

Polymers

from structure to properties

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Cover: Polarized optical microscopy image of spherulites of polyhydroxy butyrate. Image was kindly provided by Pauline Schmit of Eindhoven University of Technology.

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Preface

Polymers, from structure to properties

This book aims to provide a comprehensive introduction into the field of Polymer Technology; to provide insight in the properties of polymers and how they relate to their macromolecular structure. The book finds its origin builds in several courses at Delft University of Technology (1978-1988), Eindhoven University of Technology (1987-present), and University of Twente (2010-present). It builds on the fundament provided by the original Dutch textbook, "Polymeren, van Keten tot Kunststof", by Prof. Anne van der Vegt †; an inspiring teacher, dedicated to making knowledge on polymers accessible at all levels. After the publication of the first edition in 1991, the textbook found wide application in university and higher professional education, as well as in post-academic courses in the Netherlands. In 2002, Anne van der Vegt decided it was time for a thorough revision and approached me to join the effort. Motivation were the developments on the field of mechanical properties of polymers, specifically with respect to structure-property relations. The new, amended fifth edition, was published in 2003, shortly after the decease of Anne.

With the steady change to English as the main language of teaching on the Universities of Technology and schools for higher technical education, there was an increasing demand for a suitable English textbook on polymer technology. Unfortunately, the number of introductory textbooks in the field of polymers is small, with surprisingly little attention for current advances in structure-property relations. Consequently, we decided to translate and revise the existing Dutch textbook. Similar to the previous version, this book attempts to give a survey of polymer properties, and of the way these are, on the one hand, governed by their molecular structure, and, on the other hand, responsible for the technological behaviour of polymers. With extensive revisions, we attempted to extend the book's practicality as a guide to available literature, without losing its function as an introductory text.

Eindhoven, November 2019

L.E. Govaert

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1 Introduction

1.1. Origin of plastics / polymers

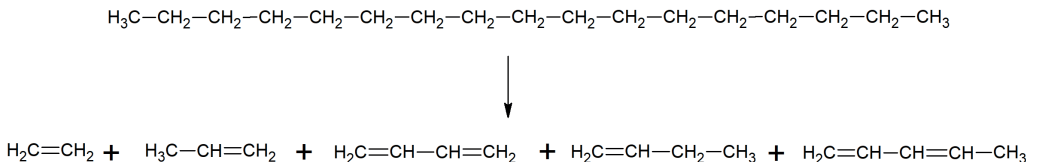
The main characteristic of polymers is, that they are composed of extremely large covalently-bonded molecules; their molecular mass ranges from 10.000 to more than 1.000.000 g/mol, in contradiction to "normal" low-molecular substances, which in general are in the order of 100 g/mol (water 18, sugar 342). Polymer molecules are often long, *thread-like chains*, which can be branched, and are sometimes chemically cross-linked with each other to form a network.

Polymers are abundantly present in nature, in plant and animal tissues (mainly as cellulose and proteins). Several polymers that are employed today in technical applications have a natural origin; they are being used as engineering materials the way they are harvested from nature ("*natural polymers*"); e.g. timber, cotton, jute, sisal, hemp, wool and silk. Other polymers are partly from a natural origin; the molecular chain has grown in living tissue but has been chemically modified into a "*half-synthetic polymer*". Examples are celluloid, cellophane, cellulose plastics, casein, leather and natural rubber.

A growing number of polymers is wholly *synthetic*; the chain molecule or the network is being build up from low-molecular components, mostly organic monomers, in a chemical process. Most of the monomers are prepared from fossil fuels, though alternative biobased sources are becoming more popular. From distillation of crude oil, a number of fuels are obtained (kerosene, petrol, gasoline, etc.) and a residue. The latter can be transformed into a series of lighter components by vacuum distillation and thermal cracking. Also, lighter fuels ("*naphtha*") can be converted to a series of various hydrocarbons by thermal cracking and fractionation.

By thermal cracking, long, saturated chains are split up into a number of shorter molecules which are *unsaturated* due to a shortage of H-atoms; they contain, therefore, one or more double bonds, which renders these molecules very suitable to be used as *monomers* in polymerization reactions.

An example is given below:



Some of these molecules, such as the first and the second (ethylene and propylene) can be used to build saturated chains (PE and PP). Other ones, such as the third one (butadiene) form unsaturated chains, which can react with sulphur to form vulcanized rubbers.

2 Molecular composition

2.1 Chain structure

A linear chain consists of a “backbone”, the main chain, at which side groups are attached. In this section a simple classification of the various types of main chain will be given, followed by a survey of frequently occurring side groups.

2.1.1. Main chain configuration

Table 2.1 Examples of main-chain configurations

| Main-chain configuration | Polymer | Example |
|---------------------------|-------------------|--|
| Saturated | Polyethylene | $\left[\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{---C---C---} \\ \quad \\ \text{H} \quad \text{H} \end{array} \right]_n$ |
| Unsaturated | Polybutadiene | $\left[\text{CH}_2\text{---CH=CH---CH}_2 \right]_n$ |
| | Polyacetylene | $\left[\begin{array}{c} \text{C}=\text{C} \\ \quad \\ \text{H} \quad \text{H} \end{array} \right]_n$ |
| Carbon & Oxygen | Polyoxymethylene | $\left[\begin{array}{c} \text{H} \\ \\ \text{---C---O---} \\ \\ \text{H} \end{array} \right]_n$ |
| | Polyethyleneoxide | $\left[\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{---C---C---O---} \\ \quad \\ \text{H} \quad \text{H} \end{array} \right]_n$ |
| Carbon & Nitrogen | Polyamide(p,q) | $\left[\begin{array}{c} \text{O} \quad \quad \text{O} \\ \quad \quad \\ \text{---C---}(\text{CH}_2)_p\text{---C---NH---}(\text{CH}_2)_q\text{---NH---} \end{array} \right]_n$ |
| Carbon, Oxygen & Nitrogen | Polyurethanes | $\left[\begin{array}{c} \text{O} \quad \quad \quad \text{O} \\ \quad \quad \quad \\ \text{---}(\text{CH}_2)_p\text{---O---C---NH---}(\text{CH}_2)_q\text{---NH---C---O---} \end{array} \right]_n$ |

4 Semi-crystalline polymers

4.1 Crystalline structure

For a share of the polymer family, under the right conditions, it is possible for the molecules to organize themselves into regular, crystalline structures. This, in contrary to glassy polymers, which consist of randomly distributed chains and are therefore amorphous. Crystals in polymers can usually be found within organized structures that are typically much larger in size than the crystals themselves.

If polymers crystallize from the melt, during, for example, an industrial cooling process, in most cases *spherulitic* structures are formed: spherical agglomerates of crystals and amorphous regions, grown from a primary *nucleus*. In a thin microtome slice they show a very attractive appearance in polarized light, see Figure 4.1. The dimensions of the spherulites are typically between 5 μm and 1 mm. When spherulites grow, in time, they will touch or impinge each other, halting the crystallization process.

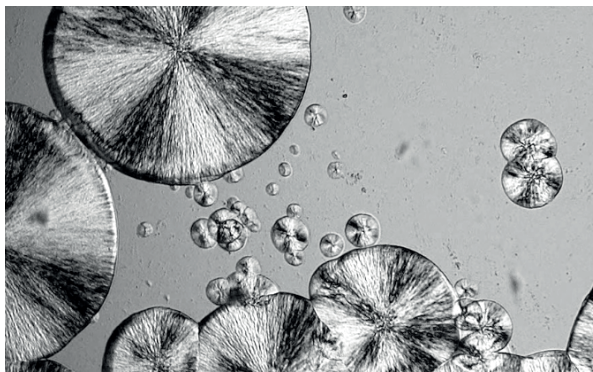


Figure 4.1 Growth of spherulites in poly(ethylene oxide)

If we further zoom into one of these spherulites, such as in Figure 4.2, the alternating layers of crystalline and amorphous layers can be observed. The crystalline layers consist of many regularly folded chains, called *lamellae*. Between the ordered layers, an amorphous section is still present. In practice, it is not possible for a polymer to fully crystallize into a material with crystals only, therefore, the term *semi-crystalline* polymers is used.

5 Rubbery and fluid state

5.1 Rubbery state

Above the glass-rubber transition temperature, T_g , large parts of the chain are free to move; their thermal energy is high enough to overcome the interaction forces, and the free volume increases with increasing temperature. The polymer is, however, not yet in the liquid condition; the coiled chains are mutually entangled, in contrast to a low-molecular amorphous material above its T_g (Figure 5.1):

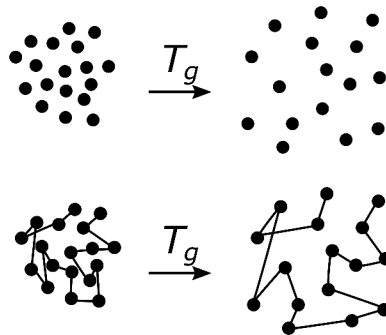


Figure 5.1 A polymer is not a liquid just above its T_g

Dependent of the amount of entanglement, thus of the chain length, a temperature region exists in which the polymer does not flow, but is very soft, rubbery and elastic. Though the chain entanglements are not permanent, because they are being disrupted with increasing temperature and also with increased time of loading, they act as temporary, physical cross-links.

We now understand that the material is, in this condition, soft and still coherent, but the question is, for non-cross-linked polymers above T_g as well as for vulcanized rubbers: why does it show spontaneous recovery after being stretched? As a model we take a single chain with freely rotating links; stretching of such a chain from a coiled state does not require any energy, while, after stretching, it retains its shape.

This model, however, is only valid for chain molecules at zero Kelvin. When $T \neq 0$ the chain parts possess thermal energy; vibration causes them to move in random directions, which always results in a contraction of the stretched chain. The chain tends to a state of higher probability, and eventually reaches a fully unoriented random conformation ("random walk conformation"). To prevent this, a force is needed, which is greater with stronger vibration and thus with a higher temperature. This implies the existence of a finite modulus of elasticity, and, also, of elastic recovery.