POLYMER DYNAMICS AND RELAXATION

Polymers exhibit a range of physical characteristics, from rubber-like elasticity to the glassy state. These particular properties are controlled at the molecular level by the mobility of the structural constituents. Remarkable changes in mobility can be witnessed with temperature, over narrow, well defined regions, termed relaxation processes. This is an important, unique phenomena controlling polymer transition behavior and is described here at an introductory level. The important types of relaxation processes from amorphous to crystalline polymers and polymeric miscible blends are covered, in conjunction with the broad spectrum of experimental methods used to study them. In-depth discussion of molecular level interpretation, including recent advances in atomistic level computer simulations and applications to molecular mechanism elucidation are discussed. The result is a self-contained, up-to-date approach to polymeric interpretation suitable for researchers and graduate students in materials science, physics and chemistry interested in the relaxation processes of polymeric systems.

RICHARD H. BOYD is a distinguished Professor Emeritus of Materials Science and Engineering and of Chemical Engineering at the University of Utah. He was awarded the Polymer Physics Prize from the American Physical Society and is the author of over 150 technical papers and book chapters.

GRANT D. SMITH is a Professor at the University of Utah. He is an NSF Career awardee and Humboldt Fellow. He is also the author of co-author of over 170 papers.

Cambridge University Press
978-0-521-81419-5 - Polymer Dynamics and Relaxation
Richard H. Boyd and Grant D. Smith
Frontmatter
More information

POLYMER DYNAMICS AND RELAXATION

RICHARD H. BOYD
Distinguished Professor Emeritus of Materials Science and Engineering and of Chemical Engineering, University of Utah

GRANT D. SMITH
Professor of Materials Science and Engineering, University of Utah

CAMBRIDGE
UNIVERSITY PRESS

CAMBRIDGE
UNIVERSITY PRESS

University Printing House, Cambridge CB2 8BS, United Kingdom

Cambridge University Press is part of the University of Cambridge.

It furthers the University's mission by disseminating knowledge in the pursuit of
education, learning and research at the highest international levels of excellence.

www.cambridge.org
Information on this title: www.cambridge.org/9780521814195

First published 2007
First paperback printing 2010

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

ISBN 978-0-521-81419-5 Hardback
ISBN 978-0-521-15291-4 Paperback

Cambridge University Press
978-0-521-81419-5 - Polymer Dynamics and Relaxation
Richard H. Boyd and Grant D. Smith
Frontmatter
More information

Contents

Cambridge University Press
978-0-521-81419-5 - Polymer Dynamics and Relaxation
Richard H. Boyd and Grant D. Smith
Frontmatter
More information

Cambridge University Press
978-0-521-81419-5 - Polymer Dynamics and Relaxation
Richard H. Boyd and Grant D. Smith
Frontmatter
More information

Cambridge University Press
978-0-521-81419-5 - Polymer Dynamics and Relaxation
Richard H. Boyd and Grant D. Smith
Frontmatter
More information

Preface

Polymers have become widely used materials because they exhibit an enormous range of behaviors and properties. They are most often processed or shaped as viscous melts. They can be used as stiff solid materials in the glassy or semicrystalline state. The rubbery or elastomeric state, obtained by cross-linking melts, is characterized by very high reversible extensibility and is unique to polymeric molecular organization. In addition, many applications are dependent upon the exhibition of behavior intermediate between that of the viscous melt and that of the relatively rigid glassy state. That is, the degree of rigidity is time dependent. In the solid state, major changes in physical properties can occur with changing temperature. Thus the same polymer can be a melt or, if cross-linked, an elastomer, or a somewhat rigid glass, or a quite rigid glass depending on the time and temperature of use. Further, these changes of properties occur in regions of time and temperature that are well defined. That is, the regions can be characterized by a variety of experimental techniques that probe the relaxation of the response following an applied perturbation such as mechanical stress or an electric field. Most polymers exhibit several such relaxation regions.

All of this rich manifold of behavior has its foundation in the ability of polymer molecules to locally change the details of the shape or conformation of the molecular chain and to accumulate these changes so that global changes in molecular shape can result. These local changes usually involve rotations about the constituent bonds and attendant responses of nearby bonds and surrounding chains. Energy barriers are involved and thus thermally activated responses result. This then leads to the time and temperature dependent character of a relaxation process. If relaxation processes are to be fully understood, then these molecular scale events have to be understood as well.

Four experimental methods are considered. Historically, perhaps the greatest early interest in relaxation phenomena centered on mechanical response as exemplified by creep and stress relaxation experiments. Concurrently, however, and

Cambridge University Press
978-0-521-81419-5 - Polymer Dynamics and Relaxation
Richard H. Boyd and Grant D. Smith
Frontmatter
More information

probably because mechanical experiments have often been considered difficult to carry out over broad ranges of time or frequency, dielectric response measurements where the short time, high frequency region is more conveniently accessed became popular. A very large literature has developed around both the mechanical and dielectric response methods. Somewhat later it was found that the decay of polarization of nuclear spins associated with the nuclear magnetic resonance (NMR) method was sensitive to motional processes and could be invoked as a tool for relaxation studies. The specificity to certain atoms in particular bonding environments is an advantage. That and the development of pulse techniques that allow wide ranges of time to be explored have led to increasingly important applications to polymer relaxations. Several scattering processes, including Rayleigh and Brillouin scattering of light and neutron scattering, are also sensitive to motional processes. But, of these, only neutron diffraction is considered here.

Experiments rarely give direct insight into the details of the molecular motions underlying relaxation processes. However, by rationalizing the results from several experimental techniques applied to groups of structurally similar but distinct polymers a reasonable mechanism can often be formulated. The process of molecular mechanism elucidation has been significantly aided by the advent of computer assisted detailed atomistic molecular modeling. Particularly valuable is the molecular dynamics method which gives the positions of every atom as a function of time. From this information time autocorrelation functions (ACF) can be constructed utilizing linear response theory that can be compared with experimental data for various techniques. The use of simulation as a tool in molecular interpretation is heavily stressed.