

Macromolecular Physics

Bernhard Wunderlich

VOLUME 1

Crystal Structure, Morphology, Defects

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Bernhard Wunderlich

*Rensselaer Polytechnic Institute
Troy, New York*

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Preface

Crystals of linear macromolecules have begun to be understood only recently. Their constituent class of molecules was discovered only in 1920, and for many years the nebulous macromolecular crystals were designated as "fringed micelles." During the early 1960's the actual birth of the field of solid-state physical chemistry of macromolecules occurred with the observation and recognition of the overriding fact of chain folding on crystallization from the random state of flexible linear high polymers. The fringed micelle was almost forgotten. Not much later, extended chain crystals were discovered and shown to be the expected equilibrium crystals. Having studied the limiting crystal types, it became obvious that the fringed micelle still holds a central position in the description of crystals of linear macromolecules (as is shown schematically in Fig. III.5). By now, however, a much more precise picture has emerged. This book is a first attempt at a unified treatment of crystals of linear macromolecules. It represents an effort to collect sufficient material to depict the breadth of the field and to show the special features arising from the long-chain nature of linear macromolecules.

Frequent references should allow quick access to the original literature. Rather than attempting to list all of the explosively increasing literature in this field, the cited references were reread and critically selected to present a typical and manageable body of information. The important ideas were traced back and documented to their origin. The literature was covered through 1971, so that this book can be looked upon as a progress report of the first 10-15 years of research on crystals of linear macromolecules. Sources to the data used are listed in addition in the text in abbreviated form. Wherever possible, tables were collected to present larger bodies of knowledge, as for example crystal structures (Tables II.9 to II.19), folded chain lamellar crystals (Table III.3), spherulites (Table III.5), and results on drawing single crystals (Table IV.14). Almost all drawings were newly made to present a uniform style and to permit in many cases the combination of data from several sources.

It must be recognized that linear macromolecules can be found among inorganic, organic, and biological materials. Our knowledge about the crystals of synthetic organic macromolecules is by far larger than that of the other types; still, in this book we attempt to unify the description of crystals of all linear macromolecules. The study of inorganic macromolecules has broadened the information on helices by pointing out the limits of the commonly accepted rules of Natta and Corradini (Sect. 2.3.5) and given an initial insight into crystallization during polymerization (Sect. 3.9). The study of biological macromolecules contributed much to advance conformational analysis of ordered macromolecules by many studies of intramolecular potential energies (Sect. 2.3.5) and represents the group of crystals with globular motifs (Table II.21).

Since knowledge about crystals of linear macromolecules cuts across many disciplines, this book attempts to serve not only the specialist. I have tried to present sufficient introductory material to make the book readable to one not expert in polymers (see Chapter I) as well as one with little prior knowledge in crystallography (see Sect. 2.2), molecular structure (see Sect. 2.3), crystal morphology (see Sect. 3.1), or recognition of polymer crystal defects (see Sect. 4.1). A reader familiar with these topics may well want to skip some or all of these sections. References in these sections are particularly restricted to more comprehensive treatises of the subjects or those of interest to the material of the body of the book. As a result, I hope the book will prove useful to a wide audience.

Obviously in a book on crystals one has many references to questions pertaining to crystallization and melting. To answer these adequately, Volume 2 is in the preparation stage entitled: "Crystallization and Melting of Linear Macromolecules," with the following subdivision: Chapter V: Nucleation, Chapter VI: Crystallization, Chapter VII: Annealing, Chapter VIII: Equilibrium Melting, Chapter IX: Irreversible Melting, Chapter X: Copolymer Melting. References to the pertinent chapters are made throughout the present book. I hope that these will prove useful in the future and will not lead to too much frustration during the time it takes to assemble the new book. Postponing the discussion of these points has enabled us to bring out the present book considerably faster and has kept it to manageable size.

Acknowledgments

An undertaking of this size can never be the work of one person alone. At this point I would like to thank the many colleges and students who have supported this work by contributing discussions, preprints, and photographs. The roots of this book go back to graduate lecture courses on the solid state of linear macromolecules given at Cornell University (1962) and Rensselaer Polytechnic Institute (1964, 1966, and 1970). The bulk of the material could only be assembled by a generous suspension of teaching load during 1970/71 arranged with the strong support of Dr. W. H. Bauer, Dean of the School of Science, and Dr. G. J. Janz, Chairman of the Department of Chemistry. For the task of typing the manuscript and making the many revisions and corrections, I would like to thank my secretary Mrs. Helen Carroll.

Financial support of travel connected with discussions on many topics of importance for this book with colleagues in all parts of the world during 1970 and 1971 was provided by the Owens Illinois Company. Most of the support for research in my own laboratory which contributed to the subject matter came from the Office of Naval Research (1962–1971), the National Aeronautics and Space Administration (1963–1972), and the National Science Foundation (1962–1966, 1968–1969).

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CHAPTER I

The Structure of Macromolecules

1.1 The Macromolecular Hypothesis

The term "macromolecule" was coined by Staudinger in 1922[†] to distinguish the molecules of linear high polymers from the much smaller common low molecular weight molecules. Naturally, there is no clear boundary between small molecules and macromolecules. A convenient dividing line is given by Staudinger (1950): Macromolecules should have a molecular weight of at least 10 000 or consist of more than 1000 atoms. This is the approximate point at which an increase by one repeating unit in the size of the molecule does not change physical properties significantly. The class of macromolecules need not be limited to strictly linear molecules; it may also include branched, cross-linked, ladder-type, sheetlike, and three-dimensional molecules. The more highly interconnected structures occur, however, only in the solid state, with, finally, one molecule making up the solid particle. In this case the subdivision of matter into molecules loses its usefulness.

Macromolecules represent the last and largest class of matter which has been characterized on a molecular level. This class contains structural material (such as cellulose and fiberglass), textiles (such as silk and nylon), elastomers (such as rubber and chloroprene), resins (such as amber and phenolics), and, finally, it contains the proteins and nucleic acids basic to the life processes. A survey of the literature by Leuchs (1968) lists 133 different partial attempts at classifying this enormous field, with no clear solution to the problem because of the great breadth of the natural and synthetic macromolecular materials.

[†] Staudinger and Fritsch (1922).

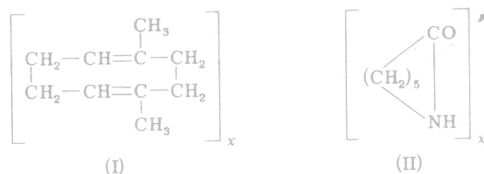
Naturally occurring macromolecules, as well as a few synthetic macromolecules, were used industrially for some time before a detailed understanding of their chemical nature on a molecular scale was arrived at. In fact, since proteins and carbohydrates are the most prominent biological structural materials, they were among the first used by early man. Long before the chemical arts necessary for the production of pottery, metal artifacts, and glass were developed, articles out of bark, wood, plant leaves and fibers, and animal skins and hair must have been in common use. [See, for example, Toulmin and Goodfield (1962)]. In biblical times several natural resins, asphalt, and fibers out of cotton, flax, wool, and silk were known. The modern plastics industry had its start about 1850 with the large-scale production of vulcanized rubber, cellulose nitrate (celluloid), and cellulose acetate. Fully synthetic materials made their entry about by 1910 in the form of phenol-formaldehyde resins (Bakelite). The large variety of presently commercially available synthetic macromolecular materials produced at a rate of more than 25 million tons annually (1970) has been developed only in the last 50 years. This exponential growth found its start with the recognition of the molecular structure of the macromolecules in the 1920s.

The roots of the understanding of macromolecular materials go back to the principles of structural organic chemistry as developed by about 1870.† By that time besides the natural macromolecules, several synthetic macromolecular substances had been made by polymerization, for example, out of vinyl chloride, styrene, and ethylene glycol. Even chain structures had been proposed for some macromolecules‡. The general acceptance of the macromolecular hypothesis was, however, delayed for another 50 years because of the difficulty in distinguishing between colloids formed by small molecules and macromolecular colloids. The name "colloid", meaning glue-like substance, was given by Graham (1861) to substances such as gelatin, albumin, and gums which showed slow diffusion in solution and an inability to pass through semipermeable membranes. Other species, able to readily diffuse in solution and to pass through semipermeable membranes, were given the name crystalloids because they could frequently also be obtained in the form of well-shaped crystals, as for example common salt and sugar. It was soon discovered that crystalloids could also be brought into the "colloidal state" by proper aggregation. This aggregation was in some cases based on secondary valences. As a consequence, it was erroneously assumed that macromolecules which always form solutions with typical colloidal properties were also made up of smaller molecules held together by secondary valences. To satisfy

† See for example, Gould, R. F. (ed.) (1966). *Kekulé Centennial*, "Advances in Chemistry Series," Vol. 61. Amer. Chem. Soc., Washington, D.C.

‡ For a detailed accounting see: Flory (1953, Chapter 1).

the stoichiometry, ring formulas were proposed for many linear high polymers. Rubber and polyamides were, for example, written as follows:



The degree of polymerization x gave the number of rings aggregated by secondary valences. One thought in this way to be able to understand all organic substances on the basis of well-defined small molecules of molecular weights of certainly less than 5000; to find the small molecule was a matter of purification and crystallization.

The acceptance of the existence of large linear, covalently linked molecules was accomplished by H. Staudinger. The first decisive paper, published in 1920, proposed a linear molecule for polyoxymethylene, polystyrene, poly(vinyl chloride), poly(malonic anhydride), polyglycols, and rubber. In Staudinger's words:

Assumptions of molecular compounds in which partial valences bring about the cohesion of the unsaturated molecules are very attractive in organic chemistry today, since a large number of well characterized compounds, for example the quinydrones, have been shown to be molecular compounds which are held together by secondary valences. Yet I believe that such assumptions need, according to the present experimental material, not to be made for the explanation of the polymerization products. Rather, one can find a satisfactory explanation through normal valence formulas for the various polymerization products as I want to show below; and especially in organic chemistry one should attempt as long as possible to represent the properties of compounds through formulas with normal valences.

This first paper was followed by many others giving indisputable proof that macromolecules must be separated from colloids formed by mere association by secondary bonds.† It took about 10 years until Staudinger's views became widely accepted. A further big advance came with the careful and thorough investigations of W. H. Carothers in the years 1929–1937 in the laboratories of the duPont Company. His work on polyamides, polyesters, and poly-anhydrides led to the commercial production of synthetic polyamides (nylon) [see, for example, Mark and Whitby (1940)].

Soon after the chemical nature of macromolecules was established, statistical methods were applied to understand molecular weight distribution,

† For a summary of the more than 800 publications, most in the field of macromolecular chemistry see, Staudinger, H. (1961). "Arbeitserrinnerungen." Hüthig Verlag, Heidelberg.

reactions, and physical properties. The status of the science of macromolecules in the 1950s is summarized by the now classic treatises by Flory (1953) and Stuart (1952–1956). The major progress in the last 20 years has been in the proliferation and refinement of syntheses leading, among others, to the polymerization of sterically regular polymers and special copolymers; the development of detailed knowledge about the crystalline solid state, the subject of this book; and a further advance into the understanding of biological macromolecules, the molecules of first interest to man.

The nomenclature of polymers described in this book is based on the IUPAC "Report on nomenclature in the field of macromolecules".† The name of the polymer is usually derived from its monomer. If the monomer name consists of more than one word, these are inclosed in parentheses. The name of the monomer follows "poly", for example: polyethylene, poly(vinyl chloride), polystyrene, poly(ethylene terephthalate).

1.2 The Synthesis of Macromolecules

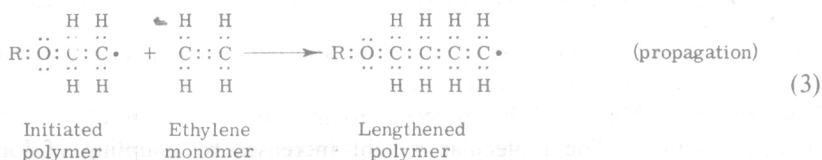
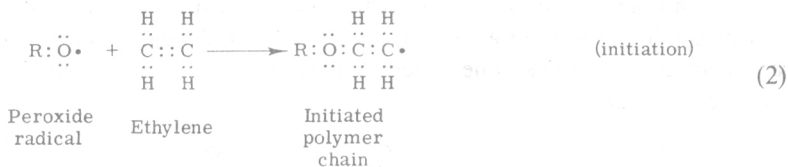
A macromolecule has a continuous backbone of covalently bonded atoms and may have any number of side groups attached to it. With valence restrictions and bond angle conditions taken into account, large one-dimensional molecules comprising many different atoms may be constructed on paper. It is the task of the synthetic polymer chemist to attempt to actually synthesize these molecules. There are many reactions that lead to linear high polymers. An example of the formation of inorganic macromolecules [see, for example, Stone and Graham (1962) or Gimblett (1963)] is the formation of polymeric sulfur. Liquid sulfur at low temperature is made up on a molecular scale mainly of rings or eight sulfur atoms. At 160°C these eight-membered rings become unstable, break up, and join with others to form very long chains. The physical properties change in accordance with the change in chemical structure from a mobile liquid to a highly viscous melt, despite the fact that the temperature has been raised to accomplish polymerization. Expressed in chemical formulas, the ring opening and polymerization are shown in Eq. (1):



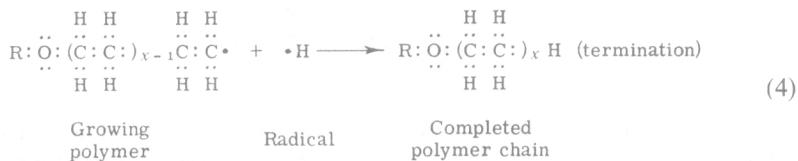
† *J. Polymer Sci.* **8**, 257 (1952). See also: Huggins, M. L., Natta, G., Desreux, V., and Mark, H. (1966). Report on nomenclature dealing with steric regularity in high polymers. *Pure Appl. Chem.* **12**, 645 (1966); Committee of Nomenclature, *Amer. Chem. Soc.* (R. B. Fox, Chairman), A structure based nomenclature for linear polymers. *Macromolecules* **1**, 193 (1968). For Indexing of polymers in Chemical Abstracts see Loenig, K. L., Metanowski, W., and Powell, W. H., *J. Chem. Documentat.* **9**, 248 (1969).

A linear chain end reacts with a ring atom and causes ring opening. The exact nature of the chain ends is not established. Tobolsky and Eisenberg (1959) assume both ends to be of the free radical type. As long as no impurities terminate the active chain ends, the molecular weight and its distribution will be determined by the polymerization equilibrium.

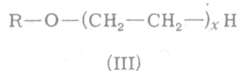
The two important types of organic reactions leading to linear high polymers are the addition reaction and the step reaction [see, for example, Lenz (1967)]. An example of an addition reaction is the synthesis of polyethylene from ethylene using a peroxide radical catalyst:



After x monomer atoms have been added, the reaction may come to a halt, because, for example, of a radical $\cdot\text{H}$ abstraction from the solvent.



The final polyethylene molecule would then have the following chemical formula:



The definition of the polymer molecule has been stretched somewhat in this case to include the two ends of the molecule which make it deviate a little from an exact multiple of the monomer.[†] The subscript x designates the degree of polymerization. The part of the molecule in parentheses (CH_2-CH_2-) is called the repeating unit.

[†] In the structure-based nomenclature the end groups are specified when necessary by preceding the polymer name by the name of the radicals prefixed by the letters α and ω , for example, $\text{Cl}(\text{CH}_2)_x\text{CCl}_3$ is α -chloro- ω -(trichloromethyl)poly(methylene).