

Cambridge University Press

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

Fumihiko Tanaka

Frontmatter

[More information](#)

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.

Cambridge University Press

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

Fumihiko Tanaka

Frontmatter

[More information](#)

Polymer Physics

Applications to Molecular
Association and
Thermoreversible
Gelation

FUMIHIKO TANAKA

Kyoto University, Japan



CAMBRIDGE
UNIVERSITY PRESS

Cambridge University Press

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

Fumihiko Tanaka

Frontmatter

[More information](#)

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

© Fumihiko Tanaka 2011

This publication is in copyright. Subject to statutory exception
and to the provisions of relevant collective licensing agreements,
no reproduction of any part may take place without the written
permission of Cambridge University Press.

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

Cambridge University Press has no responsibility for the persistence or
accuracy of URLs for external or third-party internet websites referred to in
this publication, and does not guarantee that any content on such websites is,
or will remain, accurate or appropriate.

Cambridge University Press

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

Fumihiko Tanaka

Frontmatter

[More information](#)

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

Miracle of polymer science

Contents

	<i>Preface</i>	<i>page</i> xiii
1	Statistical properties of polymer chains	1
	1.1 Conformation of polymers	1
	1.1.1 Internal coordinates of a polymer chain and its hindered rotation	1
	1.1.2 Coarse-grained models of polymer chains	3
	1.2 The ideal chain	5
	1.2.1 Single-chain partition function	5
	1.2.2 Tension–elongation curve	8
	1.2.3 Distribution of the end-to-end vector	10
	1.3 Fundamental properties of a Gaussian chain	11
	1.4 Effect of internal rotation and stiff chains	13
	1.4.1 Characteristic ratio	13
	1.4.2 Persistence length and the stiff chain	15
	1.5 Excluded-volume effect	16
	1.6 Scaling laws and the temperature blob model	19
	1.7 Coil–globule transition of a polymer chain in a poor solvent	21
	1.8 Coil–helix transition	23
	1.9 Hydration of polymer chains	33
	1.9.1 Statistical models of hydrated polymer chains	33
	1.9.2 Models of the globules and hydrated coils	38
	1.9.3 Competitive hydrogen bonds in mixed solvents	39
	References	44
2	Polymer solutions	46
	2.1 Thermodynamics of phase equilibria	46
	2.1.1 Gibbs’ phase rule and phase diagrams	46
	2.1.2 Stability of a phase	48
	2.1.3 Liquid–liquid separation by a semipermeable membrane	52
	2.1.4 Spontaneous liquid–liquid phase separation	55
	2.2 Characteristic properties of polymer solutions	57
	2.2.1 Vapor pressure and osmotic pressure	58

viii	Contents	
	2.2.2	Viscosity 61
	2.2.3	Diffusion of a polymer chain 65
2.3		Lattice theory of polymer solutions 69
	2.3.1	The free energy of mixing 69
	2.3.2	Properties of polymer solutions predicted by Flory–Huggins lattice theory 74
	2.3.3	Extension to many-component polymer solutions and blends 79
	2.3.4	Refinement beyond the simple mean field approximation 81
2.4		Scaling laws of polymer solutions 87
	2.4.1	Overlap concentration 87
	2.4.2	Correlation length 89
	2.4.3	Radius of gyration 90
	2.4.4	Osmotic pressure 91
	2.4.5	Phase equilibria (reduced equation of states) 92
	2.4.6	Molecular motion 94
		References 95
3	Classical theory of gelation	97
	3.1	What is a gel? 97
	3.1.1	Definition of a gel 97
	3.1.2	Classification of gels 97
	3.1.3	Structure of gels and their characterization 98
	3.1.4	Examples of gels 100
	3.2	Classical theory of gelation 103
	3.2.1	Random branching 104
	3.2.2	Polycondensation 106
	3.2.3	Polydisperse functional monomers 111
	3.2.4	Cross-linking of prepolymers 113
	3.3	Gelation in binary mixtures 114
	3.3.1	Finding the gel point using the branching coefficient 114
	3.3.2	Molecular weight distribution function of the binary mixtures $R\{A_f\}/R\{B_g\}$ 116
	3.3.3	Polydisperse binary mixture $R\{A_f\}/R\{B_g\}$ 118
	3.3.4	Gels with multiple junctions 119
	3.A	Moments of the Stockmayer distribution function 121
	3.B	Cascade theory of gelation 122
		References 127
4	Elasticity of polymer networks	128
	4.1	Thermodynamics of rubber elasticity 128
	4.1.1	Energetic elasticity and entropic elasticity 128
	4.1.2	Thermoelastic inversion 131
	4.1.3	Gough–Joule effect 131

Contents		ix
4.2	Affine network theory	133
4.2.1	Local structure of cross-linked rubbers	133
4.2.2	Affine network theory	134
4.2.3	Elastically effective chains	139
4.2.4	Simple description of thermoelastic inversion	141
4.3	Phantom network theory	142
4.3.1	Micronetworks of tree form	143
4.3.2	Fluctuation theorem and the elastic free energy	145
4.4	Swelling experiments	146
4.5	Volume transition of gels	150
4.5.1	Free swelling	153
4.5.2	Swelling under uniaxial elongation	154
4.6	Networks made up of nonlinear chains	156
	References	159
5	Associating polymer solutions and thermoreversible gelation	160
5.1	Historical survey of the study of associating solutions	160
5.2	Statistical thermodynamics of associating polymers	161
5.2.1	Pregel regime	167
5.2.2	Sol–gel transition and postgel regime	168
5.3	Renormalization of the interaction parameters	168
5.4	Phase separation, stability limit, and other solution properties	169
5.5	Scattering function of associating polymer mixtures	170
5.A	Renormalization of the interaction parameters	173
5.B	Scattering function in RPA	175
5.C	Spinodal condition in RPA	177
	References	178
6	Nongelling associating polymers	180
6.1	Dimer formation as associated block-copolymers	180
6.2	Linear association and ring formation	186
6.3	Side-chain association	189
6.4	Hydration in aqueous polymer solutions and closed-loop miscibility gaps	197
6.5	Cooperative hydration in solutions of temperature-responsive polymers	200
6.6	Hydrogen-bonded liquid-crystalline supramolecules	207
6.7	Polymeric micellization	212
	References	219
7	Thermoreversible gelation	222
7.1	Models of thermoreversible gelation	222
7.2	Application of the classical theory of gelation	224

x	Contents	
	7.2.1	Pregel regime 226
	7.2.2	The gel point 227
	7.2.3	Postgel regime 228
	7.2.4	Phase diagrams of thermoreversible gels 232
7.3	Thermodynamics of sol–gel transition as compared with Bose–Einstein condensation 233	
7.4	Thermoreversible gels with multiple cross-linking 235	
	7.4.1	Multiple association 235
	7.4.2	Distribution function of multiple trees 237
	7.4.3	The average molecular weight and the condition for the gel point 240
	7.4.4	Solution properties of thermoreversible gels with multiple junctions 242
	7.4.5	Simple models of junction multiplicity 243
	References	245
8	Structure of polymer networks	247
	8.1	Local structure of the networks–cross-linking regions 247
	8.2	Global structure of the networks – elastically effective chains and elastic modulus 250
	8.2.1	Fundamental parameters of the network topology 250
	8.2.2	Structure parameters of multiply cross-linked gels 252
	8.2.3	The number of elastically effective chains 258
	8.3	Percolation model 262
	8.3.1	Percolation threshold 262
	8.3.2	Distribution function of clusters 265
	8.3.3	Percolation in one dimension 266
	8.3.4	Site percolation on the Bethe lattice 268
	8.4	Self-similarity and scaling laws 269
	8.4.1	Static scaling laws 269
	8.4.2	Viscoelastic scaling laws 273
	8.5	Percolation in continuum media 276
	8.5.1	Critical volume fraction of percolation 276
	8.5.2	Gelation of sticky hard spheres (Baxter’s problem) 277
	References	279
9	Rheology of thermoreversible gels	281
	9.1	Networks with temporal junctions 281
	9.1.1	Models of transient networks 282
	9.1.2	Equilibrium solutions 286
	9.1.3	Stress–strain relation 289
	9.1.4	Integral form of the equation 290
	9.1.5	Generalization of the model 292

Contents	xi
9.2 Linear response of transient networks	292
9.2.1 The Green–Tobolsky limit	295
9.2.2 Exponential dissociation rate	296
9.2.3 Power-law dissociation rate	297
9.2.4 Coupling to the tension	298
9.3 Stationary flows	299
9.3.1 GT limit and quadratic β	300
9.3.2 Coupling to the tension	302
9.3.3 Expansion in powers of the shear rate	303
9.3.4 Elongational flows	305
9.4 Time-dependent flows	309
9.4.1 Transient flows of Gaussian networks in the GT limit	309
9.4.2 Start-up shear flows with tension–dissociation coupling	311
9.4.3 Nonlinear stress relaxation	316
9.A Expansion in powers of the shear rate and time	321
9.B Solvable model of the quadratic dissociation rate	322
9.B.1 Start-up and stationary flows	323
9.B.2 Stress relaxation	328
References	329
10 Some important thermoreversible gels	331
10.1 Polymer–surfactant interaction	331
10.1.1 Modification of the gel point by surfactants	333
10.1.2 Surfactant binding isotherms	335
10.1.3 CMC of the surfactant molecules	336
10.1.4 High-frequency elastic modulus	338
10.2 Loop-bridge transition	339
10.3 Competing hydration and gelation	345
10.3.1 Models of competitive hydration and gelation	345
10.3.2 Degree of hydration and the gel point	349
10.4 Coexisting hydration and gelation	352
10.5 Thermoreversible gelation driven by polymer conformational change	359
10.5.1 Models of conformational transition	361
10.5.2 Theory of gelation with conformation change	363
10.5.3 Simple models of excitation	367
10.6 Thermoreversible gelation driven by the coil–helix transition of polymers	370
10.6.1 Models of helix association	372
10.6.2 Multiple helices	374
10.6.3 Multiple association of single helices	378
References	379
<i>Index</i>	383

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 hydrophobic 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.

Cambridge University Press

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

Fumihiko Tanaka

Frontmatter

[More information](#)

Preface

xv

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