# **Polymer Physics**

### MICHAEL RUBINSTEIN

University of North Carolina, Chapel Hill, North Carolina, USA

and

RALPH H. COLBY

Pennsylvania State University, University Park, Pennsylvania, USA



ISBN-10: 0-19-852059-X ISBN-13: 978-0-19-852059-7 Publication date: 26 June 2003 454 pages, 246x189 mm

#### corrections from

http://felix.metsce.psu.edu/rheology/principal/papers\_local/CorrectionsFor2004Printing.pdf http://felix.metsce.psu.edu/rheology/principal/papers\_local/CorrectionsFor2007Printing.pdf are included

### **Preface**

This book introduces the reader to the fascinating field of polymer physics. It is intended to be utilized as a textbook for teaching upper level undergraduates and first year graduate students about polymers. Any student with a working knowledge of calculus, chemistry, and physics should be able to read this book. The essential tools of the polymer physical chemist or engineer are derived in this book without skipping any steps. Hence, the book is a self-contained treatise that should also serve as a useful reference for scientists and engineers working with polymers.

While the book assumes no prior knowledge of polymers, it goes far beyond introductory polymer texts in the scope of what is covered. The fundamental concepts required to fully understand polymer melts, solutions and gels in terms of both static structure and dynamics are explained in detail. Problems at the end of each chapter provide the reader with the opportunity to apply what has been learned to practice. More challenging problems are denoted by an asterisk.

The book is divided into four parts. After an introduction in Chapter 1, where the necessary concepts from a first course on polymers are summarized, the conformations of single polymer chains are treated in Part 1. Part 2 deals with the thermodynamics of polymer solutions and melts, including the conformations of chains in those states. Part 3 applies the concepts of Part 2 to the formation and properties of polymer networks. Finally, Part 4 explains the essential aspects of how polymers move in both melt and solution states. In all cases, attention is restricted to concepts that are firmly entrenched in the field, with less established uses of those concepts relegated to the problems.

The motivation for our writing this book comes from the fact that its primary antecedent, written by Paul Flory, is now 50 years old. Many of the same concepts are re-introduced in modern language. Other concepts introduced by eminent scientists over the past half-century are derived in simpler ways, with the intention of making them accessible to a broader audience. These include many of the important concepts discussed in the excellent monographs by de Gennes and by Doi and Edwards.

The book is titled Polymer Physics largely because the authors share the viewpoint of Lord Ernest Rutherford:

'Science is divided into two categories, physics and stamp-collecting.'

The foundations of this book arose from debates between the authors while they were employed for 10 glorious years at the Eastman Kodak Company. While the authors continue to debate many aspects of science, the contents of this book have emerged as the essence of what they claim to

#### Preface

understand in polymer physics, bearing in mind the wisdom of Werner Heisenberg:

'Science progresses not only because it helps to explain newly discovered facts, but also because it teaches us over and over again what the word understanding may mean.'

The authors thank Jack Chang, Dennis Massa, Glen Pearson, and John Pochan for giving the authors the freedom to ponder polymer physics. The authors also thank David Boris, Andrey Dobrynin, Mark Henrichs, Christine Landry, Mike Landry, Charlie Lusignan, Don Olbris, Ravi Sharma, Yitzhak Shnidman, and Jeff Wesson for their participation in our arguments during informal weekly meetings during the Kodak years. The readers of this book are indebted to Mireille Adam, Peter Bermel, Andrey Dobrynin, Randy Duran, Brian Erwin, Liang Guo, Alexander Grosberg, Jean–Francois Joanny, Sanat Kumar, Eugenia Kumacheva, Tom Mourey, Katherine Oates, Jai Pathak, Nopparat Plucktaveesak, Jennifer Polley, Ed Samulski, Sergei Panyukov, Jay Schieber, and Sergei Sheiko for comments on the text that greatly improved the clarity of the presentation. We thank the Institute for Theoretical Physics for hospitality during the completion of the book.

## **Contents**

1	Int	roduc	tion the state of	]	
	1.1	Histor	ry of polymer science	1	
	1.2	Polym	ner microstructure	1	
	1.3	Homo	opolymers and heteropolymers		
	1.4	Fracta	al nature of polymer conformations	-	
	1.5	Types	s of polymeric substances	12	
		1.5.1	Polymer liquids	12	
		1.5.2	Polymer solids	13	
		1.5.3	Liquid crystal polymers	13	
	1.6	Mola	r mass distributions	10	
		1.6.1	Binary distributions	19	
		1.6.2	Linear condensation polymers	20	
		1.6.3	Linear addition polymers	2:	
	1.7	Mola	r mass measurements	20	
		1.7.1	Measuring $M_n$ by osmotic pressure	20	
		1.7.2	Measuring $M_{\rm w}$ by scattering	29	
		1.7.3	Intrinsic viscosity	3.	
		1.7.4	Size exclusion chromatography	3:	
	1.8	Sumn	nary	33	
	Prol	olems		3!	
	Bibli	iograph	y	4:	
			I Single chain conformations		
2	Ide	eal ch	ains	4	
	2,1	Flexil	bility mechanisms	49	
	2.2	2 Conformations of an ideal chain		5	
	2.3	3 Ideal chain models			
		2.3.1	Freely rotating chain model	5:	
		2.3.2	Worm-like chain model	5	
		2.3.3	Hindered rotation model	5	
		2.3.4	Rotational isomeric state model	5	
	2.4	Radiı	us of gyration	6	
		2.4.1	Radius of gyration of an ideal linear chain	6	
			Radius of gyration of a rod polymer	6	
		2.4.3	Radius of gyration of an ideal branched polymer		
			(Kramers theorem)	6	

vii

11	Contents	
	2.5 Distribution of end-to-end vectors	66
	2.6 Free energy of an ideal chain	70
	2.6.1 Scaling argument for chain stretching	72
	2.6.2 Langevin dependence of elongation on force	74
	2.7 Pair correlations of an ideal chain	78
	2.8 Measurement of size by scattering	79
	2.8.1 Scattering wavevector	79
	2.8.2 Form factor	81
	2.8.3 Measuring $R_g^2$ by scattering at small angles	83
	2.8.4 Debye function	85
	2.9 Summary of ideal chains	88
	Problems	90
	Bibliography	96
3	Real chains	97
_	3.1 Excluded volume and self-avoiding walks	98
	3.1.1 Mayer f-function and excluded volume	98
	3.1.2 Flory theory of a polymer in good solvent	102
	3.2 Deforming real and ideal chains	104
	3.2.1 Polymer under tension	104
	3.2.2 Polymer under compression	107
	3.2.3 Adsorption of a single chain	110
	3.3 Temperature effects on real chains	113
	3.3.1 Scaling model of real chains	113
	3.3.2 Flory theory of a polymer in a poor solvent	115
	3.3.3 Temperature dependence of the chain size	117
	3.3.4 Second virial coefficient	119
	3.4 Distribution of end-to-end distances	121
	3.5 Scattering from dilute solutions	122
	3.6 Summary of real chains	125
	Problems	127
	Bibliography	133
	II Thermodynamics of blends and solutions	
4	Thermodynamics of mixing	137
	4.1 Entropy of binary mixing	137
	4.2 Energy of binary mixing	140
	4.3 Equilibrium and stability	146
	4.4 Phase diagrams	150
	4.5 Mixtures at low compositions	154
	4.5.1 Osmotic pressure	155
	4.5.2 Polymer melts	157
	4.6 Experimental investigations of binary mixtures	159
	4.7 Summary of thermodynamics	163
	Problems	165
	Bibliography	170

	Contents	ix
5	Polymer solutions	171
_	5.1 Theta solvent	171
	5.2 Poor solvent	173
	5.3 Good solvent	176
	5.3.1 Correlation length and chain size	176
	5.3.2 Osmotic pressure	181
	5.4 Semidilute theta solutions	183
	5.4.1 Correlation length	183
	5.4.2 Osmotic pressure	184
	5.5 The Alexander – de Gennes brush	186
	5.6 Multichain adsorption	187
	5.7 Measuring semidilute chain conformations	189
	5.8 Summary of polymer solutions	190
	Problems	191
	Bibliography	196
	III Networks and gelation	
6	Random branching and gelation	199
	6.1 Introduction	199
	6.1.1 Percolation around us	202
	6.1.2 Percolation in one dimension	205
	6.2 Branching without gelation	206
	6.2.1 Hyperbranched polymers	206
	6.2.2 Regular dendrimers	211
	6.3 Gelation: concepts and definitions	213
	6.4 Mean-field model of gelation	215
	6.4.1 Gel point	216
	6.4.2 Sol and gel fractions	217
	6.4.3 Number-average molar mass below the gel point	218
	6.4.4 Weight-average molar mass below the gel point	219
	6.4.5 Molar mass distribution	220
	6.4.6 Size of ideal randomly branched polymers	224
	6.5 Scaling model of gelation	227
	6.5.1 Molar mass distribution and gel fraction	227
	6.5.2 Cutoff functions	231
	6.5.3 Size and overlap of randomly branched polymers	234
	6.5.4 Vulcanization universality class	237
	6.6 Characterization of branching and gelation	241
	6.7 Summary of branching and gelation	244
	Problems	247
	Bibliography	252
7	Networks and gels	253
	7.1 Thermodynamics of rubbers	253
	7.1.1 Flory construction	255
	7.2 Unentangled rubber elasticity	255

X Contents

7.2.1 Affine network model

7.2.3 Finite extensibility

7.2.2 Phantom network model

255

259

263

7.3	Entangled rubber elasticity	264
	7.3.1 Chain entanglements and the Edwards tube model	264
	7.3.2 The Mooney–Rivlin model	268
	7.3.3 Constrained fluctuations models	269
7.4	Swelling of polymer gels	274
	7.4.1 Swelling in $\theta$ -solvents	276
	7.4.2 Swelling in athermal solvents	277
	7.4.3 Swelling in good solvents	278
7.5	ŭ ŭ	280
7.6	2,	282
	7.6.1 Stress relaxation after a step strain	284
	7.6.2 The Boltzmann superposition principle	285
	7.6.3 Steady shear	286
	7.6.4 Creep and creep recovery	288
	7.6.5 Oscillatory shear	290
7.7	-,	294
	blems	295
Bib	liography	305
	IV Dynamics	
8 Un	entangled polymer dynamics	309
8.1	• • •	311
8.2	Zimm model	312
8.3	Intrinsic viscosity	314
8.4	Relaxation modes	319
	8.4.1 Rouse modes	319
	8.4.2 Zimm modes	323
8.5	Semidilute unentangled solutions	325
8.6	Modes of a semiflexible chain	330
	8.6.1 Bending energy and dynamics	330
	8.6.2 Tensile modulus and stress relaxation	333
8.7	Temperature dependence of dynamics	334
	8.7.1 Time-temperature superposition	334
	8.7.2 Transition zone of polymer melts	339
	8.7.3 Short linear polymer melts	340
8.8	Randomly branched polymers	341
8.9	Dynamic scattering	345
8.10	Summary of unentangled dynamics	350
Prob		352
Biblic	ography	360

	Contents	
) Ent	angled polymer dynamics	3
9.1		3
9.2	Reptation in polymer melts	3
	9.2.1 Relaxation times and diffusion	3
	9.2.2 Stress relaxation and viscosity	3
9.3	Reptation in semidilute solutions	3
	9.3.1 Length scales	3
	9.3.2 Entanglement concentration	3
	9.3.3 Plateau modulus	3
	9.3.4 Relaxation times and diffusion	3
	9.3.5 Stress relaxation and viscosity	3
9.4	Dynamics of a single entangled chain	
	9.4.1 Chain in an array of fixed obstacles	3
	9.4.2 Entangled star polymers	
	9.4.3 H-polymers and combs	:
	9.4.4 Monomer displacement in entangled linear melts	
	9.4.5 Tube length fluctuations	;
9.5	Many-chain effects: constraint release	
	9.5.1 Relaxation times and diffusion	
	9,5.2 Stress relaxation	
9.6	Computer simulations in polymer physics	
	9.6.1 Molecular dynamics	
	9.6.2 Monte Carlo	
9.7	Summary of entangled dynamics	
Pro	plems	
Bibl	iography	
Notati	ions	
Index		
Corre	ctions	

