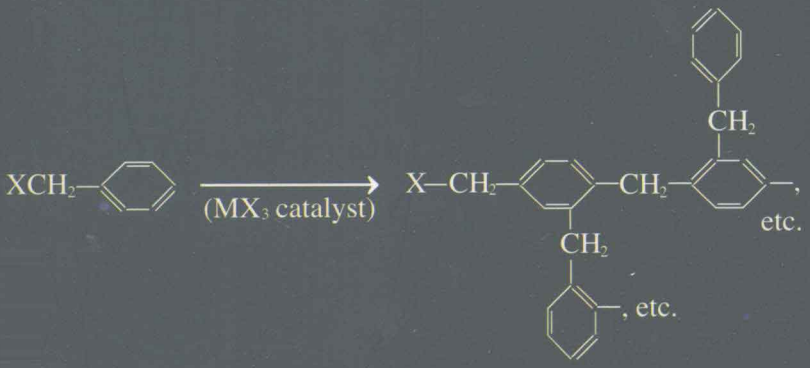
Principles of Polymer Chemistry

高分子化学原理

Paul J.Flory



Cornell University Press
世界图书出版公司

PRINCIPLES OF POLYMER CHEMISTRY

By Paul J. Flory

四川师范学院图书馆 藏书

Cornell University Press

ITHACA AND LONDON

Copyright © 1953 Cornell University

All rights reserved. Except for brief quotations in a review, this book, or parts thereof, must not be reproduced in any form without permission in writing from the publisher. For information, address Cornell University Press, Sage House, 512 East State Street, Ithaca, New York 14850.

First published 1953 by Cornell University Press

International Standard Book Number 0-8014-0134-8

Printed in the United States of America

Cornell University Press strives to use environmentally responsible suppliers and materials to the fullest extent possible in the publishing of its books. Such materials include vegetable-based, low-VOC inks and acid-free papers that are recycled, totally chlorine-free, or partly composed of nonwood fibers.

This reprint edition is specially licensed by the original publisher, Cornell University Press, for sale in China only.

书　　名：Principles of Polymer Chemistry
作　　者：P. J. Flory
中 译 名：高分子化学原理
出 版 者：世界图书出版公司北京公司
印 刷 者：北京世图印刷厂
发　　行：世界图书出版公司北京公司 (北京朝内大街 137 号　100010)
联系电话：010-64015659, 64038347
电子信箱：kjsk@vip.sina.com
开　　本：大 32　　印　张：21.75
出版年代：2003 年 6 月
书　　号：7-5062-6016-6/ O・405
版权登记：图字:01-2003-3128
定　　价：68.00 元

世界图书出版公司北京公司已获得 Cornell University Press 授权在中国大陆独家重印发行。

Preface

IT WAS the author's privilege to hold the George Fisher Baker Nonresident Lectureship in Chemistry at Cornell University during the spring of 1948. This book had its inception at that time. The uncompleted manuscript was laid aside shortly thereafter, and the work was not resumed until 1951. During the intervening years much new material became available from the ever-increasing literature, and major revision of manuscript and outlines consequently was necessary. The momentum of extensive investigations on the kinetics of addition polymerization, undertaken in various laboratories at the close of the war, carried this phase of the subject to an advanced stage of development. The material on dilute polymer solutions, appearing in the later chapters, had to be completely recast and expanded in the face of recent theories and experiments. The book consequently goes considerably beyond the Baker lectures both in scope and in the inclusion of new developments.

The field of polymer science has grown very large indeed, and it would scarcely be possible in a single volume to do justice to all the excellent researches in various branches of the subject. Even with a less ambitious objective, selection of material to be included is difficult and an element of arbitrariness is unavoidable. The author has been guided in his choice of material by a primary concern with principles. Out of the vast research effort carried on by many investigators over the past twenty years, and especially during the last decade, certain reasonably well-defined generalizations have emerged. It was felt that the time had come when these should be brought together in a book. In accordance with this objective, experimental results have been introduced primarily for illustrative purposes and to develop the basis for these principles. Descriptions of the properties of specific polymers and extensive cataloging of accumulated data, except as they may serve the foregoing objective, lie outside the intended scope

此为试读,需要完整PDF请访问: www.ertongbook.com

of this project. Some of the more important experimental methods are summarized, but there has been no attempt to offer detailed descriptions of apparatus or procedures.

Even in the selection of that which may be regarded as having achieved the status of a principle, the author admittedly exercised arbitrary judgment, and to a degree that may evoke censure. In particular, he may be criticized for myopic preoccupation with his own work. While granting that the allegation may be well founded, he would nevertheless call attention to the desirability of a unified point of view in a book of this sort, and he could scarcely have hoped to maintain a proper perspective from the outlook of someone else. However this may be, it is undeniably true that some important subject matter has been omitted. The subject of mechanical properties has been slighted, dynamic behavior having been omitted altogether. Originally a chapter on these topics was contemplated, but before Chapter XIV was completed the book had considerably exceeded its projected size and the author's patience. He therefore sought a measure of comfort in the dubiously tenable position that the subject of dynamic properties, being in the process of rapid growth on the one hand while deficient in theoretical interpretations on the other, should perhaps be postponed for some other volume, or possibly for a revision of this one—preferably by another author.

There are two introductory chapters. The first presents an interpretation of early developments which proved rewarding to the author, though it may seem an unnecessary embellishment to some readers. The second chapter, written primarily for the newcomer, is intended to set forth essential definitions and elementary concepts. The next three chapters deal with polymerization and copolymerization reaction mechanisms and kinetics. Chapters VI through IX cover the broad field of polymer constitution, including structure, molecular weight determination, and molecular distribution. The final five chapters treat molecular configuration and associated properties of polymers and their solutions. Familiarity with the material ordinarily included in courses in organic chemistry, physical chemistry, physics, and calculus are prerequisites, and some knowledge of thermodynamics and statistical mechanics is assumed in the later chapters. Explanation of standard topics belonging to these fields has not, in general, been attempted; the consultation of textbooks by the reader to the extent required seemed a preferable solution. No previous knowledge of polymers has been assumed, and the various chapters are addressed primarily to the beginner. At the same time it is hoped that some of the subject matter may prove useful to the experienced investigator as

well. Certain derivations, possibly of less interest to the general reader, have been included in Appendixes to a number of the chapters. In addition to the usual indexes, a glossary of the more widely used symbols has been included.

The author takes pleasure in acknowledging the generous assistance of many of his colleagues. He is especially indebted to Prof. P. Debye, who tendered the invitation to the Baker Lectureship; to Drs. T. G. Fox, Jr., L. Mandelkern, W. R. Krigbaum, and A. R. Shultz, whose expertly conducted investigations while officially collaborators of the author are repeatedly referred to in this book; to Prof. R. M. Fuoss for many valuable criticisms of the manuscript and to Prof. H. A. Scheraga and Dr. L. Mandelkern for reading and criticizing portions of the manuscript; to Dr. Helen Bedon, Mr. T. E. Dumitru, and Mr. A. T. McIntyre for proofreading and assistance with the indexing.

Permissions granted by the following journals and publishers are gratefully acknowledged: Academic Press, Inc., Annual Reviews, Inc., *Canadian Journal of Research, Chemische Berichte, Die Makromolekulare Chemie, India Rubber World, Industrial and Engineering Chemistry,* Interscience Publishers, Inc., *Journal of the American Chemical Society, Journal of Applied Physics, Journal of Chemical Physics, Journal of the Chemical Society* (London), *Journal of Colloid Science, Journal of Polymer Science, Journal of Research of the National Bureau of Standards, Transactions of the Faraday Society,* Williams and Wilkins Company, and *Zeitschrift für physikalische Chemie.*

P. J. F.

Ithaca, New York
September 3, 1953

Contents

Preface v

CHAPTER I

HISTORICAL INTRODUCTION 3

1. Early Investigations on Naturally Occurring Polymers 4
2. Early Encounters with Condensation Polymers 12
3. Vinyl Polymers 20
4. Rise of the Macromolecular Hypothesis 21
References. 25

CHAPTER II

TYPES OF POLYMERIC SUBSTANCES: DEFINITIONS AND CLASSIFICATIONS

1. Primary Definitions 29
2. Classification of Polymers 37
3. Condensation Polymers and Condensation Polymerization . . . 40
4. Addition Polymers from Unsaturated Monomers 51
5. Polymerization of Cyclic Compounds 57
6. Anomalous Condensation Polymerizations 61
7. Inorganic Polymers 63
8. Concluding Remarks on the Structure and Properties of High Polymers 65
References. 66

CHAPTER III

MOLECULAR SIZE AND CHEMICAL REACTIVITY; PRINCIPLES OF CONDENSATION POLYMERIZATION 69

1. Chemical Reactivity in Homologous Series of Monomeric Compounds 70

2. Theory of the Reactivity of Large Molecules 75
3. Kinetics of Condensation Polymerization 79
4. Kinetics of Degradation of Condensation Polymers 83
4a. Hydrolysis of Cellulose and Cellulose Derivatives . . . 83
4b. Hydrolysis of Polyamides 85
4c. Alcoholysis of Polyesters 86
4d. Interchange Reactions in Condensation Polymers . . . 87
5. Molecular Weights of Linear Condensation Polymers 91
6. Ring Formation *vs.* Chain Polymerization 95
7. Summary and Conclusions: The Principle of Equal Reactivity of All Functional Groups 102
References. 104

CHAPTER IV

POLYMERIZATION OF UNSATURATED MONOMERS BY FREE RADICAL MECHANISMS 106

1. The Conversion of Monomer to Polymer 110
1a. Kinetic Scheme for Polymerization in the Presence of an Initiator 110
1b. Dependence of Initial Rates on the Concentrations of Initiator and Monomer 115
1c. Initiator Efficiencies 117
1d. Evaluation of Parameters 122
1e. The Course of the Conversion of Monomer to Polymer; Autoacceleration 124
1f. Kinetics of Thermal Polymerization 129
2. Chain Lengths 132
2a. Kinetic Chain Length and Degree of Polymerization . . 132
2b. Kinetics of Chain Transfer. 136
2c. Chain Transfer in Undiluted Monomer; Evaluation of Parameters 138
2d. Chain Transfer with Solvents 141
2e. Dependence of the Degree of Polymerization on Temperature 145
2f. Regulators 146
3. Absolute Values of the Rate Constants for Individual Steps . . 148
3a. Methods for Determining the Mean Lifetime of an Active Center. 149
3b. Experimental Results 155
4. Inhibition and Retardation of Polymerization 161
4a. Reaction Mechanisms 162
4b. Kinetics of Inhibition and Retardation 169
4c. Allylic Polymerization; Autoinhibition 172
References. 174

Chapter V

COPOLYMERIZATION, EMULSION POLYMERIZATION AND IONIC POLYMERIZATION

1. The Composition of Addition Copolymers 178
1a. Kinetics of Chain Propagation in Copolymerization . . 178
1b. Evaluation of Monomer Reactivity Ratios 185
1c. Monomer Reactivity in Relation to Structure 189
1d. Radical Reactivity in Relation to Structure. 194
1e. Alternating Effects 195
2. The Rate of Addition Copolymerization 199
3. Emulsion Polymerization 203
3a. Qualitative Theory 204
3b. Quantitative Theory 208
3c. The Number of Particles 212
3d. Concluding Remarks on Heterophase Polymerization . . 214
4. Ionic Polymerization. 217
4a. Cationic Polymerization 217
4b. Anionic Polymerization. 224
4c. Ionic Copolymerization. 226
References. 228

Chapter VI

THE STRUCTURE OF VINYL POLYMERS

1. Arrangement of Units in Polymers Derived from Monovinyl Monomers 231
2. Structure and Arrangement of Units in Polymers from Dienes. . 238
2a. Diene Polymers Formed by Free Radical Mechanisms. . 238
2b. Diene Polymers Formed by Ionic Mechanisms 245
3. Steric Hindrance in Polymer Chains 246
3a. Interactions between Substituents of Successive Units. . 246
3b. Steric Interaction and the Heat of Polymerization . . . 249
4. Nonlinearity in the Macro-Structure of Vinyl Polymers . . . 256
4a. Branching in Vinyl Polymers 256
4b. Cross-Linking in Diene Polymers 260
5. Summary 262
References. 263

Chapter VII

DETERMINATION OF MOLECULAR WEIGHTS 266

1. Osmotic Methods. 269
1a. Theory 269
1b. The Number Average Molecular Weight. 273

1c. Experimental Methods 275
1d. Treatment of Data 279
2. Determination of Molecular Weights and Polymer Dimensions by Light Scattering 283
2a. Experimental Methods 284
2b. Theory for Particles Small Compared with the Wavelength of the Light 287
2c. The Weight Average Molecular Weight 291
2d. Light Scattering by Polymer Particles with Dimensions Approaching the Wavelength of the Light 293
2e. Dependence of Scattering on Concentration 297
2f. Treatment of Data 299
3. Determination of Molecular Weights with the Ultracentrifuge . . 303
3a. Molecular Weights from the Sedimentation and Diffusion Constants 304
3b. Sedimentation Equilibrium 307
4. Intrinsic Viscosities in Relation to Molecular Weights of High Polymers 308
4a. Evaluation of the Intrinsic Viscosity 309
4b. Intrinsic Viscosity–Molecular Weight Relationship . . 310
4c. The Viscosity Average Molecular Weight and the Influence of Molecular Heterogeneity 311
References 314

Chapter VIII

MOLECULAR WEIGHT DISTRIBUTIONS IN LINEAR POLYMERS 317

1. Condensation Polymers 318
1a. Linear Chain Molecules; the Most Probable Distribution . 318
1b. Experimental Confirmation of the Most Probable Size Distribution 323
1c. Average Molecular Weights for the Most Probable Distribution 325
1d. Cyclic Condensation Polymers 326
1e. Multichain Condensation Polymers 331
2. Addition Polymers 334
2a. Vinyl Polymers 334
2b. Polymers Formed by Monomer Addition without Termination 336
3. Polymer Fractionation 339
References 346

此为试读,需要完整PDF请访问: www.ertongbook.com

CHAPTER IX

MOLECULAR WEIGHT DISTRIBUTIONS IN NONLINEAR POLYMERS AND THE THEORY OF GELATION 347

1. Critical Conditions for the Formation of Infinite Networks . . 348
   1a. Polyfunctional Condensation Polymerization 348
   1b. Experimentally Observed Gel Points in Polyfunctional Condensations. 354
   1c. Cross-Linking of Polymer Chains 356
   1d. General Conditions for the Formation of Infinite Networks 360
2. Molecular Distributions in Polyfunctional Condensations . . . 361
   2a. Special Case of Random Branching without Network Formation. 361
   2b. Molecular Size Distribution Obtained by Condensing A—R—B_{f-1} Monomers 365
   2c. The Distribution in Ordinary Polyfunctional Condensations 370
   2d. Post-Gelation Relationships 374
3. Molecular Distributions in Cross-Linked Systems 378
   3a. Molecular Size Distributions 378
   3b. The Partitioning of Components between Sol and Gel . 379
4. Branching and Cross-Linking in Vinyl Addition Polymers . . . 384
   4a. Branching by Chain Transfer 384
   4b. Cross-Linking in the Polymerization of Dienes 386
   4c. Copolymerization of Divinyl with Monovinyl Monomers . 391
5. Summary 392

Appendix A. Derivation of the Molecular Distribution for the Random Condensation of Bifunctional with Polyfunctional Monomers 393

Appendix B. The Complexity Distribution 395

References. 398

CHAPTER X

CONFIGURATION OF POLYMER CHAINS 399

1. Statistical Distribution of End-to-End Dimensions 402
   1a. The Freely Jointed Chain in One Dimension 402
   1b. The Freely Jointed Chain in Three Dimensions. . . . 404
   1c. The Distribution at High Extensions. 409
   1d. Influence of Bond Angle Restrictions. 410
2. Calculation of Average Dimensions for Various Polymer Chain Structures. 414
   2a. The Freely Rotating Polymethylene Chain 414
   2b. Hindered Polymer Chains 415

2c. The Silicone Chain 420
2d. Cellulosic Chains 421
2e. Natural Rubber and Gutta-Percha 421
2f. Nonlinear Polymer Molecules 422
3. Configuration of Polymer Molecules in Dilute Solution . . . 423
3a. Long-Range Intramolecular Interactions. 423
3b. The Unperturbed Polymer Chain 425
Appendix A. Derivation of the Gaussian Distribution for a Random Chain in One Dimension 426
Appendix B. Exact Treatment for the Freely Jointed Chain (or Equivalent Chain) 427
Appendix C. The Mean-Square Distance of a Chain Element from the Center of Mass 428
References. 431

CHAPTER XI

RUBBER ELASTICITY 432

1. Thermodynamics of Rubber Elasticity 434
1a. Historical Background 434
1b. Thermodynamic Relationships 440
1c. The Results of Stress-Temperature Measurements . . . 444
1d. The Ideal Rubber 450
1e. Natural Rubber at High Elongations. 451
2. The Structure of Vulcanized Rubber 454
2a. Vulcanization Processes 454
2b. Quantitative Characterization of Network Structures . . 458
3. The Statistical Theory of Rubber Elasticity 464
4. Experimental Stress-Strain Behavior of Vulcanized Rubbers at Moderate Elongations 470
4a. The Stress-Strain Curve 471
4b. The Force of Retraction in Relation to Network Structure . 475
4c. Effects of Fillers in Rubber Vulcanizates 480
5. The Stress-Strain Curve at High Elongations 482
5a. Crystallinity and Tensile Strength 482
5b. Experimental Results on the Relationship between Tensile Strength and Network Structure 483
5c. Tensile Strength in Noncrystallizing Rubbers 488
Appendix A. The Force-Temperature Coefficient at Constant Elongation 489
Appendix B. Deformation of a Swollen Network. 492
References. 493

Chapter XII

STATISTICAL THERMODYNAMICS OF POLYMER SOLUTIONS 495

1. General Thermodynamic Relations for Polymer Solutions . . . 497
1a. The Entropy of Mixing according to Liquid Lattice Theory. 497
1b. Approximations and Limitations of the Lattice Treatment . 503
1c. An Alternate Derivation 505
1d. The Heat and Free Energy of Mixing 507
1e. Partial Molar Quantities 511
1f. Experimental Results 514
2. Dilute Polymer Solutions 519
2a. Thermodynamic Interaction within a Region of Uniform Average Segment Concentration 520
2b. The Excluded Volume 523
2c. Thermodynamic Relations for Dilute Polymer Solutions . 530
2d. Application to Experimental Data 534
Appendix. Integration of the Interaction Free Energy for a Pair of Molecules 539
References 539

Chapter XIII

PHASE EQUILIBRIA IN POLYMER SYSTEMS

1. Phase Equilibria in Liquid Systems 541
1a. Theory of Binary Systems 542
1b. Experimental Results on Binary Systems 546
1c. Ternary Systems Consisting of a Single Polymer Component in a Binary Solvent Mixture 548
1d. Ternary Systems Consisting of Two Polymeric Components in a Single Solvent. 554
1e. Theory of Polymer Fractionation 559
2. Phase Equilibria in Semicrystalline Systems 563
2a. The Nature of the Crystalline State in Polymers . . . 563
2b. Theory of the Melting Point Depression. 568
2c. Experimental Results 571
3. Swelling of Network Structures. 576
3a. Theory of Swelling 577
3b. Experimental Results on the Swelling of Nonionic Network Systems 581
3c. Swelling of Ionic Networks 584
Appendix A. Calculation of the Binodial in the Phase Diagram for the Two-Component System Comprising a Solvent and a Single Polymer Species 590
Appendix B. Donnan-Type Equilibria in Polyelectrolyte Gels . . 590
References. 593

Chapter XIV

CONFIGURATIONAL AND FRICTIONAL PROPERTIES OF THE POLYMER MOLECULE IN DILUTE SOLUTION 595

1. Intramolecular Interactions and the Average Molecular Extension . 596
2. Frictional Properties of the Polymer Molecule in Solution . . . 602
   - 2a. The Free-draining Molecule 602
   - 2b. The Equivalent Sphere Model. 605
   - 2c. Real Polymer Chains with Large Frictional Interactions . 606
3. Treatment of Experimental Results: Intrinsic Viscosities of Non-ionic Polymers 611
   - 3a. The Intrinsic Viscosity of the Theta Point and the Evaluation of K 612
   - 3b. The Universal Parameter Φ; Unperturbed Dimensions of Linear Polymers 616
   - 3c. The Molecular Expansion Factor α and the General Dependence of Intrinsic Viscosity on Molecular Weight . 620
   - 3d. Intrinsic Viscosity–Temperature Relations and Thermodynamic Parameters. 622
4. Treatment of Experimental Results: Frictional Coefficients . . . 626
5. Linear Polyelectrolytes 629
   - 5a. General Characteristics. 629
   - 5b. Intrinsic Viscosities of Polyelectrolytes 633

References. 657

Glossary of Principal Symbols 640

Author Index 653

Subject Index 663

PRINCIPLES OF POLYMER CHEMISTRY

此为试读,需要完整PDF请访问: www.ertongbook.com