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978-0-521-86429-9 - Polymer Physics: Applications to Molecular Association and Thermoreversible Gelation
Fumihiko Tanaka
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Polymer Physics

The field of polymer science has advanced and expanded considerably in recent years, encompassing broader ranges of materials and applications. In this book, the author unifies the subject matter, pulling together research to provide an updated and systematic presentation of polymer association and thermoreversible gelation, one of the most rapidly developing areas in polymer science. Starting with a clear presentation of the fundamental laws of polymer physics, subsequent chapters discuss a new theoretical model that combines thermodynamic and rheological theory. Recent developments in polymer physics are explored, along with important case studies on topics such as self-assembly, supramolecules, thermoreversible gels, and water-soluble polymers. Throughout the book, a balance is maintained between theoretical descriptions and practical applications, helping the reader to understand complex physical phenomena and their relevance in industry. This book has wide interdisciplinary appeal and is aimed at students and researchers in physics, chemistry, and materials science.

Fumihiko Tanaka is Professor in the Department of Polymer Chemistry at the Graduate School of Engineering, Kyoto University. Professor Tanaka has published extensively and his current research interests are in theoretical aspects of phase transitions in polymeric systems, polymer association, and thermoreversible gelation.

Polymer Physics

Applications to Molecular Association and Thermoreversible Gelation

FUMIHIKO TANAKA

Kyoto University, Japan

CAMBRIDGE
UNIVERSITY PRESS

CAMBRIDGE UNIVERSITY PRESS
Cambridge, New York, Melbourne, Madrid, Cape Town,
Singapore, São Paulo, Delhi, Tokyo, Mexico City

Cambridge University Press
The Edinburgh Building, Cambridge CB2 8RU, UK

Published in the United States of America by Cambridge University Press, New York

www.cambridge.org
Information on this title: www.cambridge.org/9780521864299

First published 2011

Printed in the United Kingdom at the University Press, Cambridge

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

Library of Congress Cataloguing in Publication data
Tanaka, F. (Fumihiko), 1947–
Polymer Physics: Applications to Molecular Association
and Thermoreversible Gelation / Fumihiko Tanaka.
p. cm.
Includes bibliographical references and index
ISBN 978-0-521-86429-9 (Hardback)
1. Polymers. 2. Gelation. 3. Polymer colloids. I. Title.
QC173.4.P65T36 2011
547′.7–dc22 2010051430

ISBN 978-0-521-86429-9 Hardback

Dedicated to the memory of
Professor Walter H. Stockmayer
and to
Sir Sam Edwards

Miracle of polymer science

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Preface

Polymer science has expanded over the past few decades and shifted its centre of interest to encompass a whole new range of materials and phenomena. Fundamental investigations on the molecular structure of polymeric liquids, gels, various phase transitions, alloys and blends, molecular motion, flow properties, and many other interesting topics, now constitute a significant proportion of the activity of physical and chemical laboratories around the world.

But beneath the luxuriance of macromolecular materials and observable phenomena, there can be found a common basis of concepts, hypotheses, models, and mathematical deductions that are supposed to belong to only few theories.

One of the major problems in polymer physics which remain unsolved is that of calculating the materials properties of self-assembled supramolecules, gels, molecular complexes, etc., in solutions of associating polymers from first principles, utilizing only such fundamental properties as molecular dimensions, their functionality, and intermolecular associative forces (hydrogen bonding, hydrophobic force, electrostatic interaction, etc.).

Theoretical studies of polymer association had not been entirely neglected, but their achievements were fragmentary, phenomenological, and lacked mathematical depth and rigor. What I have tried to do, therefore, is to show how certain physically relevant phenomena derive from the defining characteristics of various simple theoretical model systems.

The goal of this book is thus to present polymer physics as generally as possible, striving to maintain the appropriate balance between theoretical descriptions and their practical applications.

During the decade that has just ended the application of the method of lattice theory (by Flory and Huggins), the scaling theory (by de Gennes) of polymer solutions, and the theory of gelation reaction (by Flory and Stockmayer) has resulted in the development of what has become known as the "theory of associating polymer solutions." This has brought the aforementioned unsolved problem markedly nearer to the resolution.

In this book special reference is made to polymer associations of various types – binding of small molecules by polymers, polymer hydration, block-copolymerization, thermoreversible gelation, and their flow properties. These topics do not, by any means, exhaust the possibilities of the method. They serve, however, to illustrate its power. The author hopes that others will be stimulated by what has already been done to attempt further applications of the theory of associating polymer solutions.

Most of the subject matter treated in the present book has been hitherto available only in the form of original papers in various scientific journals. These have been very diverse and fragmented. Consequently, they may have appeared difficult to those who start the research and practice on the subjects. The opportunity has therefore been taken to develop the theoretical bases from the unified view and to give the practical applications in somewhat greater detail.

The first four chapters, making up the fundamental part, contain reviews of the latest knowledge on polymer chain statistics, their reactions, their solution properties, and the elasticity of cross-linked networks. Each chapter starts from the elementary concepts and properties with a description of the theoretical methods required to study them. Then, they move to an organized description of the more advanced studies, such as coil–helix transition, hydration, the lattice theory of semiflexible polymers, entropy catastrophe, gelation with multiple reaction, cascade theory, the volume phase transition of gels, etc. Most of them are difficult to find in the presently available textbooks on polymer physics.

Next, Chapter 5 presents the equilibrium theory of associating polymer solutions, one of the major theoretical frameworks for the study of polymer association and thermoreversible gelation.

This is followed by three chapters on the application of the theory to nongelling and gelling solutions. Chapter 6 on nongelling associating solutions includes block polymerization by hydrogen bonding, hydration of water-soluble polymers, hydrogen-bonding liquid crystallization, and micellization by hydophobic aggregation. Chapter 7 treats more interesting but difficult gelling solutions, with stress on phase separation and thermoreversible gelation with junctions of variable multiplicity. Chapter 8 presents two major methods for the study of gels near the sol–gel transition point. One is the topological method on the basis of graph theory, and the other is scaling theory on the basis of the percolation picture.

Chapter 9 presents the transient network theory of associating polymer solutions, which is the other one of the two major theories treated in this book. It studies the dynamic and rheological flow properties of structured solutions from a molecular point of view. Thus, linear complex modulus, nonlinear stationary viscosity, start-up flows, and stress relaxation in reversible polymer networks are studied in detail.

Chapter 10 presents an application of the two theoretical frameworks to more complex, but important systems, such as a mixture of polymers and surfactants, and network formation accompanied by polymer conformational transitions.

This work is a result of the research the author has done over the past two decades with many collaborators. I would like to thank Dr. A. Matsuyama and Dr. M. Ishida (Shoji) for their outstanding contribution to the hydration and thermoreversible gelation of water-soluble polymers while they were graduate students at Tokyo University of Agriculture and Technology. I would also like to thank Dr. Y. Okada who, while studying for his Ph.D under my supervision at Kyoto University, took the initiative of studying the cooperative hydration of temperature-sensitive polymers, giving me no option but to get up to date on this topic. The contribution by Dr. T. Koga to the rheological study of transient networks must also be acknowledged.

It is also a great pleasure to thank Professor Françoise M. Winnik for her research collaboration over the past decade: she has never stopped stimulating and encouraging me with her enthusiasm in the research of water-soluble polymers.

Finally, it is my great pleasure and honor to thank Professor Ryogo Kubo and Sir Sam Edwards, who in my early career introduced me to the fascinating world of statistical mechanics.

Fumihiko Tanaka
Kyoto July 2010