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 $\sim 10^5\ \mathrm{g \cdot mol^{-1}}$.

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*.

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

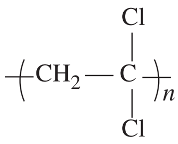
Monomeric units that are part of a polymer chain can be linked one to another by a varying number of bonds; we suggest to call this number *valence*.[†] This term should be preferred to *functionality*, which can be misleading (see page 216). Thus, monomeric units can be mono-, di-, tri-, tetra-, or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

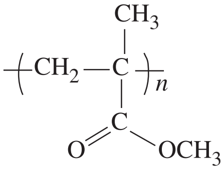
Depending upon the level of precision and the type of information required, one has at one's disposal different adequate representations of the polymer structure. To represent the macromolecular nature of a linear polymer, a mere continuous line as shown in Figure 1.1 is perfectly relevant. Representations 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.

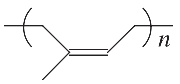


$$-\!\!\left(CH_2-\underset{Cl}{\overset{Cl}{\underset{|}{\overset{|}{C}}}}\right)\!\!-_n$$

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

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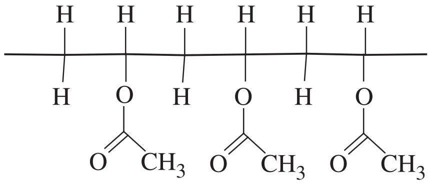
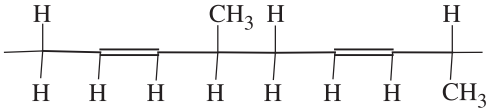
[†] The term valence of monomers or of monomeric units is proposed by anology with the valence of atoms which corresponds to the number of orbitals available for bonding. The valence of a monomer thus corresponds to the number of covalent bonds that it forms with the nearest monomeric units.

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:

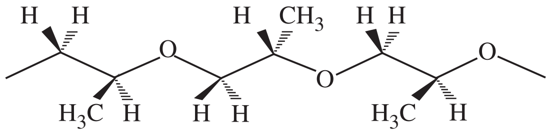


Sequence of 3 successive units *(triad)* of poly(vinyl acetate) presenting the same configuration



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);

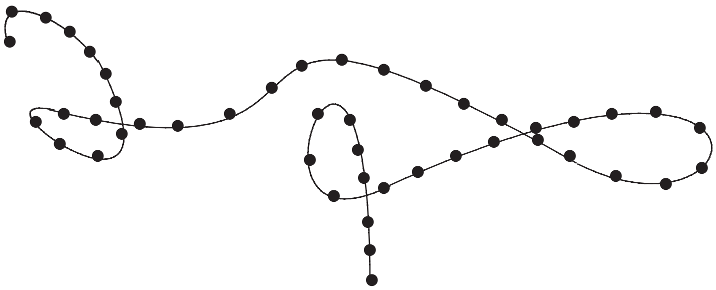


Figure 1.1. Representation of the chain of a linear polymer.

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

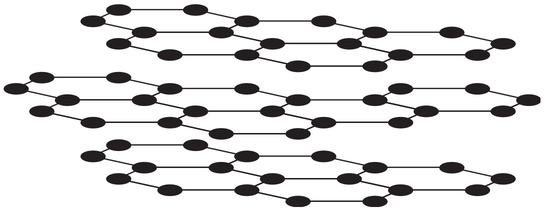


Figure 1.2. Schematic representation of a two-dimensional polymer, here carbon graphite.

- **Three-dimensional** polymers result either from the polymerization of monomers whose average valence is higher than two or from the cross-linking of linear polymers (formation of a three-dimensional network) through physical or chemical means. Their molecular dimension can be regarded as infinite for all covalently linked monomeric units of the sample are part of only one simple macromolecule. Chains grow at the same time in the three dimensions of space, and a volume element of such a system can be represented as shown in Figure 1.3.

This last mode of classification is extremely useful since all the properties of the macromolecular systems—mechanical properties in particular—are very strongly affected by the dimensionality of the polymer systems. Monographs on the various families of synthetic polymers will be presented in two different chapters to highlight this point.

Remark. Irrespective of their dimensionality and/or their topology, synthetic polymers can be classified as homopolymers and copolymers, depending on their molecular structure (see Section 3.2).

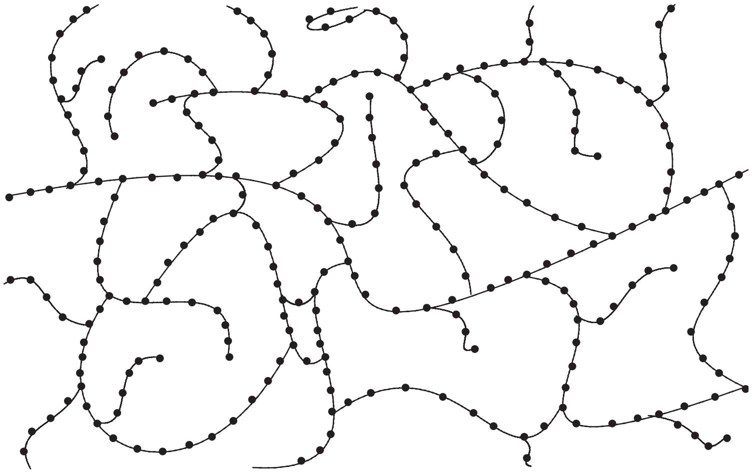


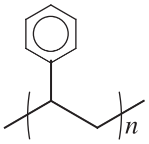
Figure 1.3. Schematic representation of a three-dimensional polymer.

1.5. NOMENCLATURE OF POLYMERS

There are three ways to name polymers.

The **first one**, which is official, follows the recommendations of the International Union of Pure and Applied Chemistry (IUPAC). It consists in naming the monomer unit according to the rules used for small organic molecules and, after insertion between brackets, in appending the prefix *poly* before it.

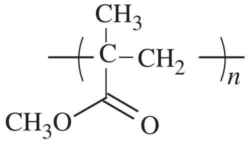
Poly(1-phenylethylene)



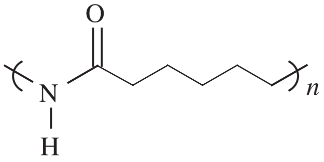
Poly(methylene) $—(CH_2)—_n$

Poly(oxyethylene) $—(O\text{-}CH_2\text{-}CH_2)—_n$

Poly[1-(methoxycarbonyl)-1-methylethylene]

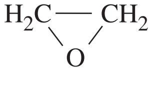


Poly[imino(1-oxohexamethylene)]

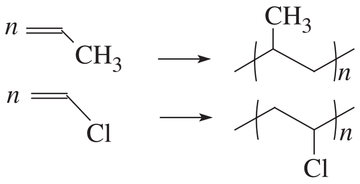


This method is based on the structure of polymer irrespective of the method of preparation.

The **second one**, which is the most frequently used, refers to the polymerization of a particular monomer and may reflect the process used. For example, poly(ethylene oxide) results from the polymerization of ethylene oxide:



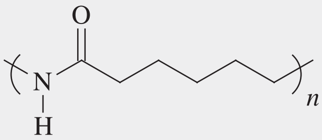
Polyethylene $-(CH_2-CH_2)_n-$ is obtained by polymerization of ethylene $H_2C=CH_2$ (which should be called ethene). Polypropylene and poly(vinyl chloride) are obtained from the polymerization of propylene (which should be called propene) and vinyl chloride, respectively:



Remarks

(a) When the monomer name consists of several words, it is inserted between brackets and the prefix “poly” is added before it.

(b) The same polymer can have several names if it can be prepared by different methods. For instance, the polyamide shown below, whose acronym is PA-6, can be called polycaprolactam or poly(ε-capramide) whether it is obtained by chain polymerization of ε-caprolactam or by self-polycondensation of ε-aminocaproic acid:



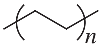
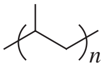
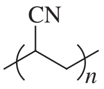
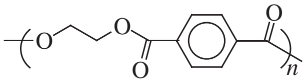
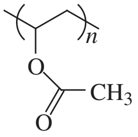
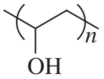
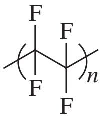
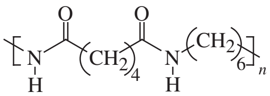
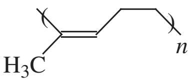
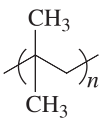
(c) Each natural polymer has its own name: cellulose, starch, keratin, lignin, and so on.

For the most commonly used polymers, a **third method**, based on acronyms, is widespread; these acronyms can designate either

- a particular polymer: PVC for poly(vinyl chloride), PS for polystyrene, and so on, or
- a family of polymers: PUR for polyurethanes, UP for unsaturated polyesters, and so on.

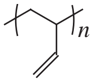
Acronyms can be also utilized to emphasize a structural characteristic; for instance, UHMWPE indicates a polyethylene with ultra-high molar mass, whereas “generic” polyethylene is simply designated by PE. Other examples of designations will be given later on—in particular in Chapter 3, which addresses the molecular structure of polymers. Table 1.2 gives the three types of naming for the most important and/or significant polymers.

Table 1.2. Designation of several common polymers

Structure of Monomeric Unit	IUPAC Designation	Common Designation	Acronym
	Poly(methylene)	Polyethylene	PE
	Poly(1-methylethylene)	Polypropylene	PP
	Poly(1-cyanoethylene)	Polyacrylonitrile	PAN
	Poly(oxyethylene-oxyterephthaloyl)	Poly(ethylene terephthalate)	PET
$\left(O - CH_2 \right)_n$	Poly(oxymethylene)	Polyformaldehyde	POM
	Poly(1-acetoxyethylene)	Poly(vinyl acetate)	PVAC
	Poly(1-hydroxyethylene)	Poly(vinyl alcohol)	PVAL
	Poly(difluoromethylene)	Polytetrafluoro-ethylene	PTFE
	Poly[imino (1,6-dioxo-hexamethylene) iminohexamethylene]	Poly(hexamethylene adipamide)	PA-6,6
	Poly(1-methylbut-1-enylene)	1,4- *cis*-Polyisoprene	NR
	Poly(1,1-dimethylethylene)	Polyisobutene	PIB

(*continued overleaf*)

Table 1.2. (*continued*)

Structure of Monomeric Unit	IUPAC Designation	Common Designation	Acronym
	Poly(1-vinylethylene)	1,2-Polybutadiene	1,2-PBD
	Poly(butenylene)	1,4-*cis*-Polybutadiene	PBD or BR

Remarks

(a) The acronyms BR and NR, which refer to polybutadiene and natural polyisoprene, correspond to the abbreviation of butadiene rubber and natural rubber, respectively.

(b) In general, chains of synthetic polydienes contain variable proportions of 1,2-, 1,4-, and 3,4-type monomer units.

(c) Designations of polymers other than linear homopolymers are the subject of specific rules. Some of them will be indicated while presenting the corresponding structure.

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J. Bandrup, E. H. Immergut, E. A. Grulke, *Polymer Handbook*, 4th edition, Wiley, New York, 1999.

W. V. Metanomski, *Compendium of Macromolecular Nomenclature*, Blackwell Scientific Publishers, Oxford, 1991.