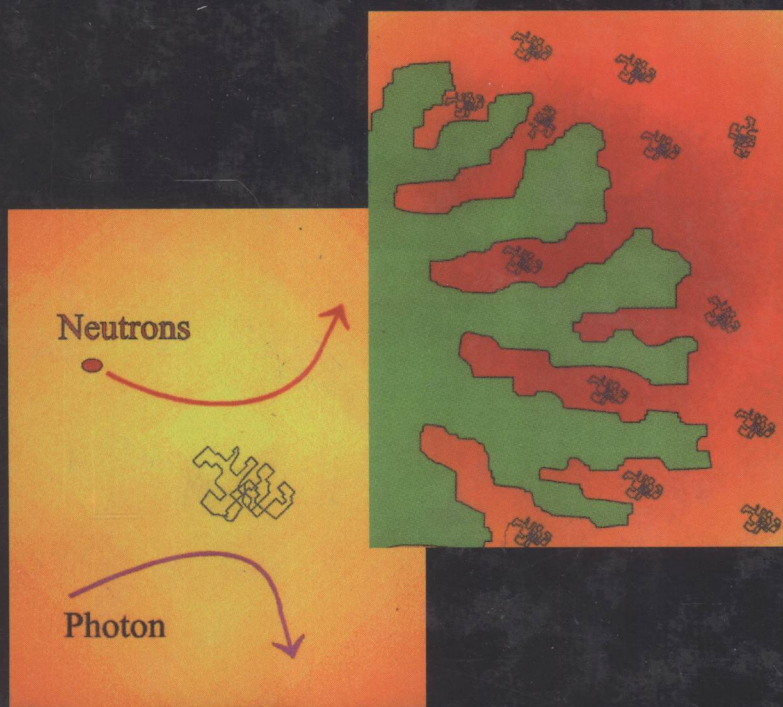


# Modern Techniques for Polymer Characterisation



*Edited by*

**R. A. Pethrick and J. V. Dawkins**

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E200000321

**JOHN WILEY & SONS**

Chichester • New York • Weinheim • Brisbane • Singapore • Toronto

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Baffins Lane, Chichester,  
West Sussex PO19 1UD, England

National 01243 779777  
International (+44) 1243 779777  
e-mail (for orders and customer service enquiries): cs-books@wiley.co.uk  
Visit our Home Page on <http://www.wiley.co.uk>  
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*Other Wiley Editorial Offices*

John Wiley & Sons, Inc., 605 Third Avenue,  
New York, NY 10158-0012, USA

WILEY-VCH Verlag GmbH, Pappelallee 3,  
D-69469 Weinheim, Germany

Jacaranda Wiley Ltd, 33 Park Road, Milton,  
Queensland 4064, Australia

John Wiley & Sons (Asia) Pte Ltd, Clementi Loop #02-01,  
Jin Xing Distripark, Singapore 129809

John Wiley & Sons (Canada) Ltd, 22 Worcester Road,  
Rexdale, Ontario M9W 1L1, Canada

***Library of Congress Cataloging-in-Publication Data***

Modern techniques for polymer characterisation/edited by R.A.  
Pethrick and J.V. Dawkins.

p. cm.

Includes bibliographical references and index.

ISBN 0-471-96097-7 (hb : alk.paper)

1. Polymers—Analysis. I. Pethrick, R.A. (Richard Arthur),  
1942— II. Dawkins, J.V.

QD139.P6M64 1999

547'.7046—dc21

98-45287

CIP

***British Library Cataloguing in Publication Data***

A catalogue record for this book is available from the British Library

ISBN 0-471-96097-7

Typeset in 10/12pt Times Roman by Laser Words, Madras, India

Printed and bound in Great Britain by Biddles Ltd, Guildford and King's Lynn

This book is printed on acid-free paper responsibly manufactured from sustainable forestation, in which at least two trees are planted for each one used for paper production

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# Preface

Recognition of macromolecules as a distinct state of matter owes much to the availability of various techniques for molar mass characterisation. In recent years, significant progress has been made into refining and developing these techniques so as to provide the experimentalist with both a more precise and more detailed picture of the products of their synthetic efforts. Traditionally, the effect of molar mass has been identified through changes in properties such as melting point, boiling point, vapour pressure and related phenomena.

Much of the early characterisation of polymeric materials relied on such techniques as viscosity, light scattering and the application of centrifugation to achieve molar mass data. These techniques provided an indication of the average molar mass of the polymer rather than precise information on the detailed distribution of chain lengths within a particular sample. Progress was made towards obtaining more detailed information with the appearance of gel permeation chromatography/size exclusion chromatography (GPC/SEC). This technique opened up measurement of molar mass distributions in a relatively easy manner to a wide group of polymer scientists. Its subsequent acceptance and exploitation is a credit to the fact that the technique has proved itself to be both relatively easy to apply to analysis, and is also relevant to the understanding of many physical properties. These techniques continue to undergo development, as evidenced by the significant number of publications on this subject. The original GPC/SEC studies were carried out using organic solvents. More recently, the use of aqueous SEC has broadened the field allowing a range of water soluble polymeric materials to be characterised. SEC is not only used for the examination of synthetic polymers, but also for a wide range of biopolymers. Over 300 papers have been published since 1995 on SEC and it has also been the subject of reviews. This book attempts to bring together some of the new emerging techniques which can assist and complement SEC and developments in some of the more conventional measurements based on fractionation and colligative property measurements.

The search for fractionation methodologies, considered to be complementary to and/or additional to GPC/SEC, continues. For complex polymers with

heterogeneities in composition/branching/tacticity, advantage can be taken of the capability of crystallisation/solubility in temperature rising elution fractionation (TREF). Field-flow fractionation is a class of separation techniques for application to a very wide range of polymeric species, avoiding potential problems which arise with some column packings in chromatographic methods. Chapters on the foundations of static scattering methods involving light and neutrons are included. These techniques have made important contributions to advances in polymer science for many years, but still have potential for development with the appearance of new polymer problems associated with new architectures. Copolymers, dendritic materials, hyperbranch co-materials and similar polymer structures are becoming more common, and hence present a challenge to those concerned with the development of techniques for polymer characterisation. Reviews of dynamic light scattering and neutron scattering studies of polymer dynamics are also included. Whereas in the past mass spectrometry (MS) has only found application to relatively low molar mass materials, the appearance of the techniques of electrospray ionisation (ES) and matrix assisted laser desorption ionisation–time of flight (MALDI–TOF) has allowed characterisation of macromolecular species. ES/MS has been largely directed to studies of biopolymers. The MALDI–TOF technique appears to provide significant potential for the future in particular for the individual mass distribution at single polymer resolution even at high molar masses. This technique opens up the possibility of obtaining detailed information on polymer structure which can be used to understand variations in physical properties or explore the subtleties of kinetic control during polymerisation. The MALDI–TOF technique is still in its development phase; however, it will surely become competitive with GPC/SEC for certain problems. More conventional techniques such as membrane osmometry, viscosity measurements, vapour phase osmometry and gel electrophoresis (for biopolymers) still have an important role to play in terms of characterisation of polymeric materials and are worthy of mention. Additionally, ultracentrifugation with new instrumentation has seen a resurgence of interest, and this chapter considers recent sedimentation data not only for determinations of molar masses and diffusion coefficients but also for binary gels.

The final chapter deals with colligative properties and amplifies the theme which is initially introduced in Chapter 11. Unfortunately, the authors had been delayed in submitting their manuscript and as a consequence it has been included out of sequence.

It was originally intended to encourage the authors to give their own experience with particular techniques and hence there is an apparent duplication in the area of TREF. The chapters deal with the subject in different ways and give the reader a deeper appreciation of the nature of the experiment. It is hoped that the reader may find these experimentally orientated review chapters of use as a source for information on the application of these techniques to polymeric problems.



The editors would like to thank Lesley Gilmour for maintaining contact with the authors and her help in the production of this book.

J.V. Dawkins

R.A. Pethrick

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# Chapter 1

# Temperature Rising Elution Fractionation

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## 1.1 INTRODUCTION

Temperature rising elution fractionation (TREF) is a technique developed to separate semicrystalline polymers according to differences in molecular structure or composition. These molecular level differences lead to changes in crystallinity and solubility. TREF has been mainly applied to the characterization of polyalkenes, especially polyethylene (PE) and its various copolymers, and more recently to polypropylene (PP) materials. In PE copolymers with  $\alpha$ -alkenes, differences in crystallinities are caused by different amounts and distributions of primarily short chain branches (SCB). Stereoisomerism in polypropylene is the controlling factor for crystallizability. TREF makes use of differences in molecular structure to fractionate polymer chains. Extensive and comprehensive reviews on the method have been published.<sup>1-3</sup>

TREF can be divided into crystallization and elution stages. In the crystallization stage, polymer is dissolved in a good solvent, and then allowed to crystallize under controlled conditions by slowly decreasing the temperature. Crystallization may take place on an inert support or the support may be added later. In the elution step, solvent is pumped through a column packed with the polymer-support mixture while the temperature is increased. Polymer elutes in the reverse order that it was crystallized, with less crystalline material eluting at lower temperatures followed by more crystalline polymer at higher temperatures.

The purpose of the present review is to provide detailed experimental procedures and indicate problems that can be anticipated using the TREF technique. In this regard an overview of the experimental conditions of various TREF