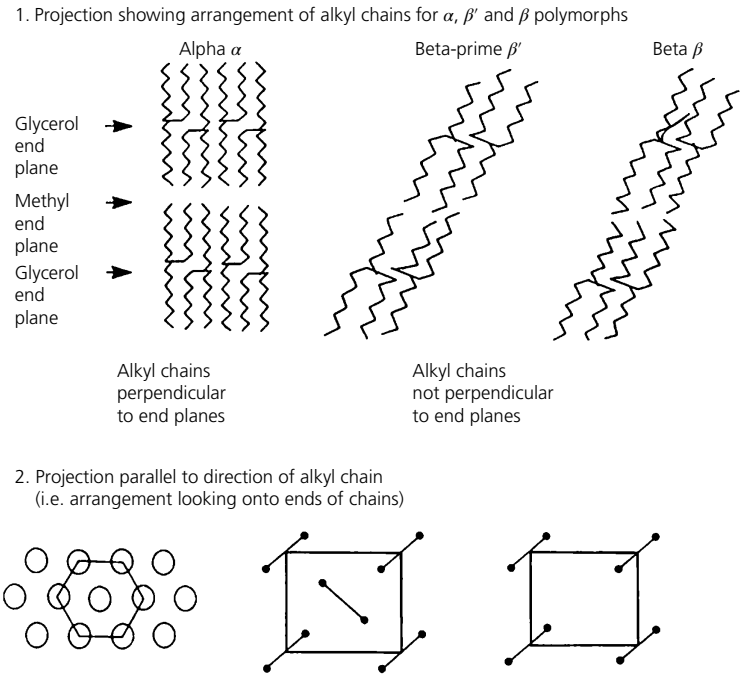

Figure 7.2 Crystal packing of triglycerides. 1. Projection showing arrangement of alkyl chains for α,β and β′ polymorphs. 2. Projection parallel to direction of alkyl chain (i.e. arrangement looking onto ends of chains). Reprinted with the permission of Loders Croklaan.

These polymorphic forms can be characterised by X-ray diffraction and, particularly by their X-ray short spacings, that is:

α Single strong line at 4.15 Å;

β′ Two lines at 3.8 and 4.2 Å;

β One strong line at 4.6 Å.

More subtle differences are observed in the X-ray diffraction patterns of the various sub-forms, for example β_V and β_{VI}. Both these forms show four smaller peaks in addition to the strong peak identified above. In the β_V form (or Form V in cocoa butter) these small peaks are of varying intensities, whereas in the β_{VI} form (or Form VI in cocoa butter) they are of intensities which increase with diffraction angle (see Figure 7.3). Note that in the context of cocoa butter β_2 and β_V are now often used interchangeably as are β_1 and β_{VI}.

In addition to these different polymorphic forms there is a further way in which different triglycerides can pack or crystallise together – the so-called double-chain length (denoted by "-2" after the Greek letter signifying the polymorphic form, e.g. β-2) and triple-chain length packing (denoted by "-3" after the Greek letter signifying the polymorphic form, e.g. β-3). Although such nomenclature can be confusing it should be remembered that β_2 and β-2 mean two different things – the former denotes the less stable of the two β forms,

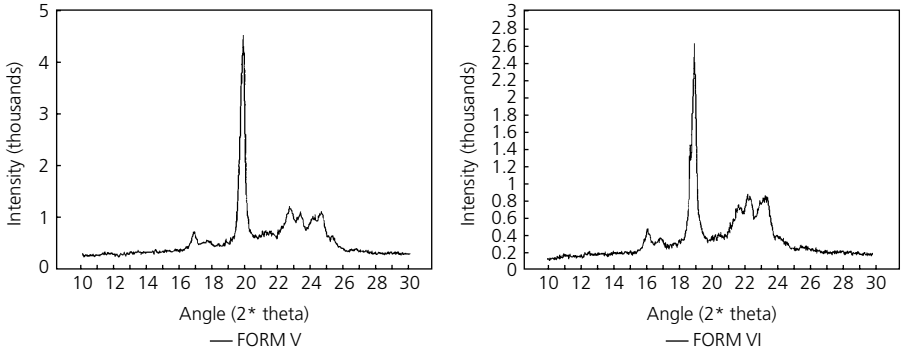

Figure 7.3 X-ray diffraction patterns of Form V and Form VI cocoa butter. Reprinted with permission of Loders Croklaan.

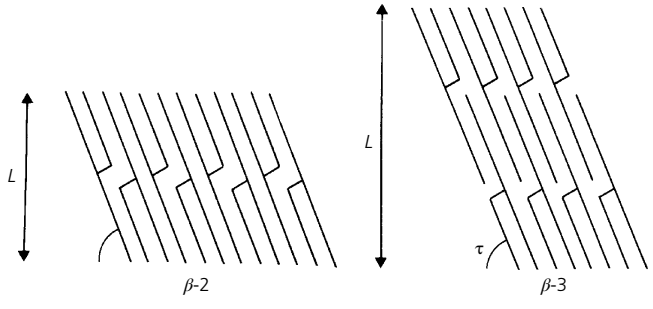

Figure 7.4 Schematic arrangement of triglycerides in the β-2 and β-3 crystalline phase. Reprinted with permission of Loders Croklaan.

the latter denotes any β form in a double-chain length configuration. The molecules shown in Figure 7.2 are depicted in a double-chain system in which the distance from one methyl end plane to the next is approximately the length of two fatty acid chains. Double and triple systems are shown schematically in Figure 7.4. These different types of chain packing are also referred to for each of the six polymorphic forms in cocoa butter in Table 7.4.

The two forms differ, therefore, in that the distance from one methyl end plane to the next is approximately the length of two fatty acid chains in the β-2 system and of three fatty acid chains in the β-3 system. X-ray long spacings will define in which of the two ways a particular fat is packed. The long spacing of β-3 is approximately 50% greater than the long spacing of β-2.

Whether a fat crystallises in a double or triple chain form is usually dictated by its triglyceride composition and, particularly, by the positional distribution of fatty acids on the triglyceride. The triglycerides in cocoa butter are predominantly of the SOS type, that is with the unsaturated oleic acid in the 2-position. The double bond in oleic acid causes an angular change in the fatty acid chain which means that it no longer has the "straight" structure of a saturated chain. If such triglycerides were to crystallise in a double chain form or β-2 the