Chapter One

Introduction to polymers, supramolecules and amphiphiles

1.1 About polymers and supramolecules

This thesis deals with polymers and supramolecules. A polymer is a long molecule consisting of in the order of fifty to thousands of repeating units, called monomers. A homopolymer has only one type of repeating unit, a copolymer several. The simplest copolymer, a diblock copolymer, consists of two chemically bonded homopolymers. Polymers can have several architectures, e.g., linear, branched, star-shaped or comb-shaped (see Fig. 1.1). Here, the emphasis is on comb-shaped copolymers.

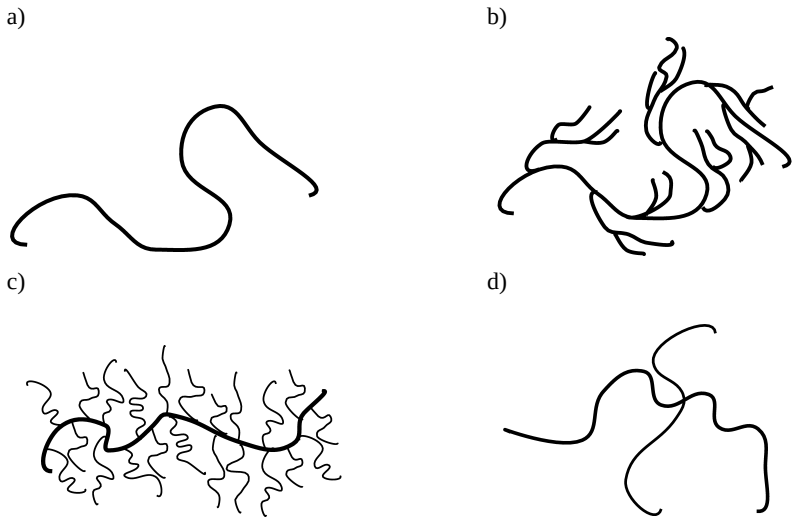

Figure 1.1 Possible architectures of polymers: a) a linear homopolymer, b) a branched polymer, c) a comb copolymer, and d) a star polymer.

A comb copolymer consists of a linear homopolymer to which side chains are chemically bonded (see Fig. 1.1c). The difference between a comb copolymer and a comb-shaped supramolecule is the fact that in the former the side chains are

permanently attached to the main chain, i.e., the polymer backbone, whereas in the second case they are dynamically bonded (see Fig. 1.2). This means that at each time interval, certain side chains will be attached to the backbone, but others will not. This can lead to additional freedom of movement of the whole complex, the comb-shaped supramolecule. This, in turn, can lead to a different response to external flow fields, such as oscillatory shear flow.

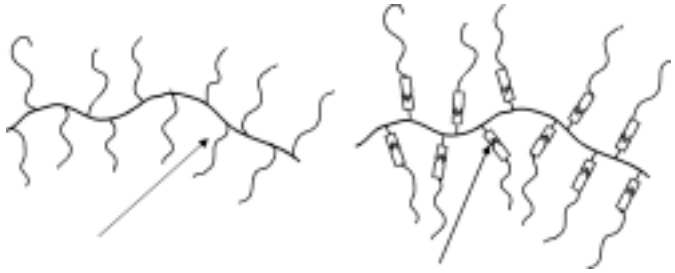

Figure 1.2. Schematic of the conformation of a) a comb copolymer and b) a comb-shaped supramolecular, where the covalent bond has been replaced by a matching physical bond. The latter is dynamic, and constantly breaks and (re-) forms.

1.2 Amphiphiles and oligomers

Amphiphiles are molecules with two sides to their nature: they have a water-loving part (hydrophilic) and a water-hating part (hydrophobic). In general, the hydrophobic part consists of a long hydrocarbon chain. The hydrophilic part can be either ionic or non-ionic. In the latter case, the polar head can exist of one or several phosphates, amines, OH-groups or acid groups. Ionic amphiphiles can be either anionic, cationic or zwitterionic, which means that they contain both an anionic and a cationic group.

Amphiphiles are commonly used as surfactant (surface active agents) in water, as they have the tendency to segregate to a water-air interface and consequently lower the surface tension. This is an important aspect of the use of surfactants as detergents. Amphiphiles in solution can form spontaneous aggregates (micelles) above a certain concentration. Depending on the temperature and concentration these can be spherical, cylindrical and lamellar or even bicontinuous. Because of the tendency to locate at the interface, they can form multilayers on a solid

substrate, when this is dipped in a monolayer of amphiphiles several times. This technique is the Langmuir-Blodgett technique.

In this thesis, the words amphiphiles and oligomers are used interchangeably. This is, because the amphiphiles used have long oligomeric tails, i.e., a chain consisting of tens of hydrocarbon units. The word oligomer refers to a chain that has more than one repeating unit, but is too small to be considered a polymer. For example, the poly(4-vinylpyridine) homopolymer used in Chapters 4 and 5 is 50 times larger than the amphiphilic pentadecyl phenol used, which has 15 repeating units.

1.3 Outline of this thesis

In Chapter 2 the comb-shaped supramolecules used are described in detail. They can form microstructures at different length scales. In Chapter 3 the effect of oscillatory shear flow on lamellar diblock copolymers is described. This background information is used in the Chapters 4 and 5, where the comb-shaped supramolecules themselves are subjected to oscillatory shear flow to induce macroscopic orientation. Having shown the feasibility of macroscopically orienting these materials, Chapters 6 to 8 work towards possible applications: nanoporous materials (Chapter 6), nanofibers (Chapter 7) and anisotropic conductivity (Chapter 8).