Summary

The fats that are present in our food are not just an energy source but they also determine important physical food properties like creaminess, spreadability, mouth feel, gloss and melting behaviour. The main components of fats are triacylglycerols (TAGs), tri-esters of a glycerol moiety and three long-chain fatty acids. The physical properties of a fat are determined by its TAG composition (e.g. acyl chain-length distribution, degree of unsaturation) and by the crystalline polymorphs formed by the co-crystallized TAGs. TAGs have a monotropic type of polymorphism. Ordered according to increasing stability, the principal polymorphs are the α, β' and β. To understand the properties of fats, knowledge about the molecular packing of the molecules in the polymorphs is essential. Application of diffraction is the most straightforward way to obtain this information. Preferably X-ray single-crystal diffraction data should be used, but as good quality and large enough TAG crystals are extremely rare, X-ray powder diffraction is a second best alternative. Crystal-structure determination from powder diffraction data is much more complicated than using single-crystal data and until a few years ago the structure determination of TAG polymorphs was considered to be a too large challenge. In the past few years the robustness of direct-space structure solution based on Monte Carlo methodology has improved considerably and with the increased computing power of PC's, crystal-structure determination of TAGs from powder diffraction data has become feasible though it is a far from routine job: high-resolution (synchrotron, laboratory) powder data are essential and a special brute-force indexing method had to be developed to overcome dominant-zone problems of the TAG powder patterns.

Chapter 2 discusses the structure-solution process of the highest-melting stable β_1 polymorph of a homologous series of *cis*-monounsaturated TAGs and of β-VI cocoa butter, a co-crystallized mixture of *cis*-monounsaturated TAGs. All the β_1 structures are crystallized in space group $P2_1/n$ and have a triple-chain length packing that arises from two symmetry-related three-packs, sets of two molecules packed together, with an unsaturated-bond layer sandwiched between two saturated layers. Comparison of this packing with an earlier published model of the lower-melting β_2 polymorph led to a re-examination of the latter.

The subject of chapter 3 is the structure determination of a set of *cis*-mono-unsaturated TAGs in the second highest melting β_2 polymorph. The set includes also β-V cocoa butter and two asymmetric *cis*-mono-unsaturated TAGs that have not been reported previously to crystallize in a β_2 polymorph. The β_2 polymorphs are crystallized in space group *Cc* and have the same amount (two) and built-up of three-packs as in the β_1 polymorphs. However, the symmetry relation between the three-packs in both polymorphs is different, in the β_2 polymorph the three-packs

are related by the *Cc* lattice-centering operation while in the β_1 they are related by inversion centers. On basis of this different packing of the β_1 and the β_2 polymorphs, the mechanism of fat bloom formation in chocolate is explained.

Chapter 4 focuses on the stable β polymorph of a series of TAGs with even-numbered saturated and *trans*-mono-unsaturated acyl chains that all are crystallized in space group $P\bar{1}$ with a double chain length packing (β-2*)*. Although replacing the *trans*-mono-unsaturated elaidoyl chain by a stearoyl increases the melting point of the corresponding TAG, in the crystal-structure packing no significant differences could be observed.

In chapter 5 the structures of the β'_1-2 polymorphs are unravelled for the same type of TAGs as in chapter 4. As it turned out, this was a very challenging problem: the structures are crystallized in space group *I*2 with a double chain length packing, just like the β-2 structures, but with two independent molecules in the asymmetric unit and different molecule conformations were established for symmetric *versus* asymmetric TAGs. Also, a novel β' polymorph of PSS has been found and its crystal structure has been solved. As its melting point is higher than that of the β'_1-2 polymorph it is denoted β'_0-2. From the difference between the crystal structures of β'-2 and the β-2 polymorphs it is concluded that a solid state β'-2 to β-2 conversion is unlikely.