PHYSICAL CHEMISTRY OF MACROMOLECULES

Basic Principles and Issues

SECOND EDITION

S. F. SUN

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Basic Principles and Issues

Second Edition

S. F. SUN
St. John's University
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PREFACE TO THE SECOND EDITION

In this second edition, four new chapters are added and two original chapters are thoroughly revised. The four new chapters are Chapter 6, Liquid Crystals; Chapter 7, Rubber Elasticity; Chapter 15, Fourier Series; and Chapter 18, Protein Molecules. The two thoroughly revised chapters are Chapter 19, Nuclear Magnetic Resonance, and Chapter 20, X-Ray Crystallography.

Since the completion of the first edition in 1994, important developments have been going on in many fields of physical chemistry of macromolecules. As a result, two new disciplines have emerged: materials science and structural biology. The traditional field of polymers, even though already enlarged, is to be included in the bigger field of materials science. Together with glasses, colloids, and liquid crystals, polymers are considered organic and soft materials, in parallel with engineering and structural materials such as metals and alloys. Structural biology, originally dedicated to the study of the sequence and structure of DNA and proteins, is now listed together with genomics, proteomics, and molecular evolution as an independent field. It is not unusual that structural biology is also defined as the field that includes genomics and proteomics.

These developments explain the background of our revision.

Chapters 6 and 7 are added in response to the new integration in materials science. In Chapter 6, after the presentation of the main subjects, we give two examples to call attention to readers the fierce competition in industry for the application of liquid crystals: crystal paint display and electronic devices. Within the next few years television and computer films will be revolutionalized both in appearance and in function. Military authority and medical industry are both looking for new materials of liquid crystals. The subject rubber elasticity in

Chapter 7 is a classical one, well known in polymer chemistry and the automobile industry. It should have been included in the first edition. Now we have a chance to include it as materials science.

Chapters 18–20 constitute the core of structural biology. Chapter 18 describes the most important principles of protein chemistry, including sequence and structure and folding and misfolding. Chapters 19 and 20 deal with the two major instruments employed in the study of structural biology: nuclear magnetic resonance (NMR) spectroscopy and x-ray crystallography. Both have undergone astonishing changes during the last few years. Nuclear magnetic resonance instruments have operated from 500 MHz in 1994 to 900 MHz in the 2000s. The powerful magnets provide greater resolution that enables the researchers to obtain more detailed information about proteins. X-ray crystallography has gained even more amazing advancement in technology: the construction of the gigantic x-ray machine known as the synchrotron. Before 1994, an x-ray machine could be housed in the confines of a research laboratory building. In 1994 the synchrotron became as big as a stadium and was first made available for use in science.

Chapter 15, Fourier Series, was given in the previous edition as an appendix to the chapter entitled Dynamic Light Scattering. Now it also becomes an independent chapter. This technique has been an integral part of physics and electrical engineering and has been extended to chemistry and biology. The purpose of this chapter is to provide a background toward the understanding of mathematical language as well as an appreciation of this as an indispensable tool to the new technologies: NMR, x-ray crystallography, and infrared spectroscopy. Equally important, it is a good training in mathematics. On the other hand, in this edition the subject of dynamic light scattering is combined with the subjects of small-angle x-ray scattering and neutron scattering to form Chapter 16.

In addition to the changes mentioned above, we have updated several chapters in the previous edition. In Chapter 5, for example, we added a section to describe the images of individual polymer chains undergoing changes in steady shear. This is related to laser technology.

Although the number of chapters has increased from 17 in the previous edition to 20 in this edition, we have kept our goal intact: to integrate physical polymer chemistry and biophysical chemistry by covering principles and issues common to both.

This book is believed to be among the pioneers to integrate the two traditionally independent disciplines. The integration by two or more independent disciplines seems to be a modern trend. Since our book was first published, not only two newly developed subjects have been the results of integrations (i.e., each integrates several different subjects in their area), but also many academic departments in colleges and universities have been integrated. In the old days, for example, we have departments with a single term: Physics, Chemistry, Biology, and so forth; now we have departments with two terms of combined subjects: Chemistry and Biochemistry, Biochemistry and Molecular Biophysics, Chemistry and Chemical Biology, Biochemistry and Molecular Biophysics, Anatomy and Structural Biology, Materials Science and Engineering, Materials and Polymers. For young science students,

the integrated subjects have broader areas of research and learning. They are challenging and they show where the jobs are.

There are no major changes in the homework problems except that two sets of problems for Chapters 7 and 15 are added in this edition. A solution manual with worked out solutions to most of the problems is now available upon request to the publisher.

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This book is dedicated to my wife, Emily.

PREFACE TO THE FIRST EDITION

Physical chemistry of macromolecules is a course that is frequently offered in the biochemistry curriculum of a college or university. Occasionally, it is also offered in the chemistry curriculum. When it is offered in the biochemistry curriculum, the subject matter is usually limited to biological topics and is identical to biophysical chemistry. When it is offered in the chemistry curriculum, the subject matter is often centered around synthetic polymers and the course is identical to physical polymer chemistry. Since the two disciplines are so closely related, students almost universally feel that something is missing when they take only biophysical chemistry or only physical polymer chemistry. This book emerges from the desire to combine the two courses into one by providing readers with the basic knowledge of both biophysical chemistry and physical polymer chemistry. It also serves a bridge between the academia and industry. The subject matter is basically academic, but its application is directly related to industry, particularly polymers and biotechnology.

This book contains seventeen chapters, which may be classified into three units, even though not explicitly stated. Unit 1 covers Chapters 1 through 5, unit 2 covers Chapters 6 through 12, and unit 3 covers Chapters 13 through 17. Since the materials are integrated, it is difficult to distinguish which chapters belong to biophysical chemistry and which chapters belong to polymer chemistry. Roughly speaking, unit 1 may be considered to consist of the core materials of polymer chemistry. Unit 2 contains materials belonging both to polymer chemistry and biophysical chemistry. Unit 3, which covers the structure of macromolecules and their separations, is relatively independent of units 1 and 2. These materials are

important in advancing our knowledge of macro molecules, even though their use is not limited to macromolecules alone.

The book begins with terms commonly used in polymer chemistry and biochemistry with respect to various substances, such as homopolymers, copolymers, condensation polymers, addition polymers, proteins, nucleic acids, and polysaccharides (Chapter 1), followed by descriptions of the methods used to create these substances (Chapter 2). On the basis of classroom experience, Chapter 2 is a welcome introduction to students who have never been exposed to the basic methods of polymer and biopolymer syntheses. The first two chapters together comprise the essential background materials for this book.

Chapter 3 introduces statistical methods used to deal with a variety of distribution of molecular weight. The problem of the distribution of molecular weight is characteristic of macromolecules, particularly the synthetic polymers, and the statistical methods are the tools used to solve the problem. Originally Chapter 4 covered chain configurations and Chapter 5 covered macromolecular thermodynamics. Upon further reflection, the order was reversed. Now Chapter 4 on macromolecular thermodynamics is followed by Chapter 5 on chain configurations. This change was based on both pedagogical and chronological reasons. For over a generation (1940s to 1970s), Flory's contributions have been considered the standard work in physical polymer chemistry. His work together with that of other investigators laid the foundations of our way of thinking about the behavior of polymers, particularly in solutions. It was not until the 1970s that Flory's theories were challenged by research workers such as de Gennes. Currently, it is fair to say that de Gennes' theory plays the dominant role in research. In Chapter 4 the basic thermodynamic concepts such as χ, θ, ψ, and κ that have made Flory's name well known are introduced. Without some familiarity with these concepts, it would not be easy to follow the current thought as expounded by de Gennes in Chapter 5 (and later in Chapters 6 and 7). For both chapters sufficient background materials are provided either in the form of introductory remarks, such as the first section in Chapter 4 (a review of general thermodynamics), or in appendices, such as those on scaling concepts and correlation function in Chapter 5.

In Chapters 6 through 17, the subjects discussed are primarily experimental studies of macromolecules. Each chapter begins with a brief description of the experimental method, which, though by no means detailed, is sufficient for the reader to have a pertinent background. Each chapter ends with various theories that underlie the experimental work.

For example, in Chapter 6, to begin with three parameters, ρ (shear stress), ε (shear strain), and E (modulus or rigidity), are introduced to define viscosity and viscoelasticity. With respect to viscosity, after the definition of Newtonian viscosity is given, a detailed description of the capillary viscometer to measure the quantity η follows. Theories that interpret viscosity behavior are then presented in three different categories. The first category is concerned with the treatment of experimental data. This includes the Mark-Houwink equation, which is used to calculate the molecular weight, the Flory-Fox equation, which is used to estimate thermodynamic quantities, and the Stockmayer-Fixman equation, which is used to

supplement the intrinsic viscosity treatment. The second category describes the purely theoretical approaches to viscosity. These approaches include the Kirkwood-Riseman model and the Debye-Buche model. It also includes chain entanglement. Before presenting the third category, which deals with the theories about viscosity in relation to biological polymers, a short section discussing Stokes' law of frictional coefficient is included. The third category lists the theories proposed by Einstein, Peterlin, Kuhn and Kuhn, Simha, Scheraga and Mendelkern. With respect to viscoelasticity, Maxwell's model is adopted as a basis. Attention is focused on two theories that are very much in current thought, particularly in connection with the dynamic scaling law: the Rouse model and the Zimm model. These models are reminiscent of the Kirkwood-Riseman theory and the Debye-Buche theory in viscosity but are much more stimulating to the present way of thinking in the formulation of universal laws to characterize polymer behavior.

Chapter 7, on osmotic pressure, provides another example of my approach to the subject matter in this book. After a detailed description of the experimental determination of molecular weight and the second virial coefficient, a variety of models are introduced each of which focuses on the inquiry into inter- and intramolecular interactions of polymers in solution. The reader will realize that the thermodynamic function μ (chemical potential) introduced in Chapter 4 has now become the key term in our language. The physical insight that is expressed by theoreticians is unusually inspiring. For those who are primarily interested in experimental study, Chapter 7 provides some guidelines for data analysis. For those who are interested in theoretical inquiry, this chapter provides a starting point to pursue further research. Upon realizing the difficulties involved in understanding mathematical terms, several appendices are added to the end of the chapter to give some background information.

Chapters 8 through 12, are so intermingled in content that they are hardly independent from each other, yet they are so important that each deserves to be an independent chapter. Both Chapters 8 and 9 are about light scattering. Chapter 8 describes general principles and applications, while Chapter 9 discusses advanced techniques in exploring detailed information about the interactions between polymer molecules in solutions. Chapters 10 and 11 are both about diffusion. Chapter 10 deals with the general principles and applications of diffusion, while Chapter 11 describes advanced techniques in measurement. However, diffusion is only part of the domain in Chapter 11, for Chapter 11 is also directly related to light scattering. As a matter of fact, Chapters 8, 9, and 11 can be grouped together. In parallel, Chapters 10 and 12, one about diffusion and the other about sedimentation, are closely related. They describe similar principles and similar experimental techniques. Knowledge of diffusion is often complementary to knowledge of sedimentation and vice versa.

It should be pointed out that all the chapters in unit 2 (Chapters 6 through 12) so far deal with methods for determining molecular weight and the configuration of macromolecules. They are standard chapters for both a course of polymer chemistry and a course of biophysical chemistry. Chapters 13 through 17 describe some of the important experimental techniques that were not covered in Chapters 6 through 12.

Briefly, Chapter 13, on optical rotatory dispersion (ORD) and circular dichroism (CD), describes the content of helices in a biological polymer under various conditions, that is, in its native as well as in its denatured states. The relationship between ORD and CD is discussed in detail. Chapter 14 provides basic knowledge of nuclear magnetic resonance phenomena and uses illustrations of several well known synthetic polymers and proteins. Chapter 15, on x-ray crystallography introduces the foundations of x-ray diffractions, such as Miller indices, Bravais lattices, seven crystals, 32 symmetries, and some relevant space groups. It then focuses on the study of a single crystal: the structure factor, the density map, and the phase problem. Chapter 16, on electron and infrared spectroscopy, provides the background for the three most extensively used spectroscopic methods in macromolecular chemistry, particularly with respect to biological polymers. These methods are ultraviolet absorption, fluorimetry, and infrared spectra. Chapter 17 belongs to the realm of separation science or analytical chemistry. It is included because no modern research in polymer chemistry or biophysical chemistry can completely neglect the techniques used in this area. This chapter is split into two parts. The first part, high-performance liquid chromatography (HPLC), describes key parameters of chromatograms and the four types of chromatography with an emphasis on size-exclusion chromatography, which enables us to determine the molecular weight, molecular weight distribution, and binding of small molecules to macromolecules. The second part, electrophoresis, describes the classical theory of ionic mobility and various types of modern techniques used for the separation and characterization of biological materials. Chapter 17 ends with an additional section field-flow fractionation, which describes the combined methods of HPLC and electrophoresis.

In conclusion, the organization of this book covers the basic ideas and issues of the physical chemistry of macromolecules including molecular structure, physical properties, and modern experimental techniques.

Mathematical equations are used frequently in this book, because they are a part of physical chemistry. We use mathematics as a language in a way that is not different from our other language, English. In English, we have words and sentences; in mathematics, we use symbols (equivalent to words) and equations (equivalent to sentences). The only difference between the two is that mathematics as a symbolic language, is simple, clear, and above all operative, meaning that we can manipulate symbols as we wish. The level of mathematics used in this text is not beyond elementary calculus, which most readers are assumed to have learned or are learning in college.

In this book, derivations, though important, are minimized. Derivations such as Flory's lattice theory on the entropy of mixing and Rayleigh's equation of light scattering are given only because they are simple, instructive, and, above all, they provide some sense of how an idea is translated from the English language to a mathematical language. The reader's understanding will not be affected if he or she skips the derivation and moves directly to the concluding equations. Furthermore the presentation of the materials in this book has been tested on my classes for many years. No one has ever complained.

The selection of mathematical symbols (notations) used to designate a physical property (or a physical quantity) poses a serious problem. The same letter, for example, α or c, often conveys different meanings (that is, different designations). The Greek letter α can represent a carbon in a linear chain (α atom, β atom, ...), one of the angles of a three-dimensional coordinate system (related to types of crystals), the expansion factor of polymer molecules in solutions (for example, $\alpha^5 - \alpha^3$), the polarizability with respect to the polarization of a molecule, and so on. The English letter c can represent the concentration of a solution (for example, g/mL, mol/L), the unit of coordinates (such as a, b, c), and so on. To avoid confusion, some authors use different symbols to represent different kinds of quantities and provide a glossary at the end of the book. The advantage of changing standard notation is the maintenance of consistency within a book. The disadvantage is that changing the well-known standard notation in literature (for example, S for expansion factor, T for polarizability, instead of α for both; or d for a unit coordinate, j for the concentration of a solution, instead of c for both), is awakward, and may confuse readers. In addressing this problem, the standard notations are kept intact. Sometimes the same letters are used to represent different properties in the same chapter. But I have tried to use a symbol to designate a specific property as clearly as possible in context by repeatedly defining the term immediately after the equation. I also add a prime on the familiar notations, for example, R' for gas constant and c' for the velocity of light. Readers need not worry about confusion.

At the end of each chapter are references and homework problems. The references are usually the source materials for the chapters. Some are original papers in literature, such as those by Flory, Kirkwood, Debye, Rouse, Des Cloizeau, deGennes, Luzzati, and Zimm, among others; and some are well-known books, such as those of Yamakawa and Hill, in which the original papers were cited in a rephrased form. Equations are usually given in their original forms from the original papers with occasional modifications to avoid confusion among symbols. It is hoped that this will familiarize readers with the leading literature. Homework problems are designed to help readers clarify certain points in the text.

A comment should be made on the title of the book, *Physical Chemistry of Macromolecules: Basic Principles and Issues*. The word "basic" refers to "fundamental," meaning "relatively timeless." In the selection of experimental methods and theories for each topic, the guideline was to include only those materials that do not change rapidly over time, for example, Fick's first law and second law in diffusion, Patterson's synthesis and direct method in x-ray crystallography, or those materials, though current, that are well established and frequently cited in the literature, such as the scaling concept of polymer and DNA sequencing by electrophoresis. The book is, therefore, meant to be "a course of study."

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