POLYMER CHEMISTRY AND ENVIRONMENTALLY DEGRADABLE POLYMERS

E. Ranucci

Department of Organic and Industrial Chemistry, University of Milan, Italy

Keywords: Polymer chemistry, polymers, polymer structure, crystalline polymers, amorphous polymers, polymer synthesis, degradable polymers, biodegradability, renewable sources.

Contents

Summary

The most relevant characteristic of a polymer is the large dimension of the macromolecules (giant molecules). Polymers are long chain hydrocarbons constituted by 1 000 – 10 000 simple chemical units. A large group of polymers are plastics, with properties ranging from rubbers to thermoplastics and fibers. Every year around 100 billions tons of diverse plastics are produced in the world. They are characterized by good properties, as low density, corrosion resistance, strength, ease to be formed, and on top of that they are usually cheap. This is the reason why plastics are currently employed to make a large number of things of practical use in our everyday-life, from

packaging, bottles, clothes, toys, tires, cables and sportswear, just to mention a few. Innovations in polymer chemistry constantly bring both improved and entirely new uses for polymers. It is therefore extremely interesting and useful to gain a general picture of the polymers' world, not only for scientists working in different fields, but also for students or even for common people. To enter this world, this chapter provides first a brief review of the basic definitions and concepts pertaining polymer structures and properties. The description of the basic principles of polymerization enables the reader to achieve a general understanding of polymer synthesis. In a separate section, the environmental aspects related to the use of plastics for the production of mass products are dealt with. General concepts as recycling and post-use, thermo-valorization, biodegradation and composting of plastics and finally the possibility to produce plastics from renewable materials are commented.

1. Introduction

Polymer chemistry is the chemistry of giant molecules. This includes the synthesis, characterization, and physical chemistry of organic polymers. Polymers (from the Greek words "poly" = many, and "meroi" = units) are long-chain hydrocarbons constituted by 1 000 – 10 000 repeating units, and a molar mass of 10^4 – 10^6 g/gram-mole. They can be either natural or synthetic, that is, produced by chemical processes, or artificial, that is, obtained by chemical modification of natural polymers (Figure 1).
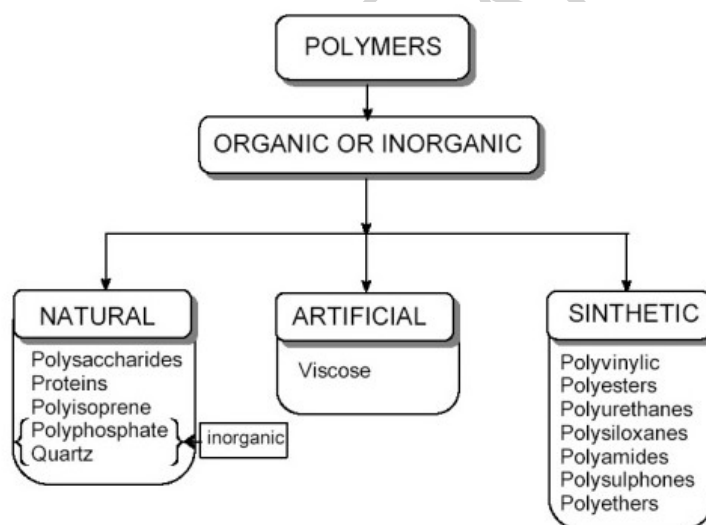

Figure 1: Classification of polymers.

The most relevant characteristic of a polymer is represented by the large dimensions of its macromolecules (giant molecules), which determine peculiar chemical, physical and mechanical properties both in the solid state and in the melt. In solvents, polymers form colloidal solutions in which the macromolecules arrange in swollen "coils" with dimensions in the range 50 - 200 Å. Such solutions are characterized by a high viscosity, which increases with increasing the length of the macromolecules. In the solid state, polymers may behave either as hard glasses, or soft rubbers, or tough fibers, according to their structure, which can vary from amorphous, through semi-crystalline to highly crystalline.

Why are polymers so important in our life? The answer can be expressed in a single word: plastics. A large group of polymers behave as plastic materials. This means that they are either easily melted and subsequently formed into complex tri-dimensional shapes into molds (thermoplastics), or cured by heating to form insoluble network-like structures that do not soften at high temperatures (thermosets). Every year around 100 billions tons of diverse plastics are currently produced in the world. The reasons for this commercial success are the low cost of precursors and the ease of processing, combined with good properties, as low density, resistance to corrosion and mechanical strength. Several commodities for different applications are currently made of plastics: films for packaging, shoppers, bottles for soft drinks, synthetic fibers, toys, tires, cables and sportswear for our every-day life; but also specialty polymers for advanced applications, as biomedical materials, or techno-polymers for aerospace industry, just to mention a few. Further, it may be predicted that several new materials will be produced in the future by taking advantage of the versatility of polymers. These can be compounded with different additives or inorganic fillers, or blended with other polymers giving rise to a variety of novel materials with tunable properties, that can be addressed to different applications.

Finally, it is worth noticing here that since the polymer chemists' community has progressively developed a highly specialized lexicon, which is not immediate even for those who are familiar with organic chemistry nomenclature, a glossary, summarizing the main concepts related to polymer chemistry is presented in Appendix 1. Glossary, related to the field of environmentally biodegradable polymers is included at the end of this chapter.

2. General Structure of Polymers

2.1. Basic Definitions

A "macromolecule" is a chemical entity that fully characterizes the chemical properties of a polymer. It is formed by several repeating (or constitutional) units covalently bound to each other. The chemical structure of a macromolecule is usually represented by drawing the raw chemical formula(s) of the repeating unit(s) within square brackets, thus showing the general arrangement of bonds and atoms in the polymer (Figure 2). The index, "n", usually reported on the bottom side of the right bracket, indicates that the macromolecule includes a large number of such repeating units. As a rule, the repeating units contain recognizable functional groups that can be used to classify the polymer (Figure 2).
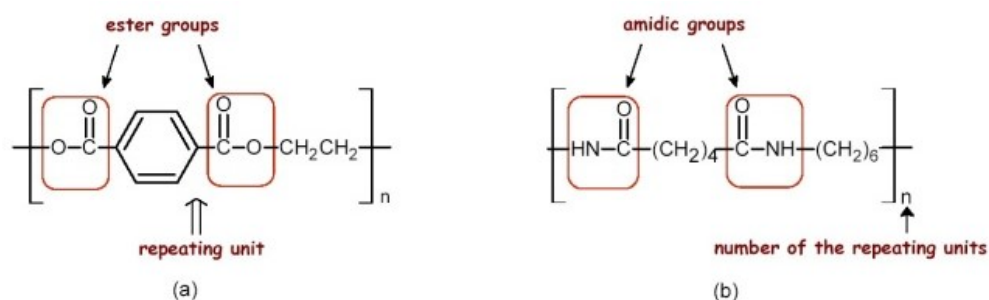

(a)   (b)

Figure 2: Structure of a polyester (a) and of a polyamide (b).

The chemical structure of the repeating units is related to that of monomers. These are the organic reagents that generate the macromolecules through specific chemical reactions, referred to as polymerization reactions. Polymers are often named according to the monomers used in their synthesis, although this is not always rigorous according to the IUPAC rules. As a matter of fact, for polymers with any complexity, the IUPAC nomenclature is too cumbersome for common use. This is why, for instance, the polymer consisting of a long chain of -CH$_2$- groups is called "polyethylene", and not "polymethylene". Similarly, the polyamide containing six carbon atoms is known as poly-ε-caprolactam (Figure 3).
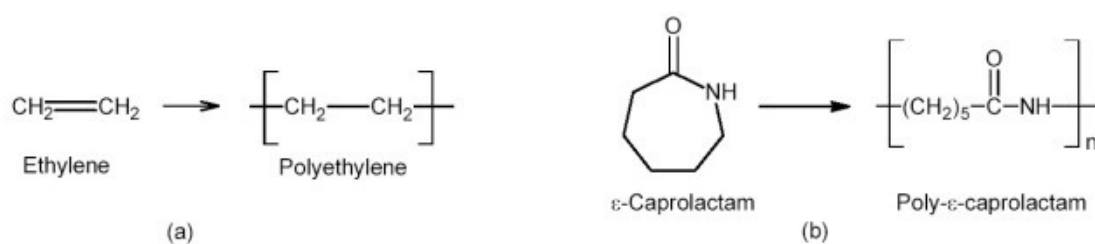

Figure 3: Structure of polyethylene (a) and poly-ε-caprolactam (b).

According to the concatenation of the repeating units in the macromolecules, polymers can be classified either as linear, or branched or cross-linked. In linear polymers, macromolecules grow along a preferential direction, while in branched ones they grow along different directions. In addition, a cross-linked polymer is obtained when linear macromolecules are chemically connected through transversal covalent bonds, which lead to a set, tri-dimensional network (Figure 4). A cross-linked polymer is not soluble in any solvents, cannot be re-melted and decomposes when heated at high temperatures.
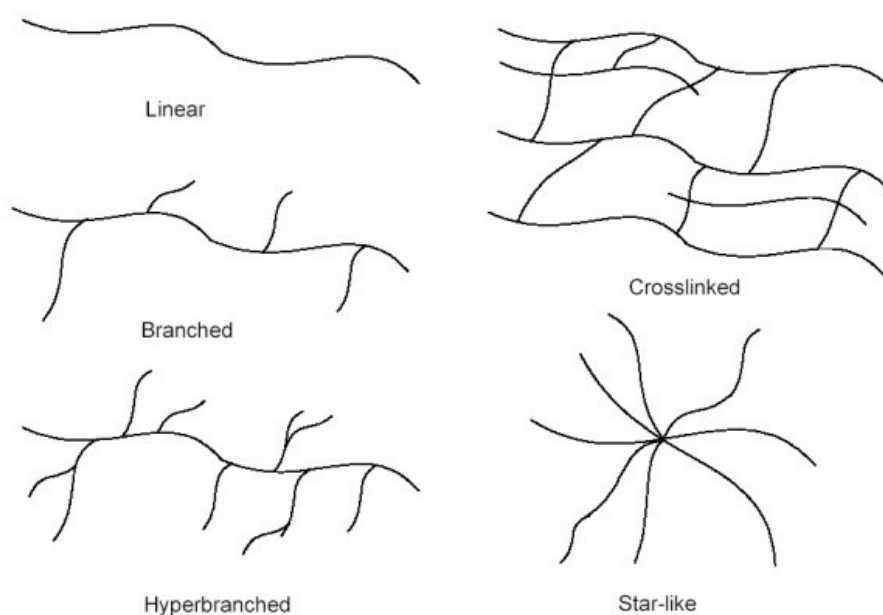
Figure 4: General structure of macromolecules.

Polymers bearing only one kind of repeating unit are referred to as homo-polymers. When the repeating units are two or more, they are termed co-polymers, ter-polymers and so on. Co-polymers can, in turn, be defined as random, alternating, or block ones according to the concatenation of the repeating units (Figure 5).

Figure 5: General structure of co-polymers.

2.2. Molecular Weights and Molecular Weight Distributions

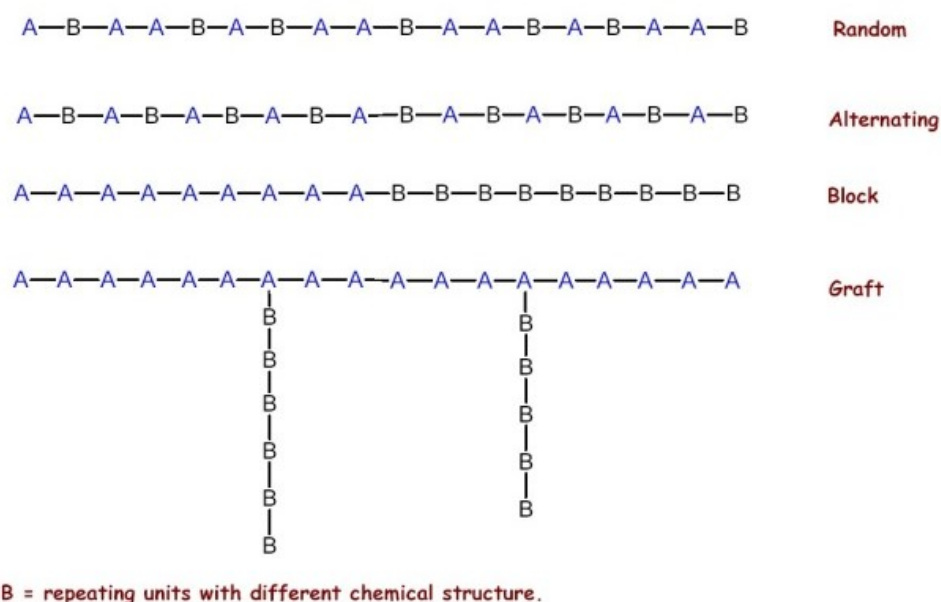Synthetic polymers are constituted by a mixture of homologous macromolecular species, which differ from each other for the number of repeating units included in the backbone, that is, for the polymerization degree. It follows that, in polymers, the molecular weight is not a univocal characteristic, as in ordinary small molecules, since it varies over a wide distribution of values (Figure 6).
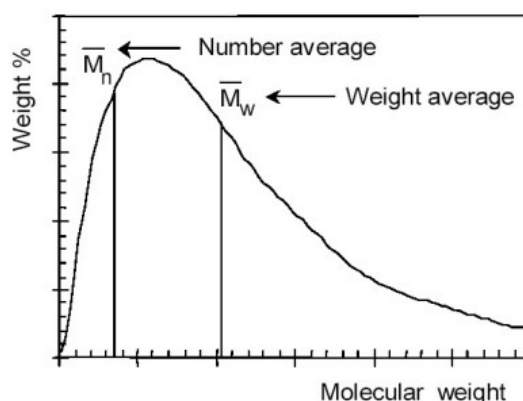

Figure 6: Molecular weight distribution of polymers.

For practical purposes, it is therefore necessary to identify reference molecular weight values, averaged over the whole range of molecular weights of the polymer. These reference values are the number average-, $\overline{M}_n$, and the weight average, $\overline{M}_w$, molecular weight, respectively. The $\overline{M}_n$ average is based on the number fractions of the populations of macromolecules with the same chain length. Similarly, the $\overline{M}_w$ average is based on the weight fractions of the populations of macromolecules with the same chain length (see below). In order to correctly understand the physical meaning of both number and weight average molecular weights, it might be helpful to provide some preliminary definitions, as reported in Eqs. (1) and (2).

The number fraction of a generic macromolecules' population bearing *j* repeating units is given by:

$$n_j = \frac{N_j}{\sum_j^n N_j} = \frac{N_j}{N_T} \tag{1}$$

where N_j represents the number of the macromolecules bearing *j* repeating units and N_T is the overall number of macromolecules. In the same way, we can define the weight fraction of the generic macromolecules' population bearing *j* repeating units as:

$$w_j = \frac{W_j}{\sum_j^n W_j} = \frac{W_j}{W_T} \tag{2}$$

where W_j represents the weight of the macromolecules bearing j repeating units and W_T is the overall weight of the polymer sample.

We can now mathematically define $\overline{M}_n$ and $\overline{M}_w$ according to Eqs. (3) and (4):

$$\overline{M}_n = \frac{\sum_{j=1}^{n} N_j \times M_j}{\sum_{j=1}^{n} N_j} \tag{3}$$

$$\overline{M}_w = \frac{\sum_{j=1}^{n} W_j \times M_j}{\sum_{j=1}^{n} W_j} \tag{4}$$

where M_j represents the molecular weight of the macromolecules bearing j repeating units. Eqs. (3) and (4) provide a correct mathematical definition *per se* of $\overline{M}_n$ and $\overline{M}_w$. However, by using the expressions of n_j and w_j reported in Eqs. (1) and (2), the new Eqs. (5) and (6) are obtained:

$$\overline{M}_n = \sum_{j=1}^{n} n_j \times M_j \tag{5}$$

$$\overline{M}_w = \sum_{j=1}^{n} w_j \times M_j \tag{6}$$

These equations add something more, in that they clearly indicate that $\overline{M}_n$ and $\overline{M}_w$ represent "statistically weighed" average values. In fact, in $\overline{M}_n$, the average molecular weight is determined by assuming as "statistic weights" the number fractions of the populations of macromolecules with the same chain length. Similarly, in $\overline{M}_w$, the average molecular weight is determined by assuming as "statistic weights" the weight fractions of the populations of macromolecules with the same chain length.

It may be observed that, for an ordinary polydispersed polymer, $\overline{M}_w$ is always larger that $\overline{M}_n$, as it may be deduced from the following considerations. From Eq. (2), and by taking into account the relationship between W_j and N_j expressed in Eq. (7), a new mathematic expression of $\overline{M}_w$ can be obtained, as reported in Eq. (8).

$$W_j \propto N_j \times M_j$$

(7)

$$\overline{M}_w = \frac{\sum\limits_{j=1}^{n} N_j \times M_j^2}{\sum\limits_{j=1}^{n} N_j \times M_j}$$

(8)

The comparison between the expressions of $\overline{M}_n$ and $\overline{M}_w$, as reported in Eqs. (1) and (8), clearly indicates that $\overline{M}_w > \overline{M}_n$, unless all M_j has identical values, as in the case of equally sized macromolecules. A useful parameter to define the molecular weight distribution of polymers is, therefore, the polydispersity index, d, defined as the ratio between the weight and the number average molecular weight (Eq. (9)).

$$d = \frac{\overline{M}_w}{\overline{M}_n}$$

(9)

High d values correspond to broad macromolecular dispersions, while the limit d value equal to 1 is typical of monodisperse polymers or, more correctly, of polymers with very narrow molecular weight distributions. Commercial polymers exhibit typically a d value greater than 2, and occasionally much greater.

As regards the practical relevance of the absolute molecular weight averages, $\overline{M}_w$ represents the most useful one, since it better accounts for the contributions of different sized chains to the overall behavior of polymers, as demonstrated by the good correlation with most of the physical properties of interest. Many relevant polymer properties (for instance T_g, mechanical compliance, tensile strength, etc.) follow a peculiar pattern as a function of the molecular weight, as depicted in Figure 7 for a general case. As shown in this figure, small molecules exhibit usually poor property values. As the chains grow to intermediate sized macromolecules (that is, oligomers) a sharp rise in properties is observed. The properties finally level off as the chains become long enough to be classified as polymers.
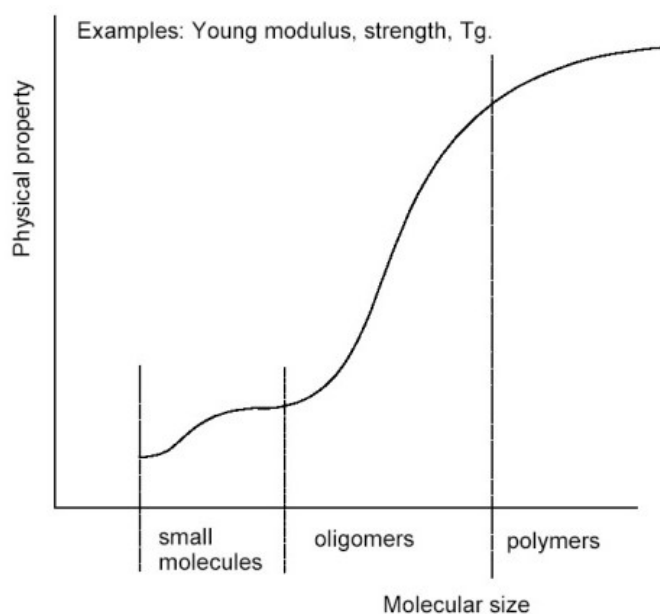
Figure 7: Dependence of polymer properties on molecular weight.

Moreover, a few properties relevant for polymer processing, like melt viscosity and solution viscosity, increase monotonically with molecular weight. As a consequence, the goal of polymer synthesis is often not to reach the largest possible molecular weights, but, rather, to make molecules large enough to get onto the plateau region. As a matter of fact, increasing the molecular weight beyond this limit does not significantly improve the physical properties, but only makes processing more difficult, due to increase in viscosity.

Finally, it worth noticing that a few physical properties of polymers, as for instance color, dielectric constant and refractive index, are dictated by the repeating units alone, and are therefore independent of polymerization degree.

-
-
-

TO ACCESS ALL THE **71 PAGES** OF THIS CHAPTER,
Visit: http://www.eolss.net/Eolss-sampleAllChapter.aspx

Bibliography

Albertsson A.-C. and Karlsson S. (1998). Biodegradable Polymers and Environmental Interaction, *Polymer Engineering Science* **38**, 1251-1253. [Classical review paper on biodegradable polymers and environment. Contains reference material to the photodegradation of polyolefins]

Amass W., Amass A. and Tighe B. (1998) A Review of Biodegradable Polymers: Uses, Current Developments in the Synthesis and Characterization of Biodegradable Polyesters, Blends of Biodegradable Polymers and Recent Advances in Biodegradation Studies. *Polymer International* **47** 89-144.[This review contains information on problems of plastics waste management, on biodegradable materials and biodegradation testing]

Chiellini E., Cinelli P., Chiellini F. and Imam S. H. (2004). Environmentally Degradable Bio-Based Polymeric Blends and Composites. *Macromol. Biosci.*, **4**, 218–231. .[This review contains information protein-based composite as biodegradable bio-based materials]

http://plc.cwru.edu/tutorial/enhanced/files/glossary/glossary.htm#C [This provides an extensive glossary for polymer science]

http://www.chem.rochester.edu/~chem421/index.htm [This provides an extensive glossary for polymer science]

Ikada Y. and Tsuji, H. (2000). Biodegradable polyesters for medical and ecological applications. *Macromol*ecular Rapid Communications **21**, 117–132. [Review on biodegradable polymers for medical and environmental uses]

Odian G., "Principles of polymerisation", 4th edition, McGraw Hill Text.

Scott G. (1999). Polymers and the environment. RSC Paperback. [Book review on the properties and applications of polymers with discussion of their environmental benefits compare with traditional materials]

Biographical Sketch

Elisabetta Ranucci, born in Gubbio, Italy (1958), received his doctor degree in Chemistry (1983) at the University of Pisa (I) working on the synthesis of macromolecular catalysts. She has worked as Assistant Professor at the University of Brescia (I) from 1986 to 1998, and as lecturer at the Royal Institute of Technology, Department of Polymer Technology, in Stockholm (SE), from 1998 to 2001, where, in 2000, she was appointed as Docent in Polymer Technology. In October 2001 she was appointed as Associate Professor in Industrial Chemistry at the University of Milan, where she is currently working. Her teaching and research interests lie in the field of macromolecular chemistry. Her research activity has mainly focused on the synthesis of bioactive and biocompatible polymers of medical interest, and of polymers from renewable resources.