

PHYSICAL CHEMISTRY OF MACROMOLECULES

Basic Principles and Issues

Second Edition

S. F. SUN

St. John's University
Jamaica, New York



A Wiley-Interscience Publication
JOHN WILEY & SONS, INC.

PHYSICAL CHEMISTRY OF MACROMOLECULES

Second Edition

PHYSICAL CHEMISTRY OF MACROMOLECULES

Basic Principles and Issues

Second Edition

S. F. SUN

St. John's University
Jamaica, New York



A Wiley-Interscience Publication
JOHN WILEY & SONS, INC.

Copyright © 2004 by John Wiley & Sons, Inc. All rights reserved.

Published by John Wiley & Sons, Inc., Hoboken, New Jersey.

Published simultaneously in Canada.

No part of this publication may be reproduced, stored in a retrieval system, or transmitted in any form or by any means, electronic, mechanical, photocopying, recording, scanning, or otherwise, except as permitted under Section 107 or 108 of the 1976 United States Copyright Act, without either the prior written permission of the Publisher, or authorization through payment of the appropriate per-copy fee to the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, 978-750-8400, fax 978-646-8600, or on the web at www.copyright.com. Requests to the Publisher for permission should be addressed to the Permissions Department, John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, (201) 748-6011, fax (201) 748-6008.

Limit of Liability/Disclaimer of Warranty: While the publisher and author have used their best efforts in preparing this book, they make no representations or warranties with respect to the accuracy or completeness of the contents of this book and specifically disclaim any implied warranties of merchantability or fitness for a particular purpose. No warranty may be created or extended by sales representatives or written sales materials. The advice and strategies contained herein may not be suitable for your situation. You should consult with a professional where appropriate. Neither the publisher nor author shall be liable for any loss of profit or any other commercial damages, including but not limited to special, incidental, consequential, or other damages.

For general information on our other products and services please contact our Customer Care Department within the U.S. at 877-762-2974, outside the U.S. at 317-572-3993 or fax 317-572-4002.

Wiley also publishes its books in a variety of electronic formats. Some content that appears in print, however, may not be available in electronic format.

Library of Congress Cataloging-in-Publication Data:

Sun, S. F., 1922-

Physical chemistry of macromolecules : basic principles and issues / S. F. Sun.—2nd ed.
p. cm.

Includes bibliographical references and index.

ISBN 0-471-28138-7 (acid-free paper)

1. Macromolecules. 2. Chemistry, Physical organic. I. Title.

QD381.8.S86 2004

547'.7045—dc22

2003063993

Printed in the United States of America.

10 9 8 7 6 5 4 3 2 1

CONTENTS

Preface to the Second Edition	xv
Preface to the First Edition	xix
1 Introduction	1
1.1 Colloids, 1	
1.2 Macromolecules, 3	
1.2.1 Synthetic Polymers, 4	
1.2.2 Biological Polymers, 7	
1.3 Macromolecular Science, 17	
References, 17	
2 Syntheses of Macromolecular Compounds	19
2.1 Radical Polymerization, 19	
2.1.1 Complications, 21	
2.1.2 Methods of Free-Radical Polymerization, 23	
2.1.3 Some Well-Known Overall Reactions of Addition Polymers, 23	
2.2 Ionic Polymerization, 25	
2.2.1 Anionic Polymerization, 25	
2.2.2 Cationic Polymerization, 27	
2.2.3 Living Polymers, 27	
2.3 Coordination Polymerization, 30	
2.4 Stepwise Polymerization, 32	

- 2.5 Kinetics of the Syntheses of Polymers, 33
 - 2.5.1 Condensation Reactions, 34
 - 2.5.2 Chain Reactions, 35
- 2.6 Polypeptide Synthesis, 40
 - 2.6.1 Synthesis of Insulin, 43
 - 2.6.2 Synthesis of Ribonucleus, 48
- 2.7 DNA Synthesis, 48
- References, 50
- Problems, 50

3 Distribution of Molecular Weight 52

- 3.1 Review of Mathematical Statistics, 53
 - 3.1.1 Binomial Distribution, 53
 - 3.1.2 Poisson Distribution, 54
 - 3.1.3 Gaussian Distribution, 55
- 3.2 One-Parameter Equation, 56
 - 3.2.1 Condensation Polymers, 57
 - 3.2.2 Addition Polymers, 58
- 3.3 Two-Parameter Equations, 59
 - 3.3.1 Normal Distribution, 59
 - 3.3.2 Logarithm Normal Distribution, 60
- 3.4 Types of Molecular Weight, 61
- 3.5 Experimental Methods for Determining Molecular Weight and Molecular Weight Distribution, 64
- References, 65
- Problems, 65

4 Macromolecular Thermodynamics 67

- 4.1 Review of Thermodynamics, 68
- 4.2 ΔS of Mixing: Flory Theory, 71
- 4.3 ΔH of Mixing, 75
 - 4.3.1 Cohesive Energy Density, 76
 - 4.3.2 Contact Energy (First-Neighbor Interaction or Energy Due to Contact), 79
- 4.4 ΔG of Mixing, 81
- 4.5 Partial Molar Quantities, 81
 - 4.5.1 Partial Specific Volume, 82
 - 4.5.2 Chemical Potential, 83
- 4.6 Thermodynamics of Dilute Polymer Solutions, 84
 - 4.6.1 Vapor Pressure, 87
 - 4.6.2 Phase Equilibrium, 89
- Appendix: Thermodynamics and Critical Phenomena, 91
- References, 92
- Problems, 93

5 Chain Configurations **96**

- 5.1 Preliminary Descriptions of a Polymer Chain, 97
- 5.2 Random Walk and the Markov Process, 98
 - 5.2.1 Random Walk, 99
 - 5.2.2 Markov Chain, 101
- 5.3 Random-Flight Chains, 103
- 5.4 Wormlike Chains, 105
- 5.5 Flory's Mean-Field Theory, 106
- 5.6 Perturbation Theory, 107
 - 5.6.1 First-Order Perturbation Theory, 108
 - 5.6.2 Cluster Expansion Method, 108
- 5.7 Chain Crossover and Chain Entanglement, 109
 - 5.7.1 Concentration Effect, 109
 - 5.7.2 Temperature Effect, 114
 - 5.7.3 Tube Theory (Reptation Theory), 116
 - 5.7.4 Images of Individual Polymer Chains, 118
- 5.8 Scaling and Universality, 119
- Appendix A Scaling Concepts, 120
- Appendix B Correlation Function, 121
- References, 123
- Problems, 124

6 Liquid Crystals **127**

- 6.1 Mesogens, 128
- 6.2 Polymeric Liquid Crystals, 130
 - 6.2.1 Low-Molecular Weight Liquid Crystals, 131
 - 6.2.2 Main-Chain Liquid-Crystalline Polymers, 132
 - 6.2.3 Side-Chain Liquid-Crystalline Polymers, 132
 - 6.2.4 Segmented-Chain Liquid-Crystalline Polymers, 133
- 6.3 Shapes of Mesogens, 133
- 6.4 Liquid-Crystal Phases, 134
 - 6.4.1 Mesophases in General, 134
 - 6.4.2 Nematic Phase, 135
 - 6.4.3 Smectic Phase, 135
 - 6.4.3.1 Smectic A and C, 136
 - 6.4.4 Compounds Representing Some Mesophases, 136
 - 6.4.5 Shape and Phase, 137
 - 6.4.6 Decreasing Order and ΔH of Phase Transition, 138
- 6.5 Thermotropic and Lyotropic Liquid Crystals, 138
- 6.6 Kerr Effect, 140
- 6.7 Theories of Liquid-Crystalline Ordering, 141
 - 6.7.1 Rigid-Rod Model, 141
 - 6.7.2 Lattice Model, 142
 - 6.7.3 De Genne's Fluctuation Theory, 144

- 6.8 Current Industrial Applications of Liquid Crystals, 145
 - 6.8.1 Liquid Crystals Displays, 146
 - 6.8.2 Electronic Devices, 147
- References, 149

7 Rubber Elasticity 150

- 7.1 Rubber and Rubberlike Materials, 150
- 7.2 Network Structure, 151
- 7.3 Natural Rubber and Synthetic Rubber, 152
- 7.4 Thermodynamics of Rubber, 154
- 7.5 Statistical Theory of Rubber Elasticity, 158
- 7.6 Gels, 162
- References, 163
- Problems, 164

8 Viscosity and Viscoelasticity 165

- 8.1 Viscosity, 165
 - 8.1.1 Capillary Viscometers, 166
 - 8.1.2 Intrinsic Viscosity, 170
 - 8.1.3 Treatment of Intrinsic Viscosity Data, 172
 - 8.1.4 Stokes' Law, 176
 - 8.1.5 Theories in Relation to Intrinsic Viscosity of Flexible Chains, 176
 - 8.1.6 Chain Entanglement, 179
 - 8.1.7 Biological Polymers (Rigid Polymers, Inflexible Chains), 181
- 8.2 Viscoelasticity, 184
 - 8.2.1 Rouse Theory, 187
 - 8.2.2 Zimm Theory, 190
- References, 192
- Problems, 193

9 Osmotic Pressure 198

- 9.1 Osmometers, 199
- 9.2 Determination of Molecular Weight and Second Virial Coefficient, 199
- 9.3 Theories of Osmotic Pressure and Osmotic Second Virial Coefficient, 202
 - 9.3.1 McMillan–Mayer Theory, 203
 - 9.3.2 Flory Theory, 204
 - 9.3.3 Flory–Krigbaum Theory, 205
 - 9.3.4 Kurata–Yamakawa Theory, 207
 - 9.3.5 des Cloizeaux–de Gennes Scaling Theory, 209
 - 9.3.6 Scatchard's Equation for Macro Ions, 213

Appendix A	Ensembles, 215
Appendix B	Partition Functions, 215
Appendix C	Mean-Field Theory and Renormalization Group Theory, 216
Appendix D	Lagrangian Theory, 217
Appendix E	Green's Function, 217
References,	218
Problems,	218

10 Diffusion 223

10.1	Translational Diffusion, 223
10.1.1	Fick's First and Second Laws, 223
10.1.2	Solution to Continuity Equation, 224
10.2	Physical Interpretation of Diffusion: Einstein's Equation of Diffusion, 226
10.3	Size, Shape, and Molecular Weight Determinations, 229
10.3.1	Size, 229
10.3.2	Shape, 230
10.3.3	Molecular Weight, 231
10.4	Concentration Dependence of Diffusion Coefficient, 231
10.5	Scaling Relation for Translational Diffusion Coefficient, 233
10.6	Measurements of Translational Diffusion Coefficient, 234
10.6.1	Measurement Based on Fick's First Law, 234
10.6.2	Measurement Based on Fick's Second Law, 235
10.7	Rotational Diffusion, 237
10.7.1	Flow Birefringence, 239
10.7.2	Fluorescence Depolarization, 239
References,	240
Problems,	240

11 Sedimentation 243

11.1	Apparatus, 244
11.2	Sedimentation Velocity, 246
11.2.1	Measurement of Sedimentation Coefficients: Moving-Boundary Method, 246
11.2.2	Svedberg Equation, 249
11.2.3	Application of Sedimentation Coefficient, 249
11.3	Sedimentation Equilibrium, 250
11.3.1	Archibald Method, 251
11.3.2	Van Holde-Baldwin (Low-Speed) Method, 254
11.3.3	Yphantis (High-Speed) Method, 256
11.3.4	Absorption System, 258
11.4	Density Gradient Sedimentation Equilibrium, 259
11.5	Scaling Theory, 260

References, 262

Problems, 263

12 Optical Rotatory Dispersion and Circular Dichroism 267

12.1 Polarized Light, 267

12.2 Optical Rotatory Dispersion, 267

12.3 Circular Dichroism, 272

12.4 Cotton Effect, 275

12.5 Correlation Between ORD and CD, 277

12.6 Comparison of ORD and CD, 280

References, 281

Problems, 281

13 High-Performance Liquid Chromatography and Electrophoresis 284

13.1 High-Performance Liquid Chromatography, 284

13.1.1 Chromatographic Terms and Parameters, 284

13.1.2 Theory of Chromatography, 289

13.1.3 Types of HPLC, 291

13.2 Electrophoresis, 300

13.2.1 Basic Theory, 300

13.2.2 General Techniques of Modern Electrophoresis, 305

13.2.3 Agarose Gel Electrophoresis and Polyacrylamide Gel Electrophoresis, 307

13.2.4 Southern Blot, Northern Blot, and Western Blot, 309

13.2.5 Sequencing DNA Fragments, 310

13.2.6 Isoelectric Focusing and Isotachopheresis, 310

13.3 Field-Flow Fractionation, 314

References, 317

Problems, 318

14 Light Scattering 320

14.1 Rayleigh Scattering, 320

14.2 Fluctuation Theory (Debye), 324

14.3 Determination of Molecular Weight and Molecular Interaction, 329

14.3.1 Two-Component Systems, 329

14.3.2 Multicomponent Systems, 329

14.3.3 Copolymers, 331

14.3.4 Correction of Anisotropy and Depolarization of Scattered Light, 333

14.4 Internal Interference, 333

14.5 Determination of Molecular Weight and Radius of Gyration of the Zimm Plot, 337

Appendix Experimental Techniques of the Zimm Plot, 341

References, 345

Problems, 346

15 Fourier Series **348**

15.1 Preliminaries, 348

15.2 Fourier Series, 350

15.2.1 Basic Fourier Series, 350

15.2.2 Fourier Sine Series, 352

15.2.3 Fourier Cosine Series, 352

15.2.4 Complex Fourier Series, 353

15.2.5 Other Forms of Fourier Series, 353

15.3 Conversion of Infinite Series into Integrals, 354

15.4 Fourier Integrals, 354

15.5 Fourier Transforms, 356

15.5.1 Fourier Transform Pairs, 356

15.6 Convolution, 359

15.6.1 Definition, 359

15.6.2 Convolution Theorem, 361

15.6.3 Convolution and Fourier Theory: Power Theorem, 361

15.7 Extension of Fourier Series and Fourier Transform, 362

15.7.1 Lorentz Line Shape, 362

15.7.2 Correlation Function, 363

15.8 Discrete Fourier Transform, 364

15.8.1 Discrete and Inverse Discrete Fourier Transform, 364

15.8.2 Application of DFT, 365

15.8.3 Fast Fourier Transform, 366

Appendix, 367

References, 368

Problems, 369

**16 Small-Angle X-Ray Scattering, Neutron Scattering, and
Laser Light Scattering** **371**

16.1 Small-Angle X-ray Scattering, 371

16.1.1 Apparatus, 372

16.1.2 Guinier Plot, 373

16.1.3 Correlation Function, 375

16.1.4 On Size and Shape of Proteins, 377

16.2 Small-Angle Neutron Scattering, 381

16.2.1 Six Types of Neutron Scattering, 381

16.2.2 Theory, 382

16.2.3 Dynamics of a Polymer Solution, 383

16.2.4 Coherently Elastic Neutron Scattering, 384

16.2.5 Comparison of Small-Angle Neutron Scattering
with Light Scattering, 384

16.2.6	Contrast Factor, 386	
16.2.7	Lorentzian Shape, 388	
16.2.8	Neutron Spectroscopy, 388	
16.3	Laser Light Scattering, 389	
16.3.1	Laser Light-Scattering Experiment, 389	
16.3.2	Autocorrelation and Power Spectrum, 390	
16.3.3	Measurement of Diffusion Coefficient in General, 391	
16.3.4	Application to Study of Polymers in Semidilute Solutions, 393	
16.3.4.1	Measurement of Lag Times, 393	
16.3.4.2	Forced Rayleigh Scattering, 394	
16.3.4.3	Linewidth Analysis, 394	
	References, 395	
	Problems, 396	
17	Electronic and Infrared Spectroscopy	399
17.1	Ultraviolet (and Visible) Absorption Spectra, 400	
17.1.1	Lambert–Beer Law, 402	
17.1.2	Terminology, 403	
17.1.3	Synthetic Polymers, 405	
17.1.4	Proteins, 406	
17.1.5	Nucleic Acids, 409	
17.2	Fluorescence Spectroscopy, 412	
17.2.1	Fluorescence Phenomena, 412	
17.2.2	Emission and Excitation Spectra, 413	
17.2.3	Quenching, 413	
17.2.4	Energy Transfer, 416	
17.2.5	Polarization and Depolarization, 418	
17.3	Infrared Spectroscopy, 420	
17.3.1	Basic Theory, 420	
17.3.2	Absorption Bands: Stretching and Bending, 421	
17.3.3	Infrared Spectroscopy of Synthetic Polymers, 424	
17.3.4	Biological Polymers, 427	
17.3.5	Fourier Transform Infrared Spectroscopy, 428	
	References, 430	
	Problems, 432	
18	Protein Molecules	436
18.1	Protein Sequence and Structure, 436	
18.1.1	Sequence, 436	
18.1.2	Secondary Structure, 437	
18.1.2.1	α -Helix and β -Sheet, 437	
18.1.2.2	Classification of Proteins, 439	
18.1.2.3	Torsion Angles, 440	
18.1.3	Tertiary Structure, 441	
18.1.4	Quarternary Structure, 441	

18.2	Protein Structure Representations, 441	
18.2.1	Representation Symbols, 441	
18.2.2	Representations of Whole Molecule, 442	
18.3	Protein Folding and Refolding, 444	
18.3.1	Computer Simulation, 445	
18.3.2	Homolog Modeling, 447	
18.3.3	De Novo Prediction, 447	
18.4	Protein Misfolding, 448	
18.4.1	Biological Factor: Chaperones, 448	
18.4.2	Chemical Factor: Intra- and Intermolecular Interactions, 449	
18.4.3	Brain Diseases, 450	
18.5	Genomics, Proteomics, and Bioinformatics, 451	
18.6	Ribosomes: Site and Function of Protein Synthesis, 452	
	References, 454	
19	Nuclear Magnetic Resonance	455
19.1	General Principles, 455	
19.1.1	Magnetic Field and Magnetic Moment, 455	
19.1.2	Magnetic Properties of Nuclei, 456	
19.1.3	Resonance, 458	
19.1.4	Nuclear Magnetic Resonance, 460	
19.2	Chemical Shift (δ) and Spin–Spin Coupling Constant (J), 461	
19.3	Relaxation Processes, 466	
19.3.1	Spin–Lattice Relaxation and Spin–Spin Relaxation, 467	
19.3.2	Nuclear Quadrupole Relaxation and Overhauser Effect, 469	
19.4	NMR Spectroscopy, 470	
19.4.1	Pulse Fourier Transform Method, 471	
19.4.1.1	Rotating Frame of Reference, 471	
19.4.1.2	The 90° Pulse, 471	
19.4.2	One-Dimensional NMR, 472	
19.4.3	Two-Dimensional NMR, 473	
19.5	Magnetic Resonance Imaging, 475	
19.6	NMR Spectra of Macromolecules, 477	
19.6.1	Poly(methyl methacrylate), 477	
19.6.2	Polypropylene, 481	
19.6.3	Deuterium NMR Spectra of Chain Mobility in Polyethylene, 482	
19.6.4	Two-Dimensional NMR Spectra of Poly- γ -benzyl-L-glutamate, 485	
19.7	Advances in NMR Since 1994, 487	
19.7.1	Apparatus, 487	
19.7.2	Techniques, 487	
19.7.2.1	Computer-Aided Experiments, 487	
19.7.2.2	Modeling of Chemical Shift, 488	
19.7.2.3	Protein Structure Determination, 489	