

From polymers to plastics

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Preface

The two words in the title of this book, “polymers” and “plastics”, could be considered as referring to two different worlds.

In the world of polymers, the properties of chain molecules are in the focus of attention, and are subject of thorough theoretical studies.

In the world of plastics, the end-use performance of the technically used materials counts, as well as their behaviour in the various processing operations in which they are transformed into finished articles.

Nevertheless, these two worlds are closely related to each other. The typical behaviour of plastics materials, strongly deviating from other materials, can only be understood on the basis of the chain properties.

In this book an attempt has been made to give a survey of polymer properties, and of the way these are, on the one hand, governed by their molecular structure, and are, on the other hand, responsible for the technological behaviour of plastics materials.

As a result of this intention, cross-references are given throughout the whole book: every aspect of polymer science and of plastics technology is closely related to practically every other aspect!

This book originates from several series of lectures at the Delft University of Technology during the years 1978 - 1988, later on integrated into a number of post-graduate and other courses. Since only a first introduction is given, more detailed treatment and more scientific depth have been sacrificed to the striving for survey and integration.

Delft, May 2001
A.K. van der Vegt

Note from the publisher

Just before he died in April 2002, Professor Em. Anne van de Vegt made a translation of his successful Dutch textbook on polymer science and technology “Polymeren, van keten tot kunststof”. Initially we published this translation only on the internet, but decided that it would be worthwhile to publish it in print as so many students and professionals took the trouble to let us know that an affordable edition on paper would be most welcome. So, we are very pleased to be able to publish Anne’s much acclaimed text. We included the - initially separate - collection of problems as well, inserted at the end of each chapter.

J.S.
January 2006

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Solutions to the problems can be downloaded from <http://www.vssd.nl/hlf/m028.htm>

1

Introduction

1.1. Origin of plastics / polymers

The main characteristic of polymers is, that they are composed of extremely large 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 are sometimes branched, sometimes chemically cross-linked with each other so that they form a network.

Polymers are abundantly present in nature, in vegetable and animal tissues (mainly as cellulose and proteins). Several technically used polymers have a natural origin; they are being used as technical materials as they are harvested from natural materials (“*natural polymers*”).

Other polymers are partly from a natural origin; the chain molecule has grown in a living tissue, but has been chemically modified into a “*half-synthetic polymer*”.

A growing number of polymers is wholly *synthetic*; the chain molecule or the network is being built up from small molecules (monomers) in a chemical process.

Some examples of these categories are given below:

Natural polymers:

- vegetable: timber, cotton, jute, sisal, hemp, cork, etc.
- animal : wool, silk, fur, etc.

Half-synthetic polymers:

- from wood: celluloid, cellophane, viscose-rayon, cellulose plastics,
- from milk: casein, from which casein plastics,
- from hides, via a tanning process: leather,
- from rubber latex, via i.a. vulcanization: technical rubber.

Synthetic polymers:

These are synthesized from low-molecular components, mostly organic monomers. Most of the monomers are prepared from fossil fuels; here we can distinguish between two main categories:

- *carbochemistry* (from coal)
- *petrochemistry* (from petroleum or natural gas).

2

Molecular composition

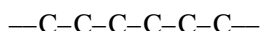
2.1. Chain structure

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.

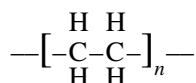
2.1.1. Main chain (Qu. 2.1 and 2.2)

Carbon atoms only:

- saturated:

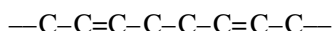


example: polyethylene (PE)

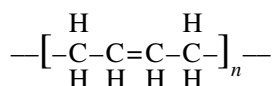


also PP, PS, PVC, PB, PMMA, PTFE, etc. (see § 2.1.2)

- unsaturated:

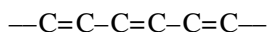


example: polybutadiene

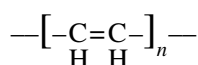


also IR, CR, etc. (see § 2.1.2)

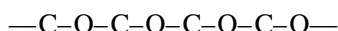
- more unsaturated:



example: polyacetylene.



Carbon and oxygen atoms:



3

Glassy state and glass-rubber transition

3.1. Glassy state

In the usual schedule “solid - liquid” the solid is crystalline and passes into the liquid state at the melting point, T_m . This transition is, in nearly all cases, accompanied by an increase in volume (one of the exceptions is water!), and with an increase in the heat content (enthalpy), the heat of melting.

The jump in volume is illustrated in Figure 3.1; the slope of the line FC is the thermal expansion coefficient of the crystalline phase; at the melting point the volume jumps from C to B, and the higher slope of BA denotes the expansion coefficient of the liquid phase.

Some substances are, however, not able to crystallize, for instance normal glass, as a result of a too irregular molecular structure. When such a substance is cooled down from the liquid state, and follows the line AB, then from B to D it still remains a fluid, which solidifies at D without showing a jump in volume. The line then continues as DE, with about the same slope as CF; the matter is, however, not in a crystalline condition, but in an unordered, amorphous, *glassy state*, and has, therefore, a greater volume.

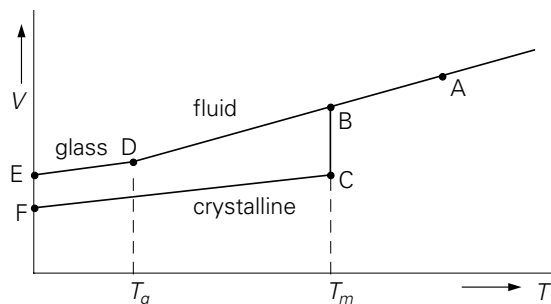


Figure 3.1. Volume as a function of temperature.

The transition at D is called the *glass transition*, occurring at the *glass transition temperature*, T_g . It follows that T_g is always lower than the melting point, T_m . It is very important to *distinguish* very carefully between T_g and T_m !!

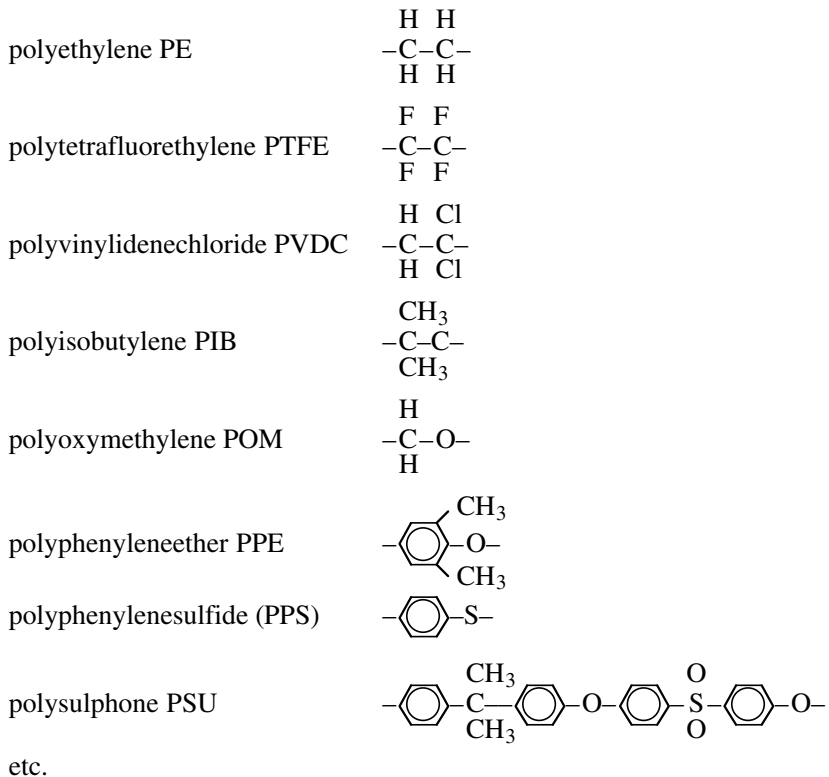
4

Crystalline polymers

4.1. Conditions for crystallization

A primary condition (although not sufficient) for crystallizability is a *regular chain* structure, which enables the formation of crystals in a lattice structure. This condition can be met in several ways:

- when the side groups on both sides of an atom in the main chain are equal, so that the chain is *symmetrical*. Examples of such chains are:



- when the side groups are *small enough to be fitted* into a crystal lattice.

Examples:

polyvinylalcohol PVAL;

5

Rubbery and liquid phases

5.1. Rubbery phase

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):

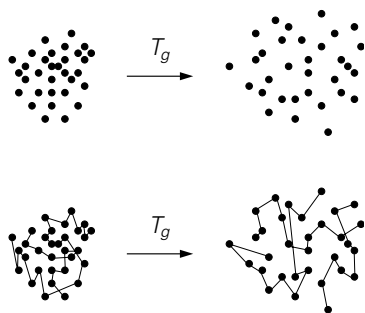


Figure 5.1. A polymer is not a liquid just above its T_g .

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 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, as described in § 2.4 (“random walk conformation”). To