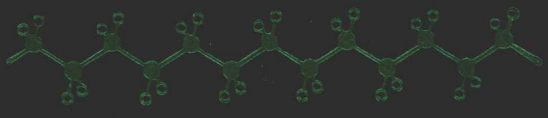
SECOND EDITION

FUNDAMENTALS OF POLYMER SCIENCE



AN INTRODUCTORY TEXT

PAUL C. PAINTER
MICHAEL M. COLEMAN

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MICHAEL M. COLEMAN
The Pennsylvania State University

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DEDICATION AND ACKNOWLEDGEMENT

This is the book that we swore we would never write after we finished our last book. But now that we have written it and the frustrations have passed, we gratefully dedicate the book to our fathers, Charles Painter and Ronald Coleman, whose lives were and much more difficult than ours and who sacrificed many things to give us a start.

We would also like to take this opportunity to acknowledge our friends at Technomic, Mike Margotta and Tony Deraco, who shrewdly managed to hide their superior golfing abilities in order not to embarrass the authors and also persuade them to complete this second edition.

PREFACE TO THE SECOND EDITION

Writing a book, particularly a textbook, can take a lot out of you:

Writing a book is an adventure: it begins as an amusement, then it becomes a mistress, then a master and finally a tyrant.

Winston S. Churchill

Things get particularly hard near the end, when you are confronted by the tedious tasks of preparing an index, editing and proof reading; especially when you look out the window, the sun is shining and you would rather be playing golf.

All morning I worked on the proof of one of my poems, and I took out a comma; in the afternoon I put it back.

Oscar Wilde

So it is perhaps inevitable that your attention slips and errors creep in. You don't realize this until later, of course, when you start to find some minor typo's or garbled sentences. This is not too bad and you can always blame your publishers:

It is with publishers as with wives: one always wants somebody else's.

Norman Douglass

But if your book is used as a text, each and every mistake will be found by your students and the number of revealed errors becomes daunting. Even worse, these errors are often brought to your attention in a manner that you believe reflects a large measure of glee:

There are those who notice mistakes in passing and those who buy books for the sole purpose of finding them.

A. K. Dewdney

It is particularly galling when your so-called friends participate in the criticism:

Of all plagues, good heaven, thy wrath can send,
Save me, oh save me from the candid friend.

George Canning

Naturally, your first instinct is to attribute their comments to mere envy:

Nothing is more humiliating than to see idiots succeed in enterprises we have failed in.

Gustave Flaubert

This base emotional response is quickly replaced by denial:

If at first you don't succeed, destroy all evidence that you have tried.

Anonymous

But in the end a measure of objectivity returns and you start to make a list of corrections. You then also notice that there are certain topics that you really made a mess of:

I know you believe you understand what you think I said, but I am not sure you realize that what you heard is not what I meant.

Anonymous

So you end up writing a second edition. You hopefully fix all the errors in the first edition, modify a little here and there to improve clarity, add some study questions (for those idle teachers who cannot be bothered to make them up!) and end up totally rewriting and reorganizing two chapters. But you no longer have the illusion that your efforts will be remotely error-free; you just hope to get some minor satisfaction from your work:

Some day I hope to write a book where the royalties will pay for the copies I give away.

Clarence Darrow

February 1997

PAUL PAINTER
MIKE COLEMAN

PREFACE TO THE FIRST EDITION

If you, dear reader, ever write a book, you will eventually find that having labored long and hard to write down and give shape to your view of a subject, an effort that can result in hundreds of pages of text and figures that perhaps (if you are lucky) only a few hundred people might ever read, you are then faced with the oppressive but suddenly daunting task of writing a preface. This is where you are supposed to explain what the book is about and why you wrote it in the first place. The problem is that you no longer remember.

But a preface has its uses. It can give readers a whiff of the author's prose style and an indication of his potential as an inducer of tedium, thus enabling them to moderate their enthusiasm, lower their sights, and so prepare themselves for the main body of the work.

Frank Muir (An Irreverent and Thoroughly Incomplete Social History of Almost Everything)

In addition, you are by now tired and fed up with the whole enterprise;

How unfit, and how unworthy a choice I have made of myself, to undertake a work of this mixture.

Sir Walter Raleigh

and you are starting to suspect that your explanation of what you know reveals even more about what you don't know;

A person who publishes a book willfully appears before the populace with his pants down.

Edna St. Vincent Millay

Even worse, you find that if your scribblings have been a collaborative effort you might no longer be on speaking terms with your co-author and one-time friend;

I have known two professors of Greek who ceased speaking to one another because of divergent views on the pluperfect subjunctive.

Stephen Leacock

Fortunately, you realize that this too will pass and you must save your disagreements for more vital matters;

I've seen lifelong friends drift apart over golf just because one could play better, but the other counted better.

Stephen Leacock

What really happens is that if you teach, then at some point you become so frustrated with what you perceive as the shortcomings of the available texts that you decide to write your own. And that is what happened to us. Of course, you then find that the books you were using were not so bad after all, its just that you wanted to emphasize or include subjects that perhaps others found uninteresting or irrelevant, but which to you are of consuming interest and central to the whole field.

So, here is our effort; the essential parts of what we teach in two courses to juniors, seniors and some first-year graduate students that have drifted into polymers from other fields. It is an introduction and survey of the subject based on a refinement of what we have taught over the last ten years. As with all books of this type, it is difficult to know what to assume as prior knowledge. We naturally suppose that the student has digested some fundamentals of organic chemistry,

Organic chemistry is the study of organs; inorganic chemistry is the study of the insides of organs.

Max Shulman

and has enough physics and physical chemistry to be comfortable with basic molecular concepts;

MOLECULE,*n*. The ultimate, indivisible unit of matter. It is distinguished from the corpuscle, also the ultimate, indivisible unit of matter, by a closer resemblance to the atom, also the ultimate, indivisible unit of matter. Three great scientific theories of the structure of the universe are the molecular, the corpuscular and the atomic. A fourth affirms, with Haeckel, the condensation or precipitation of matter from ether–whose existence is proved by the condensation or precipitation. The present trend of scientific thought is toward the theory of ions. The ion differs from the molecule, the corpuscle and the atom in that it is an ion. A fifth theory is held by idiots, but it is doubtful if they know any more about the matter than the others.

Ambrose Bierce

(The Devil's Dictionary)

However, it has been our experience that the average student has only imperfectly digested certain fundamentals before starting their studies of polymers, so in our lectures and in this book we attempt to start at a simple level with brief reviews of what should be (but usually isn't) well-known material. Of course, we have to guard against carrying this to extremes and we have tried to overcome a tendency to over-explain;

I am standing on the threshold about to enter a room. It is a complicated business. In the first place I must shove against an atmosphere pressing with a force of fourteen pounds on every square inch of my body. I must make sure of landing on a plank travelling at twenty miles a second round the sun–a fraction of a second too early or too late, the plank would be miles away. I must do this whilst hanging from a round planet head outward into space, and with a wind of aether blowing at no one knows how many miles a second through every interstice of my body. The plank has no solidity of substance. To step on it is like stepping on a swarm of flies. Shall I not slip through? No, if I make the venture one of the flies hits me and gives a boost up again; I fall again and am knocked upwards by another fly, and so on. I may hope that the net result will be that I remain about steady; but if unfortunately I should slip through the floor or be boosted too violently up to the ceiling, the occurrence would be, not a violation of the laws of Nature, but a rare coincidence. These are some of the minor difficulties. I ought really to look at the problem four-dimensionally as concerning the intersection of my world-line with that of the plank. Then again it is necessary to determine in which direction the entropy of the world is increasing in order to make sure that my passage over the threshold is an entrance not an exit.
Verily, it is easier for a camel to pass through the eye of a needle that for a scientific man to pass through a door.

Sir Arthur Eddington
(The Nature of the Physical World)

Keeping this warning in mind, we have tried to say what we have to say simply;

Don't quote Latin; say what you have to say, and then sit down.

Arthur Wellesley
Duke of Wellington

and in so doing we have deliberately adopted a conversational tone to our writing. Some might find this irritating and unrigorous;

This is the sort of English up with which I will not put.

Winston S. Churchill

but in the final analysis this is the way we like to write and if you don't like it, write your own damned book!

February 1994

PAUL PAINTER
MIKE COLEMAN

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CHAPTER 1

The Nature of Polymeric Materials

"He fixed thee mid this dance
of plastic circumstance"
—Robert Browning

A. WHAT ARE POLYMERS—WHAT IS POLYMER SCIENCE?

Simply stated, polymers are very large molecules (macromolecules) that are comprised or built up of smaller units or monomers. The arrangements of these units, the various types of chains that can be synthesized and the shapes that these chains can bend themselves into, result in a class of materials that are characterized by an enormous and intriguing range of properties. Some of these are unique to polymers (e.g., rubber elasticity) and, as we shall see, are simply a consequence of their size and chain-like structure.

Polymer science is also a relatively new discipline and one that is characterized by extraordinary breadth. It involves aspects of organic chemistry, physical chemistry, analytical chemistry, physics (particularly theories of the solid state and solutions), chemical and mechanical engineering and, for some special types of polymers, electrical engineering. Clearly, no one person has an in-depth knowledge of all these fields. Most polymer scientists seek a broad overview of the subject that is then usually supplemented by a more detailed knowledge of a particular area. This book is a first step towards the former and to give a flavor for the diversity of this subject matter we will commence with an outline of some of the areas we will cover.

Polymer Synthesis

Many polymer scientists think that it is unlikely that we will ever again see any new thermoplastic take the world by storm (i.e., achieve levels of production comparable to polyethylene or polystyrene), but it should be kept in mind that similar things were being said round about 1950, just before high density polyethylene and isotactic polypropylene made their debut (some of this terminology will be defined shortly). Today, there are two good reasons to think they may be right, however. First, all the monomers that can be readily polymerized already have been; second, commercializing a new *commodity* plastic would probably cost more than $1 billion (*The Economist*, May 1980). This is not promising in an industry that has become infected by MBA's with a

six month time-horizon. Fortunately, this does not mean that polymer synthetic chemists are out of business. There is considerable interest in using new catalysts (for example) to produce commodity plastics more cheaply, or in producing better defined chain structures to give controlled properties; synthesizing "specialty" polymers such as those with stiff chains and strong intermolecular attractions to give thermal resistance and high strength; or chains with the types of delocalized electronic structures that result in unusual electrical and optical properties. These materials would be produced in smaller quantities than "bulk" plastics, but can be sold at a much higher price. Our intention is only to give you a start in this area, however, so you won't find any discussion of advanced synthetic methods in this book. In chapter 2 we simply cover the basics of polymer synthesis, but this is enough for you to grasp the essentials of how the majority of commercial polymers are produced.

Polymer Characterization

What a chemist *thinks* he or she has made is not always the stuff that is lying around the bottom of his or her test tube. Accordingly, there is an enormous field based on characterization. This is now a particularly exciting area because of recent advances in instrumentation, particularly those interfaced with high-powered yet small and relatively cheap dedicated computers. These novel analytical techniques are not only useful in studying new materials, but answering questions that have intrigued polymer scientists for decades. For example, spectroscopic techniques are used to examine "local" chemical structure and interactions in polymer systems. Electron and other microscopies and the scattering of electromagnetic radiation are used to characterize overall structure or morphology; i.e., how components of a system phase separate into various types of structures; how chains fold into crystals; and the shape of an individual chain in a particular environment. Some techniques are so expensive that national facilities are required, e.g., synchotron radiation and neutron scattering. Our focus in this book will be on the basics, and in particular we will discuss the measurement of molecular weight and the use of molecular spectroscopy to characterize chain structure.

Polymer Physical Chemistry

Paul Flory was awarded the Nobel Prize in Chemistry for his work in this area and we will mention his name often in this book. Polymer physical chemistry is a subject that demands a knowledge of theory and the ability to perform carefully controlled experiments, often using the types of instruments mentioned above. (The areas of characterization and polymer physical chemistry overlap considerably and they are artificially separated here merely to illustrate the different types of things polymer scientists do.) The simplest way to get a "feel" for this subject is get a copy of Flory's book *Principles of Polymer Chemistry*, still a classic after forty years, and scan the chapters on, for example, the theories of rubber elasticity, solution thermodynamics, phase behavior, etc.

This subject is still attracting enormous interest, and there has been much recent emphasis on polymer blends or alloys and polymer liquid crystals.

Polymer Physics

Polymer physics and polymer physical chemistry are overlapping disciplines that are not, in many cases, easily delineated. Historically, however, it is possible to point to an enormous impact by theoretical physicists starting in the late 1960's and early 1970's. Until then most theory was based on almost classical physical chemistry, but a number of leading physicists (notably de Gennes and Edwards) started to apply modern theories of statistical physics to the description of long chain molecules. The result has been a revolution in polymer theory, one that is not easily assimilated by "traditional" polymer scientists and is still ongoing.

Polymer physics is not confined to theory, however. Experimental polymer physics continues to focus on areas such as chain conformation, viscoelastic and relaxation properties, phenomena at interfaces, kinetics of phase changes and electrical and piezoelectric properties. In our discussions of polymer physics and physical chemistry we will focus on chain conformation and morphology (structure), thermal properties (crystallization, melting and the glass transition), solution properties and the determination of molecular weight.

Polymer Engineering

Last, but by no means least, there is a vast area that is involved with chemical engineering (the processing of polymers) and mechanical engineering (studies of strength, fatigue resistance, etc.) as applied to polymeric materials. For example, there is enormous interest in producing ultra-high strength polymer fibers. It turns out that even "common or garden" polymers like polyethylene or polypropylene can be processed to give "high-tech" properties. The trick is to align the chains as perfectly as possible; not an easy task. Once made of course, the mechanical properties of these materials have to be determined. This involves more than stretching a fiber until it breaks. The mechanical properties of polymers are complicated by all sorts of factors (defects, relaxation processes, etc.) and the field is an intriguing combination of mechanical measurements, structural characterization and theory. The last chapter in this book will deal with mechanical properties of polymers.

B. SOME BASIC DEFINITIONS - THE ELEMENTS OF POLYMER MICROSTRUCTURE

It may seem a bit like putting the cart before the horse, but we will first describe some basic molecular characteristics of the chain structure of polymers before we consider the chemistry of how these materials are produced. By arranging the subject matter in this manner it immediately becomes clear why