federal Laboratories for Materials
Science and Technology (Empa)
CH-8600 Dübendorf
Switzerland
e-mail: beat.keller@empa.ch

František Lednický
Institute of Macromolecular Chemistry
Academy of Sciences of the Czech
Republic
Heyrovsky Sq. 2
162 06 Prague 6
Czech Republic
e-mail: ledn@imc.cas.cz

Filippo Mangolini
Department of Materials Science and
Engineering
University of Pennsylvania
Philadelphia, PA 19104
USA
e-mail: mfilippo@seas.upenn.edu

Fabio Palumbo
Chemistry Department
University of Bari Aldo Moro
Via Orabona 4
70126 Bari
Italy
e-mail: fabio.palumbo@cnr.it

Antonella Rossi
Dipartimento di Scienze Chimiche e Geologiche
Università degli Studi di Cagliari
INSTM Unit – Cittadella Universitaria di Monserrato
S.S. 554 Bivio per Sestu
I-09042 Monserrato, Cagliari
Italy
e-mail: rossi@unica.it

Luigia Sabbatini
Chemistry Department
University of Bari Aldo Moro
Via Orabona 4
70126 Bari
Italy
e-mail: luigia.sabbatini@uniba.it

Miroslav Šlouf
Institute of Macromolecular Chemistry
Academy of Sciences of the Czech Republic
Heyrovsky Sq. 2
162 06 Prague 6
Czech Republic
e-mail: slouf@imc.cas.cz

Taťana Vacková
Institute of Macromolecular Chemistry
Academy of Sciences of the Czech Republic
Heyrovsky Sq. 2
162 06 Prague 6
Czech Republic
e-mail: vackova@imc.cas.cz

Petr Wandrol
FEI
Podnikatelská 6
612 00 Brno
Czech Republic
e-mail: Petr.Wandrol@fei.com

Dalia Yablon
Surfacechar LLC
Sharon, MA 02067
USA
e-mail: dalia.yablon@surfacechar.com

Contents

Stefania Cometa and Luigia Sabbatini

1 Introductory remarks on polymers and polymer surfaces

1.1 Why polymers?

1.1.1 Generality

Polymers are everywhere in our everyday life. Both synthetic and natural polymers have unique properties (chemical, mechanical, electrical, thermal), which make them irreplaceable in the particular job they are called to do. The most impressive aspect in the world of polymers is the enormous variety of applications, which span from everyday consumer goods (house wares, toys, bottles, packaging, textiles, furniture), heavily used electrical and electronic items (computer, cable insulation, household appliances), construction (housing, pipes, adhesives, coatings, insulation), transportation (tires, appliance parts, hardware, carpeting), medical and hospital furniture and goods (gloves, syringes, catheters, bandage), to high-performance, sophisticated materials for aerospace, bulletproof vests, nonflammable fabric, artificial organs, degradable device for controlled release of drugs or chemicals, high-power-density batteries, high-strength cables for oceanic platforms, etc.

From a chemical point of view, polymers are high-molecular-weight compounds made up of simple repeating units called monomers. Molecular weights range from thousands to millions of atomic mass units, which makes writing a definitive molecular structure for these materials close to impossible. Polymer structures are therefore represented by enclosing the repeating unit (monomer) in brackets and placing "n" as subscript (Fig. 1.1a).

Polymers having more than one kind of repeating units are called copolymers; the units can be distributed either randomly in the chains or in an ordinate alternate sequence or in blocks. Moreover, the chains of the polymer structure may arrange in linear, branched, network, stars, ladder, or dendrimer fashion (Fig. 1.1b). Complex structures such as networks are formed when cross-linking occurs, i.e. the formation of covalent bonds between polymer chains; this process leads to a remarkable increase in molecular weight, and this in turn strongly influences chemical, physical, and mechanical properties of the material as well as its processability.

1.1.2 Synthesis

The first synthetic polymer that was produced on a commercial scale was Bakelite, a phenol-formaldehyde resin (by its inventor, the Belgian chemist Leo Baekeland [1]), at the beginning of 1900; however, it is the German chemist Hermann Staudinger who is

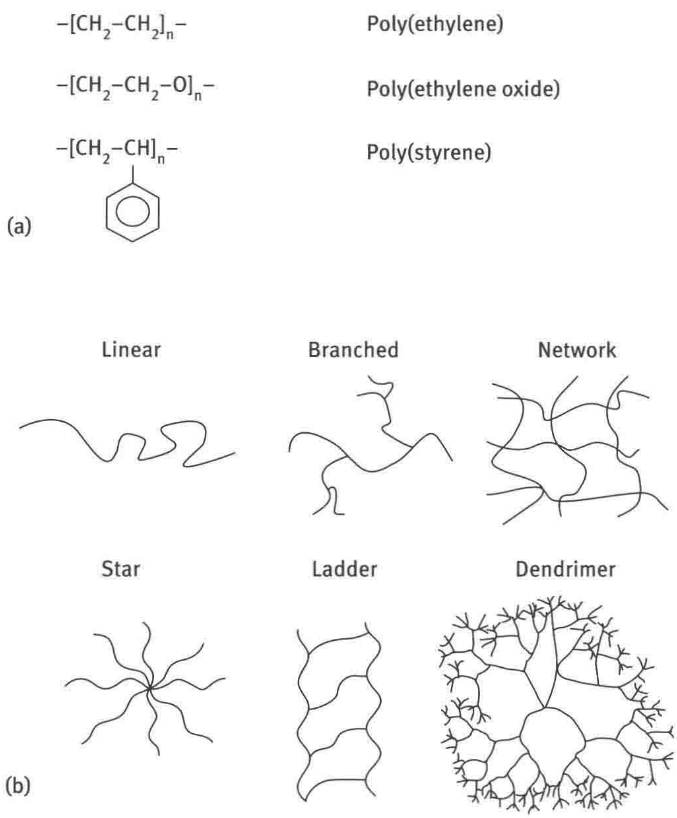


Fig. 1.1: (a) Conventional representation of polymers structures. (b) Arrangement of chains in the polymer structure.

rightly recognized as the father of the chemistry of macromolecules; for his studies on the relationship between structure of polymers and their properties, he received the Nobel Prize in Chemistry in 1953. During those years, polymer chemistry experienced the most significant advances and the beginning of a true revolution in the polymer industry, thanks to the work of Giulio Natta in Italy, who, for the first time, synthesized polymers having controlled stereochemistry [2] using the coordination catalysts developed by the German chemist Karl Ziegler [3]. The two scientists were awarded by the Nobel Prize in Chemistry in 1963. It was clearly demonstrated that polymers with similar chemical composition but exhibiting different molecular orientation have different morphology and their mechanical properties too may differ markedly. It is therefore vital, in view of commercial exploitation of polymer materials, to have full knowledge and control of the polymerization process. In brief, two reaction mechanisms are possible: step reaction (generally, a condensation reaction) and chain reaction (generally, an addition reaction). In the former, poly-functional monomers react randomly to give dimers, trimers, and oligomers, which can react with other monomers or among themselves: monomers are consumed rapidly, but polymer chains do