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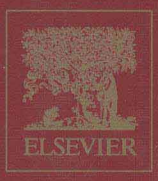

COMPREHENSIVE ANALYTICAL CHEMISTRY

EDITED BY

D. BARCELÓ

VOLUME 53

MOLECULAR CHARACTERIZATION AND ANALYSIS OF POLYMERS

EDITED BY

JOHN M. CHALMERS

ROBERT J. MEIER

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VOLUME **53**

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ELSEVIER

Amsterdam • Boston • Heidelberg • London
New York • Oxford • Paris • San Diego
San Francisco • Singapore • Sydney • Tokyo

Elsevier
Radarweg 29, PO Box 211, 1000 AE Amsterdam, The Netherlands
Linacre House, Jordan Hill, Oxford OX2 8DP, UK

First edition 2008

British Library Cataloguing in Publication Data
A catalogue record for this book is available from the British Library

Library of Congress Cataloging-in-Publication Data
A catalog record for this book is available from the Library of Congress

ISBN: 978-0-444-53056-1
ISSN: 0166-526X

Printed and bound in Hungary

08 09 10 11 12 10 9 8 7 6 5 4 3 2 1

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PREFACE

When, over three years ago, we were asked to commission a book on polymer analysis, our initial reaction was to decline, since we both believed that there was enough excellent books already published that dealt with the subject matter. However, we then contemplated that most existing books cover the subject from a technique point of view, that is, they tend to have a format in which individual chapters focus specifically on a single technique, such as mass spectrometry, nuclear magnetic resonance, vibrational spectroscopy, thermal analysis methods, chromatographic methods, etc. Occasionally, the scope is wider, if we can put it that way, but in these cases the focus is on a particular segment of the world of polymers. It was during our discussions on this viewpoint when our industrial experience kicked in, for which we recognised that the paramount desire of the "customer for polymer molecular characterization and analysis" is that of problem solving, not of championing a single or set of particular techniques. What these customers ideally require is a solution or information that enables them to solve or overcome a problem on a timescale that is relevant to the customers' business needs, whether they be research-related, production-related, property-related, service-related, marketing-related, competitive product deformulation,... It was with this mindset that we agreed to try to commission a book, the result of which you have in front of you, in which each chapter addresses a particular problem or property, for example, chain structure or chain end characterization, polymer degradation, molecular orientation, product failure,..., and in which the techniques were secondary, that is "a means to an end" rather than "how can I solve this problem/measure this property by the technique for which I am a recognised specialist?" The task we set for many of our authors was therefore often a very difficult one: that of providing as balanced a viewpoint as possible of the various techniques and methods that may be used to tackle a particular problem or property characterization, and how they may optimally complement each other, and their comparative limitations and strengths. This was our ultimate aim; that is, a text from which the essential information to tackle a problem, for which polymer analysis is required, could be readily distilled from its pages, and from which the supportive, confirmatory and complementary positions of the various measurement techniques could be readily grasped.

Our industrial experience should have forewarned us: while it is relatively easy to find well-recognised technique specialists, it did turn out, however, to be not trivial to find authors fully comfortable with covering the issues and all techniques from a problem-solving/property-related point of view. Some chapters might, therefore, from some specialist readers and reviewers perceptions, still have some missing issues albeit relevant. In other cases, for example, polymer degradation, optimum coverage has been achieved by including multiple chapters. Nevertheless, considering all the possible topics to be covered and the complexity of the issues involved, we believe most topics are well covered by the contributing authors, and, notwithstanding, we believe the coverage is comprehensive, and provides a unique text on the molecular characterization and analysis of polymers, and approaches our ideal closely.

As intimated above, reaching this point, that is publication of this book, has not been a straightforward task; the road has been sometimes rocky, with various professional and personal problems causing both the need to refine our original outline and the need along the way to commission late in the project new authors. To all our chapter authors, we are therefore truly indebted. For those whose chapters we have "sat on" for nearly two years, we especially thank you for your understanding and patience! For those who "stepped into the breach" near the end, we especially thank you for coming to our aid! We are also very thankful to the publishers, Elsevier Science B.V., for their patience too!

This book is divided up into sections. The first three chapters provide a background; sections that follow contain chapters dealing with polymer chain analysis, polymer morphology and structure, polymer degradation, polymer product analysis and support techniques. These are listed in more detail in Chapter 1, which also expands more fully on our industrial perception of the requirements for competence and appreciation in all techniques and methods for polymer molecular characterization and analysis. We hope you find this book of value and its approach both unique and technically informative and useful.

John Chalmers
Robert J. Meier
November 2008

SERIES EDITOR'S PREFACE

This volume on "Molecular Characterization and Analysis of Polymers" has been edited by John M. Chalmers and Robert J. Meier, both of whom have considerable experience in the industrial sector. They have compiled a broad compilation of chapters on the various aspects of polymer analysis and placed a clear and useful emphasis on problem solving, rather than on the techniques used.

The first three chapters layout the background; the following chapters deal with polymer chemistry and microstructure and polymeric materials, polymer chain analysis, polymer morphology and structure, polymer degradation, polymer product analysis, and polymer product development support techniques. The book contains a considerable amount of information on the techniques and methods used for polymer molecular characterization and analysis. Various techniques covered include analytical options for polymer product analysis, like size exclusion chromatography, thermal methods, nuclear magnetic resonance spectroscopy, electron spin resonance spectroscopy, mass spectrometry, infrared spectroscopy, gas chromatography-mass spectrometry and liquid chromatography-mass spectrometry.

The book is a useful addition to the *Comprehensive Analytical Chemistry* series and it is the first on the topic of polymer analysis in the series. A tremendous effort was made by the editors to achieve this compilation and as they say in their Preface "the road has been sometimes rocky".

Thanks to the editors and all contributing authors for their time and efforts in preparing this comprehensive compilation of research papers that will make this book on molecular characterization and analysis of polymers a unique reference in this field.

D. Barceló
Barcelona, April 14, 2008

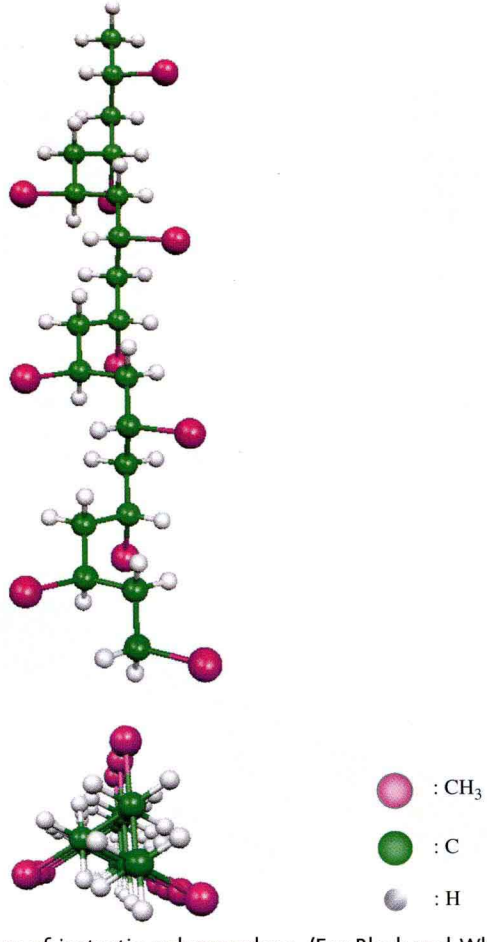

Plate 1 Helical structure of isotactic polypropylene. (For Black and White version, see page 33.)

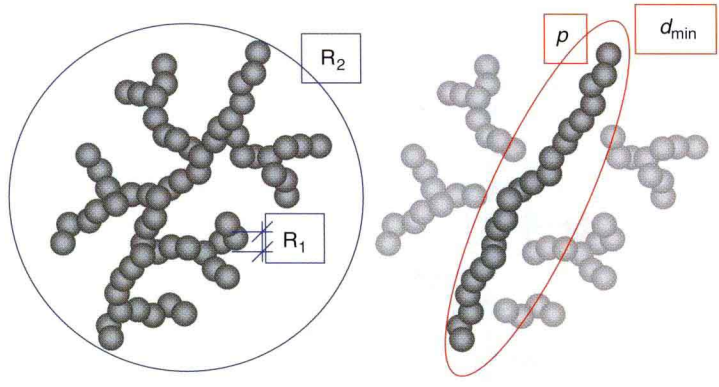

Plate 2 (a) Branched chain aggregate, (b) Branched chain aggregate; decomposed into the minimum path, *p*, and the branches [83]. Reprinted with permission from Beaucage [83]. Copyright 2004, American Physical Society. (For Black and White version, see page 151.)

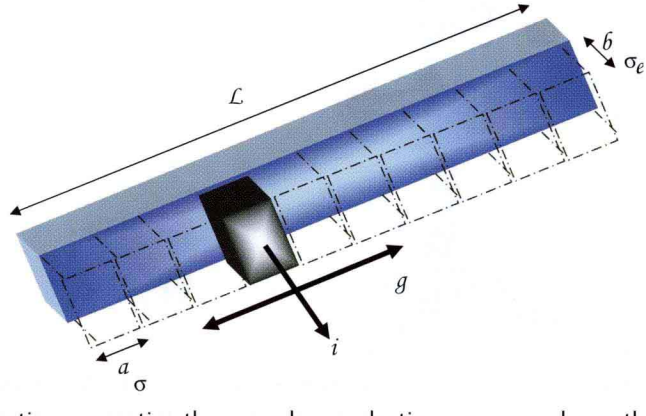

Plate 3 Schematic representing the secondary nucleation process and growth at the crystal face by spreading. The rates of these two processes are *i* and *g*, respectively. (For Black and White version, see page 154.)

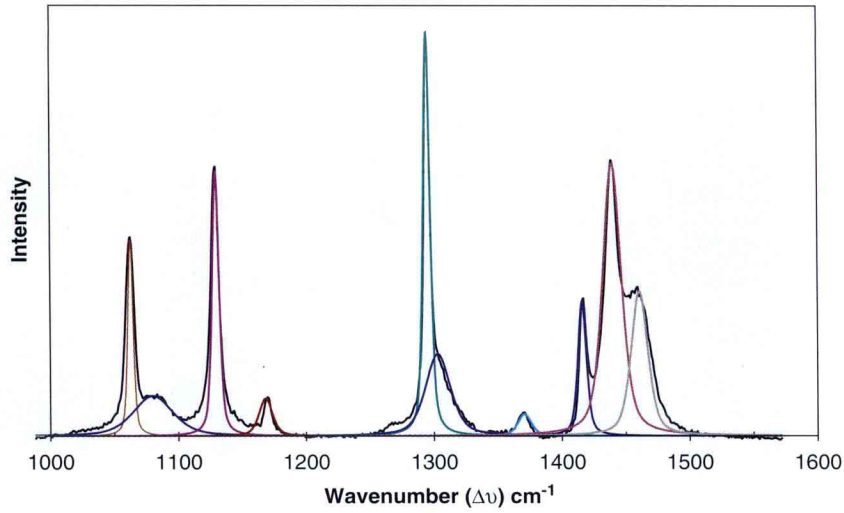

Plate 4 Raman spectra of orthorhombic ethylene 1-hexene copolymer with band fitting. The crystalline band at 1,416 cm^{-1}, and amorphous bands at 1,303 cm^{-1} and 1,080 cm^{-1} are used to compute the crystallinity content: $a_c = 0.52$, and the amorphous content: $a_a = 0.42$. (For Black and White version, see page 264.)

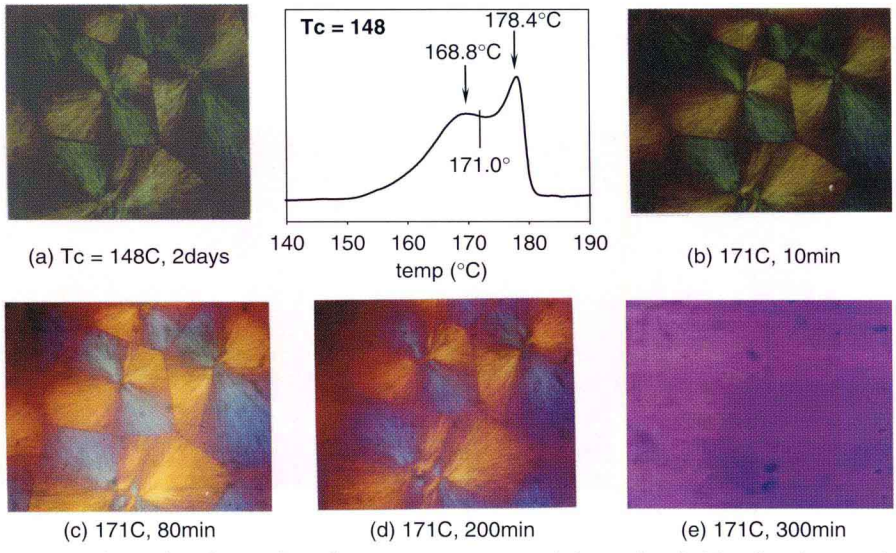

Plate 5 Isothermal melting of Ziegler–Natta isotactic poly(propylene). (a) Spherulites with mixed birefringence at $T_c = 148°C$. The top middle figure displays the melting for the same thermal history. (b) Subsequent to crystallization, the temperature was raised to 171°C; spherulites acquire negative birefringence. (c), (d) and (e) Isothermal melting at 171°C for 80, 200 and 300 min, respectively. Reproduced with permission from W.T. Huang, Dissertation, Florida State University, 2005. (For Black and White version, see page 281.)