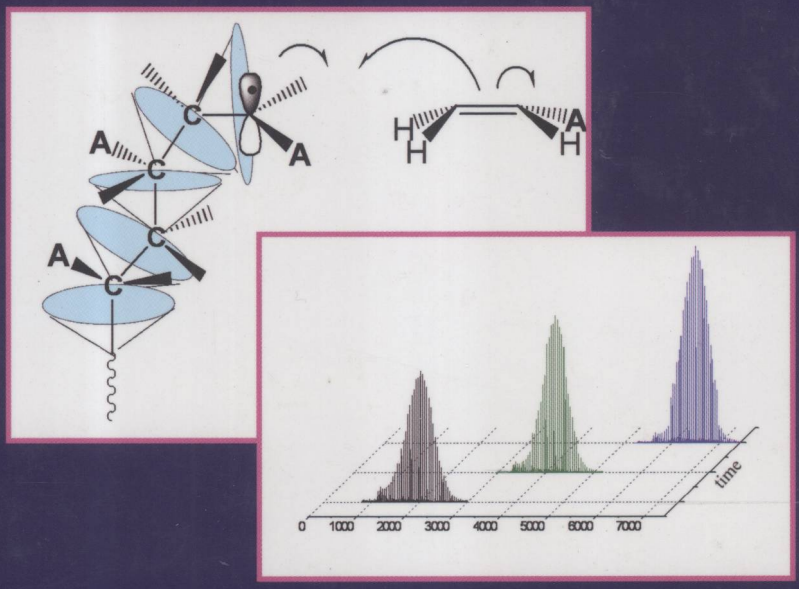
WILEY

ORGANIC AND PHYSICAL CHEMISTRY OF POLYMERS



YVES GNANOU
MICHEL FONTANILLE

Foreword by Professor Krzysztof Matyjaszewski
from the Department of Chemistry at Carnegie Mellon University

ORGANIC AND PHYSICAL CHEMISTRY OF POLYMERS

Yves Gnanou
Michel Fontanille

WILEY-INTERSCIENCE
A JOHN WILEY & SONS, INC., PUBLICATION

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

Library of Congress Cataloging-in-Publication Data:

Gnanou, Yves.
Organic and physical chemistry of polymers / by Yves Gnanou and Michel Fontanille.
p. cm.
Includes index.
ISBN 978-0-471-72543-5 (cloth)
1. Polymers. 2. Polymers—Synthesis. 3. Chemistry, Physical and theoretical. I. Fontanille, M. (Michel), 1936– II. Title.
QD381.G55 2008
547′.7—dc22

2007029090

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

ORGANIC AND PHYSICAL CHEMISTRY OF POLYMERS

FOREWORD

Polymers, commonly known as plastics, are perhaps the most important materials for society today. They are employed in nearly every device. The interior of every automobile is essentially entirely made of polymers; polymers are also used for body parts and for under-the-hood applications. Progress in the aerospace industry has been aided by new light, strong nanocomposite polymeric materials. Many construction materials (e.g., insulation, pipes) and essentially all adhesives, sealants, and coatings (paints) are made from polymers. The computer chips used in our desktops, laptops, cell phones, Ipods, or Iphones are enabled by polymers used as photoresists in microlithographic processes. Many biomedical applications require polymers for tissue or bone engineering, drug delivery, and also for needles, tubing, and containers for intravenous delivery of medications. Some new applications call for smart or "intelligent" polymers that can respond to external stimuli and change shape and color to be used as artificial muscles or sensors.

Thus, it is not surprising that the annual production of polymers approaches 200 million tons and 50% of the chemists in USA, Japan or Western Europe work in one way or other with polymeric materials. However, polymer awareness has not yet reached the appropriate level, for many of those chemists do not fully comprehend nor do they take advantage of concepts of free volume, glass transition, and microphase separation; consequently they do not know how to precisely control polymer synthesis. One may also argue that some polymer scientists do not sufficiently appreciate most recent developments in organic and physical chemistry, although polymer science has a very interdisciplinary character and bridges synthetic chemistry with precise characterization techniques offered by the methodologies of physical chemistry.

Organic and Physical Chemistry of Polymers by Yves Gnanou and Michel Fontanille provides a unique approach to combine fundamentals of organic and physical chemistry and apply them to explain complex phenomena in polymer science. The authors employ a very methodical way, straightforward for polymer science novices and at the same time, attractive for more experienced polymer scientists. On reading this book, one can easily comprehend not only how to make conventional and new polymeric materials, but also how to characterize them and use them for classic and new advanced applications.

I read the book with a great interest, and I am convinced that this book will become an excellent polymer science textbook for senior undergraduate and graduate students.

KRZYSZTOF MATYJASZEWSKI

J.C. Warner University Professor of Natural Sciences
Carnegie Mellon University
Fall 2007, Pittsburgh, USA

PREFACE

Although the uses of polymers in miscellaneous applications are as old as humanity, polymer science began only in the 1920s, after Staudinger conclusively proved to sceptics the concept of long chain molecules consisting of atoms covalently linked one to another. Then came the contributions of physicists: Kuhn first accounted for the flexibility of certain polymers and understood the role of entropy in the elasticity of rubber. Flory subsequently explained most of the physical properties of polymers using very simple ideas, and Edwards found a striking analogy between the conformation of a polymer chain and the trajectory of a quantum mechanical particle.

The aim of this textbook is to do justice to the interdisciplinary nature of polymer science and to break the traditional barriers between polymer chemistry and the physical chemistry and physics of polymers. Through the description of the structures found in polymers and the reactions used to synthesize them, through the account of their dynamics and their energetics, are conveyed the basic concepts and the fundamental principles that lay the foundations of polymer science. We tried to keep in view this primary emphasis throughout most of the book, and chose not to elaborate on applicative and functional aspects of polymers.

At the core of this book lie three main ideas:

1. —the synthesis of polymer chains requires reactions exhibiting high selectivity, including regio-, chemo- and sometimes stereoselectivity. Mother Nature also produces macromolecules that are useful for life (proteins, DNA, RNA) but with a much higher selectivity;
2. —polymers represent a class of materials that are by essence ambivalent, exhibiting at the same time viscous and elastic behaviors. Indeed, a polymer chain never behaves as a purely elastic material or as an ideal viscous liquid. Depending upon the temperature and the polymer considered, the time scale of the stress applied, either the viscous or the elastic component dominates in its response;
3. —an assembly of polymer chains can adopt a variety of structures and morphologies and self-organize in highly crystalline lamellae or exist as a totally disordered amorphous phase and intermediately as mesomorphic structures.

Polymers are thus materials with peculiar physical properties which are controlled by their methods of synthesis and their internal structure. The first chapters (I to III) introduce the notions of configuration and conformation of polymers, their dimensionality, and how their multiple interactions contribute to their overall cohesion. The three next chapters are concerned with physical chemistry, namely the thermodynamics of polymer solutions (IV), the structures typical of polymer assemblies (V), and the experimental methods used to characterize the size, the shape and the structures of polymers (VI). Four chapters (VII to IX) then follow that elaborate on the methods of synthesis and modification of polymers, and the engineering of complex architectures (X). Chapters XI to XIII subsequently describe the thermal transitions and relaxations of polymers, their mechanical properties and their rheology. These thirteen chapters are rounded off by monographs (chapters XIV to XVI) of natural polymers and of some common monodimensional and tridimensional polymers.

Since the 1920s, polymer science has moved on at a dramatic rate. Significant advances have been made in the synthesis and the applications of polymeric materials, paving the way for the award of the Nobel Prize in five instances to polymer scientists. Staudinger in 1953, Ziegler and Natta in 1963, Flory in 1974, de Gennes in 1991, and more recently McDiarmid, Shirakawa and Heeger in 2000 indeed received this distinction. Their contributions and the many developments witnessed in the area of specialty polymers have made necessary to write a book that provides the basics of polymer science and a bridge to an understanding of the huge primary literature now available. This book is intended for students with no prior knowledge or special background in mathematics and physics; it can serve as a text for a senior-level undergraduate or a graduate-level course.

In spite of our efforts, some mistakes certainly remain; we would appreciate reports about these from readers.

Last but not least, we wish to mention our debt and express our gratitude to Professors Robert Pecora (Standford University), Marcel van Beylen (Leuven University) and colleagues from our University who read and checked most of the chapters. We are also indebted to Professor K. Matyjaszewski for accepting to write the foreword of this book.

YVES GNANOU
MICHEL FONTANILLE

Summer 2007, Bordeaux, France.

CONTENTS

1

INTRODUCTION

1.1. HISTORY

The term *polymer* is quite old and has been used since 1866 after Berthelot mentioned that "When styrolene (now called *styrene*) is heated up to 200°C for several hours, it is converted into a resinous polymer...." Is it the first synthetic polymer recognized as such? Probably, yes. However, the concept of polymeric chain as we understand it today had to wait for the work of Staudinger (Nobel Prize laureate in 1953) before being fully accepted. It is only from that time onward—approximately the 1920s—that the "macromolecular" theory ultimately prevailed over the opposite "micellar" theory.

Meanwhile, artificial and synthetic polymers had acquired due acceptance and began to be utilized as substitutes for rare substances (celluloid in lieu of ivory, artificial silk, etc.) or in novel applications (bakelite, etc.) due to their peculiar properties.

The variety of synthetic polymers discovered by Staudinger is impressive, and a number of today's polymeric substances were prepared for the first time by this outstanding scientist. His work soon attracted the keen interest and attention of the chemical industry, and as soon as 1933 the ICI company obtained a grade of polyethylene whose world production is still several tens of million tons per annum. A little later (1938), and after some failures in the field of polyesters, scientists

Organic and Physical Chemistry of Polymers, by Yves Gnanou and Michel Fontanille

headed by Carothers at DuPont de Nemours discovered the polyamides (known as "nylons"). This breakthrough illustrated the ability of polymer chemists to design and invent materials with mechanical characteristics surpassing those of materials originating from the vegetable or animal worlds.

By the end of the Second World War, polymers had shown their ability to replace many traditional materials, but were somehow plagued by a reputation of affording only poor-quality products. From the research work carried out in both academic laboratories and industrial research centers since then, many unexpected improvements have been accomplished in terms of processes and properties, so that today's polymers are present in most advanced sectors of technology.

It is no surprise that the name of several Nobel laureates appear on the list of scientists who have contributed the most to polymer science. In addition to Staudinger, these include Ziegler, Natta, Flory, de Gennes, McDiarmid, Shirakawa, Heeger, and, recently, Chauvin, Grubbs, and Schrock. There are also many scientists whose names are known only to experts and whose contributions were instrumental in the development of the polymer field. Owing to the economic significance of polymer materials, industry has also been keen on supporting research work in the field of polymers. They are indeed present everywhere and appear in almost all aspects of our daily life. With the continuous improvement of their properties, the old tendency to look down on polymers has given way to attention and consideration; more than ever, the current perception is: "There are no bad polymers but only bad applications."

Table 1.1 contains important dates that have marked the progress witnessed in the field of polymers throughout the last 150 years or so. Most of them correspond to the discovery of new methodologies and materials, followed by their industrial development. These successes have been possible because of a sustained investment in basic research and the surge of knowledge that has resulted from it.

1.2. SEVERAL DEFINITIONS

What is a polymer? Several answers can be given, but, for the moment, the most common and generally accepted definition is: a system formed by an assembly of macromolecules—that is, a system of molecular entities with large dimension, which are obtained by the covalent linking of a large number of constitutional repeat units, more commonly called monomeric units. The macromolecular structures corresponding to this definition have molecular dimensions (characterized by their molar mass) much larger than those of the simple molecules. This, in turn, provides the polymer considered with properties of practical application—in particular, in the field of materials.

It is difficult to precisely define the change induced by the transition from the simple molecular level to the macromolecular one. Depending upon the property considered, the macromolecular effect will be indeed perceptible at a lower or higher threshold of molar mass; for example, the majority of industrially produced linear polymers used in daily life are in the range of $\sim 10^5$ g·mol^{-1}.

Table 1.1. Main dates in the history of polymers

1838: A. Payen succeeded in extracting from wood a compound with the formula $(C_6H_{10}O_5)_n$, which he called *cellulose*.

1844: C. Goodyear developed the vulcanization of natural rubber.

1846: C. Schonbein obtained nitrocellulose (which was the first "artificial" polymer) by action of a sulfo-nitric mixture on cellulose.

1866: M. Berthelot discovered that upon heating "styrolene" up to 200°C for several hours, the latter is converted into a "resinous polymer."

1883: H. de Chardonnet obtained "artificial silk" by spinning a collodion (concentrated solution) of nitrocellulose.

1907: A. Hofmann prepared the first synthetic rubber by polymerization of conjugated dienes.

1910: L. Baekeland developed the first industrial process for the production of a synthetic polymer; formo-phenolic resins were produced under the name of "bakelite."

1919: H. Staudinger introduced the concept of macromolecule and then carried out the polymerization of many vinyl and related monomers. He can be viewed as the father of macromolecular science.

1925: Th. Svedberg presented experimental evidence of the existence of macromolecules by measuring their molar mass using ultracentrifugation.

1928: K. Meyer and H. Mark established the relationship between the chemical and crystallographic structures of polymers.

1933: E. Fawcett and R. Gibson, working for I.C.I., carried out the free radical polymerization of ethylene under high pressure.

1938: W. Carothers (of DuPont de Nemours) and his team prepared the first synthetic polyamides (known under the "nylon" tradename).

1942: P. Flory and M. Huggins proposed a theory accounting for the behavior of macromolecular solutions.

1943: O. Bayer synthesized the first polyurethane.

1947: T. Alfrey and C. Price proposed a theory of chain copolymerization.

1953: F. Crick and J. Watson identified the double helix structure of DNA using X-ray crystallography. They shared the Nobel Prize in 1962.

1953: K. Ziegler discovered the polymerization of ethylene under low pressure, using a catalyst generated from $TiCl_4$ and AlR_3.

1954: G. Natta obtained and identified isotactic polypropene.

1955: M. Williams, R. Landel, and J. Ferry proposed a relation (WLF equation) between the relaxation time of polymer chains at a certain temperature and that measured at the glass transition temperature.

1956: M. Szwarc established the principles of "living" polymerizations based on his work on the anionic polymerization of styrene.

1957: A. Keller obtained and characterized the first macromolecular monocrystal.

1959: J. Moore developed size exclusion chromatography as a technique to fractionate polymers.

1960: Discovery of thermoplastic elastomers and description of the corresponding morphologies.

1970–1980: P.-G. de Gennes formulated the scaling concepts which accounted for the variation of the characteristic sizes of a polymer with its concentration. He introduced with Doi and Edwards the concept of reptation of polymer chains in the molten state.

(*continued overleaf*)

Table 1.1. (*continued*)

1974: Development of aromatic polyamides by DuPont de Nemours.
1980: W. Kaminsky and H. Sinn discovered the effect of aluminoxanes on the polymerization of olefins catalyzed by metallocenes.
1982: A DuPont de Nemours team working under O. Webster and D. Sogah discovered the group transfer polymerization of acrylic monomers and initiate various research works related to the controlled polymerization of these monomers.
1982: T. Otsu introduced the concept of controlled radical polymerization. This concept was applied by E. Rizzardo and D. Solomon (1985) then by M. George (1992) to the controlled radical polymerization of styrene.
1986: D. Tomalia described the synthesis of the first dendrimers.
1992: D. Tirrell synthesized the first perfectly uniform polymer using methods of genetic engineering.
1994: M. Sawamoto and K. Matyjaszewski developed a new methodology of controlled radical polymerization by atom transfer.
2000: After more than 20 years of work on intrinsically conducting polymers, H. Shirakawa, A. Heeger, and A. McDiarmid were awarded the Nobel Prize in Chemistry.
2005: Y. Chauvin, R. Grubbs, and R. Schrock have been awarded the 2005 Nobel Prize in Chemistry for improving the metathesis reaction, a process used in making new polymers.

Remark. The terms *polymer* and *macromolecule* are often utilized without discrimination. Some specialists prefer using the term *macromolecule* for compounds of biological origin, which often have more complex molecular structure than synthetic polymers. For our part, we will utilize the two terms interchangeably.

The number of monomer units constituting a polymer chain is called the *degree of polymerization** (DP); it is directly proportional to the molar mass of the polymer. An assembly of a small number of monomer units within a macromolecular chain is called *sequence* and the first terms of the series of sequences are referred to as *dyad, triad, tetrad, pentad*, and so on. Chains made up of a small number of monomer units are called *oligomers*; typically, the degrees of polymerization of oligomers vary from 2 to a few tens. Synthetic polymers are obtained by reactions known as polymerization reactions, which transform simple molecules called monomer molecules (or monomers) into a covalent assembly of monomer units or polymer. When a polymer is obtained from the polymerization of different monomer molecules (indicated in this case by *comonomers*) exhibiting different molecular structure, it is called a *copolymer*.

*The symbol recommended by IUPAC for the average number of monomeric units in a polymeric chain is $\overline{X}$, D*P* being the abbreviation for the degree of polymerization.

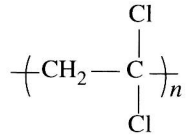
Monomeric units that are part of a polymer chain can be linked one to another by a varying number of bonds; we suggest to call this number *valence*.† This term should be preferred to *functionality*, which can be misleading (see page 216). Thus, monomeric units can be mono-, di-, tri-, tetra-, or plurivalent and so are the corresponding monomer molecules.

The average valence of monomeric units in a macromolecular chain determines its *dimensionality* (see Section 1.4.3).

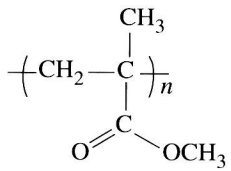
1.3. REPRESENTATION OF POLYMERS

Depending upon the level of precision and the type of information required, one has at one's disposal different adequate representations of the polymer structure. To represent the macromolecular nature of a linear polymer, a mere continuous line as shown in Figure 1.1 is perfectly relevant. Representations appearing in Figures 1.3 and 3.1 (see the corresponding paragraphs) illustrate more complex architectures and for the first one of higher dimensionality.

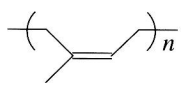
The most suitable representation of the chemical structure of a macromolecular compound is a monomeric unit flanked by two brackets and followed by a number, n, appearing as an index to indicate the degree of polymerization. Such a representation disregards the chain ends, which are necessarily different from the main chain, as well as possible defects along the polymer backbone (Section 3.2). This is illustrated in the following three examples, which are based on conventions borrowed from organic chemistry.



Poly(vinylidene chloride)



Poly(methyl methacrylate)

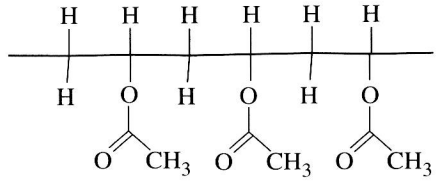


cis-1,4-Polyisoprene

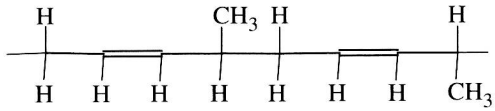
To address configurational aspects, one generally relies on the Fischer projections used in organic chemistry, with a rotation $\pi/2$ of the line representing the main chain. However, in the case of polymers, it is the relative configuration of

†The term valence of monomers or of monomeric units is proposed by anology with the valence of atoms which corresponds to the number of orbitals available for bonding. The valence of a monomer thus corresponds to the number of covalent bonds that it forms with the nearest monomeric units.

a sequence of monomer units that is considered, which implies that several such units are represented. The two following examples take into consideration these conventions:

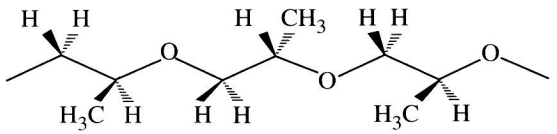


Sequence of 3 successive units *(triad)* of poly(vinyl acetate) presenting the same configuration



Sequence of 2 successive units *(dyad)* of *cis*-1,4-polypentadiene, presenting opposite chiralities and the same geometrical configurations

This method of representation is certainly easier to use than the one based on the principles established by Cram, which is illustrated below:



[S][S][S] triad of poly(propylene oxide)

1.4. CLASSIFICATION OF ORGANIC POLYMERS

1.4.1. Depending upon their **origin**, one can classify polymers into three categories:

- **Natural polymers** are obtained from vegetable or animal sources. Their merits and utility are considerable, but they will be only briefly described in the first part of this work. To this category belong all families of polysaccharides (cellulose, starch, etc.), proteins (wool, silk, etc.), natural rubber, and so on;
- **Artificial polymers** are obtained by chemical modification of natural polymers in order to transform some of their properties; some of them, such as cellulose esters (nitrocellulose, cellulose acetate, etc.), have been economically important for a long time;
- **Synthetic polymers** are exclusively the result of human creation; they are obtained by polymerization of monomer molecules. There exists a large variety of such polymers, and henceforth they will be described in detail.

1.4.2. A classification by **applications** would not be exhaustive because of the extreme variability of the polymer properties and the endless utilization of polymers, particularly in the field of materials. However, one can identify three main categories of polymers as a function of the application contemplated:

- **Large-scale** polymers (also called **commodity** polymers), whose annual production is in the range of millions of tons, are used daily by each of us. Polyethylene, polystyrene, poly(vinyl chloride), and some other polymers are included in this category of polymers of great economic significance;
- **Technical** polymers (also called **engineering** plastics) exhibit mechanical characteristics that enable them to replace traditional materials (metals, ceramics, etc.) in many applications; polyamides, polyacetals, and so on, are part of this family;
- **Functional** polymers are characterized by a specific property that has given rise to a particular application. Conducting polymers, photoactive polymers, thermostable polymers, adhesives, biocompatible polymers, and so on, belong to this category.

Depending on whether they are producers, formulators, or users of polymers, experts do not assign the same definition to each of these categories even if they broadly agree on the terms.

1.4.3. Polymers can also be classified into three categories as a function of their **structure** (dimensionality):

- **Linear** (or **monodimensional**) polymers, which consist of a (possibly) high (but finite) number of monomeric units; such systems are obtained by the polymerization of bivalent monomers, and a linear macromolecule can be schematically represented by a continuous line divided into intervals to indicate the monomer units (Figure 1.1); an assembly of polymer chains consists of entities with variable length, a characteristic designated by the term *dispersity*;[‡]
- **Two-dimensional** polymers are mainly found in Nature (graphite, keratin, etc.); two-dimensional synthetic polymers are objects that have not yet crossed the boundaries of laboratories. They appear in the form of two-dimensional layers with a thickness comparable to that of simple molecules (Figure 1.2);

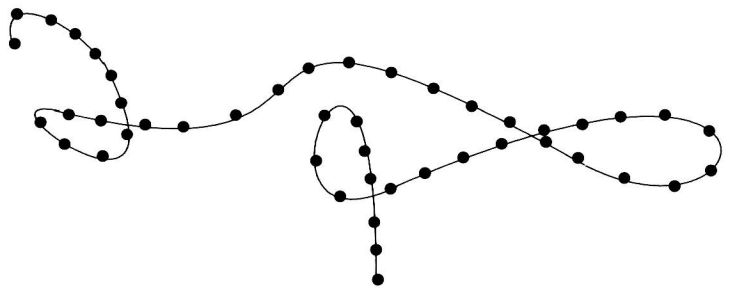


Figure 1.1. Representation of the chain of a linear polymer.

[‡]term recommended in 2007 by the IUPAC Subcommittee on Macromolecular Nomenclature to replace *polydispersity*.