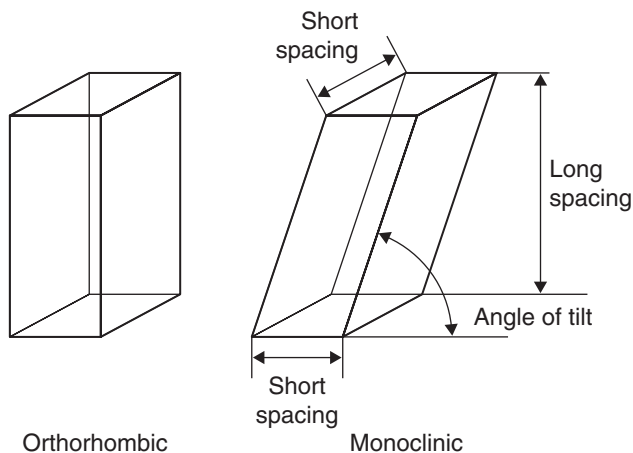


# Physical Properties

## 5.1 Polymorphism, crystal structure, and melting point

In the solid state long-chain compounds frequently exist in more than one crystalline form and consequently have more than one melting point. This property (polymorphism) is of both scientific and technical interest. Understanding this phenomenon is essential for the satisfactory blending and tempering of fat-containing materials (such as spreads and confectionery fats) which must attain a certain physical appearance during preparation and maintain it during storage. Problems of graininess in margarine and bloom in chocolate, for example, are both related to polymorphic changes (Sections 8.3 and 8.7). The experimental methods used most extensively to examine melting and crystallisation phenomena involve low-resolution pulsed  $^1\text{H}$  NMR spectroscopy, differential scanning calorimetry, infrared (IR) spectroscopy, and X-ray diffraction (Larsson *et al.*, 2006).

X-ray investigations indicate that the unit cell for long-chain compounds is a prism with two short spacings and one long spacing as indicated in Figure 5.1. When the long spacing is less than the molecular dimension calculated from known bond lengths and bond angles, it is assumed that the molecule is tilted with respect to its end planes. Sometimes, however, the length is such as to indicate a dimeric or trimeric unit for the most stable form. The molecules assume the angle of tilt at which they are most closely packed. This will give the greatest physical stability and the highest melting point.



**Figure 5.1** The unit cell of long-chain compounds (kindly supplied by my colleague Dr C. M. Scrimgeour).

## 5.2 Alkanoic and alkenoic acids

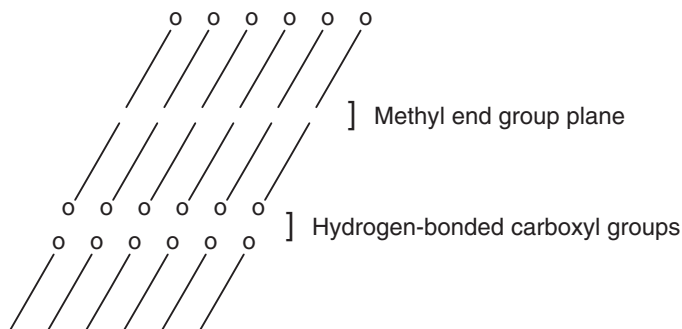
The melting points of some long-chain acids and their methyl esters are listed in Table 1.1. These values show alternation with increasing chain length, a phenomenon commonly displayed in the physical properties of long-chain compounds in the solid state and related to the arrangement of molecules in the crystals. The melting points of acids with an even number of carbon atoms in the molecule and their methyl esters plotted against chain length fall on smooth curves lying above similar curves for the odd acids and their methyl esters. Odd acids melt lower than even acids with one less carbon atom. The two curves for saturated acids converge at 120–125°C.

The melting points of unsaturated acids depend on chain length and on the number, position, and configuration of the unsaturated centres. For example stearic (70°C), oleic ( $\Delta 9c$ , 11°C), elaidic ( $\Delta 9t$ , 45°C), and stearolic acids ( $\Delta 9a$ , 46°C) have the melting points shown. Note the considerable difference between *cis* and *trans* isomers. Among polyunsaturated acids those with conjugated unsaturation are higher melting than their methylene-interrupted isomers (Tables 1.1 and 5.1).

Alkanoic acids exist in three polymorphic forms designated A, B, and C for acids with an even number of carbon atoms. Form C has the highest melting point and is the most stable (physically). It is obtained by crystallisation either from the melt or from polar solvents.

**Table 5.1** Melting points (°C) of some mono and poly-unsaturated acids

<i>Monoenes</i>	
16:1 (9c)	0.5
18:1 (9c)	16.3
20:1 (9c)	25
22:1 (13c)	33.4
<i>Polyenes with methylene-interrupted unsaturation</i>	
18:2 (9c12c)	-5
18:2 (9c12t)	-3
18:2 (9t12t)	29
18:3 (9c12c15c)	-11
18:3 (9t12t15t)	30
<i>Polyenes with conjugated unsaturation</i>	
18:2 (9c11t)	22
18:2 (9t11t)	54
18:3 (9c11t13c)	44
18:3 (9c11t13t)	49
18:3 (9t11t13c)	32
18:3 (9t11t13t)	71



**Figure 5.2** Schematic arrangement of alkanolic acid molecules in the crystalline form. The o represents the polar head group (COOH) and the line represents the alkyl chain which will assume a zig-zag arrangement of successive carbon atoms.

Crystallisation from non-polar solvents gives form A or forms B and C. The molecules crystallise in dimeric layers. Alternation of melting point for odd and even chain-length compounds results from the fact that the methyl groups in the end group plane interact differently in the odd and even series (Figure 5.2).

### 5.3 Glycerol esters

For most technical purposes the melting behaviour of triacylglycerols is more important than that of the fatty acids. It has long been known that fats show multiple melting points and as far back as 1853 glycerol tristearate was reported to have three melting points at 52°C, 64°C, and 70°C. When the melt of a simple triacylglycerol (GA<sub>3</sub>) is cooled quickly it solidifies in its lowest melting form ( $\alpha$ ) with perpendicular alkyl chains in its unit cell (the angle of tilt is 90°). When heated slowly this melts but, held just above this melting point, it will re-solidify in the  $\beta'$  (beta prime) crystalline form. In the same way a still more stable  $\beta$  form can be obtained from the  $\beta'$  form. The  $\beta$  form with the highest melting point is obtained directly by crystallisation from solvent. The  $\beta'$  and  $\beta$  forms have tilted alkyl chains which permit more efficient packing of the triacylglycerols in the crystal lattice. Glycerol esters with only one type of acyl chain are easy to make and have been thoroughly studied. The results have provided useful guidance but such molecules are not generally significant components of natural fats (except after complete hydrogenation). With mixed saturated triacylglycerols such as PStP (P = palmitic, St = stearic) the  $\beta$  form is only obtained with difficulty and such compounds usually exist in their  $\beta'$  form. Among triacylglycerols with saturated and unsaturated acyl chains, symmetrical compounds (SUS and USU) have higher melting (more stable)  $\beta$  forms but the unsymmetrical compounds (USS and UUS) have stable  $\beta'$  forms (S = saturated and U = unsaturated acyl chains) (Table 5.2).

The stable  $\beta$  form generally crystallises in a double chain length arrangement (DCL or  $\beta_2$ ) but if one acyl group is very different from the others either in chain length or in degree of unsaturation the

**Table 5.2** Characteristics of  $\alpha$ ,  $\beta'$ , and  $\beta$  forms of crystalline triacylglycerols

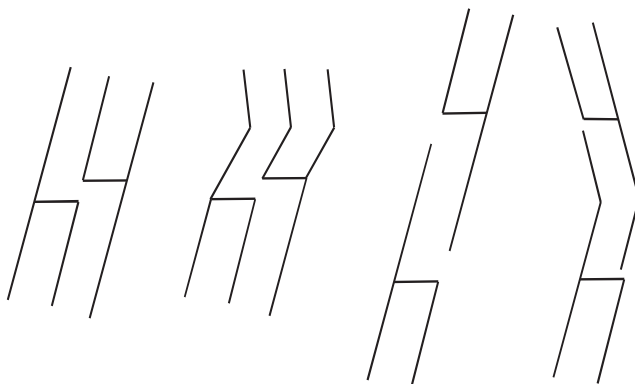
Form	MP	Short spacings (nm)	IR absorption (cm <sup>-1</sup> )	Hydrocarbon chain	Subcell
$\alpha$	Lowest	0.4	720	Perpendicular	Orthorhombic
$\beta'$	Intermediate	0.42–0.43 and 0.37–0.40	726 and 719	Tilted	Orthorhombic
$\beta$	Highest	0.46 and 0.36–0.39	717	Tilted	Triclinic

crystals assume a triple chain length arrangement (TCL or  $\beta_3$ ) to allow more efficient packing of alkyl chains and head groups. These crystals have the short spacing expected of a  $\beta$  crystalline form but the long spacing is about 50% longer than usual (Figure 5.3).

In the DCL arrangement the molecules align themselves (like tuning forks or chairs) with two chains in extended line (to give the DCL) and a third parallel to these (Figure 5.3). Some mixed glycerol esters which have a TCL form when crystallised on their own, give high-melting (well-packed) mixed crystals with a second appropriate glycerol ester (e.g. CPC and PCP or OPO and POP where C = capric, P = palmitic, and O = oleic). This has been described as 'compound formation'.

The methyl groups at the top and bottom of each triacylglycerol layer do not usually lie on a straight line, but form a boundary with a structure depending on the lengths of the several acyl groups. This is called the 'methyl terrace'. The molecules tilt with respect to their methyl end planes to give the best fit between the upper methyl terrace of one row of glycerol esters with the lower methyl terrace of the next row of esters. There may be several  $\beta_2$  modifications differing in the slope of the methyl terrace and in their angle of tilt.

Crystallisation occurs in two stages: nucleation and growth. A crystal nucleus is the smallest crystal that can exist in a solution and is dependent on concentration and temperature. Spontaneous (homogeneous) nucleation rarely occurs in fats. Instead heterogeneous nucleation occurs on solid particles (dust, etc.) or on the walls of the container. Once crystals are formed fragments may drop off



**Figure 5.3** DCL and TCL structures (kindly supplied by my colleague Dr C. M. Scrimgeour).

and either re-dissolve or act as nuclei for further crystals. The latter is not desirable in fat crystallisation so agitation during crystallisation should be kept to the minimum required to facilitate heat transfer. Nucleation rates for the different polymorphs are in the order  $\alpha > \beta' > \beta$  so that  $\alpha$  and  $\beta'$  crystals are more readily formed in the first instance even though the  $\beta$  polymorph is the most stable and is favoured thermodynamically. Crystal nuclei grow by incorporation of other molecules from the adjacent liquid layer at a rate depending on the amount of supercooling and the viscosity of the melt (Timms in Gunstone and Padley, 1997; Sato, 2001; Lawler and Dimick, 2002).

In the production of margarines and shortenings the  $\beta'$  crystalline form is preferred to the  $\beta$  form.  $\beta'$  Crystals are relatively small and can incorporate a large amount of liquid. This gives the product a glossy surface and a smooth texture.  $\beta$  Crystals, on the other hand, though initially small, grow into needle-like agglomerates. These are less able to incorporate liquids and produce a grainy texture. Margarines and shortenings, made from rape/canola, sunflower, or soybean oil after partial hydrogenation, tend to develop  $\beta$  crystals. This can be inhibited or prevented by the incorporation of some hydrogenated palm oil or palm olein which stabilise the crystals in the  $\beta'$  form. These changes in crystallisation pattern are linked with the larger amount of palmitic acid in the palm products. Glycerol esters with  $C_{16}$  and  $C_{18}$  acyl chains are more likely to be stable in the  $\beta'$  form than glycerol esters with three  $C_{18}$  chains.

Because of the importance of its melting behaviour the polymorphism displayed by cocoa butter has been thoroughly investigated. This material is particularly rich in three 2-oleo-1,3-disaturated glycerol esters namely POP, POST, and StOSt. The solid fat has been identified in six crystalline forms designated I–VI with the melting points and DCL/TCL nature indicated in Table 5.3. Of these, form V ( $\beta_2$ ) is the one preferred for chocolate. This crystalline form gives good demoulding characteristics, has a stable gloss, and shows a favourable snap at room temperature. All of these are important properties

**Table 5.3** Polymorphism in cocoa butter

	I	II	III	IV	V	VI
MP (°C)	17.3	23.3	25.5	27.3	33.8	36.3
Chain length*	D	D	D	D	T	T

\*D = double chain length, T = triple chain length.

in good chocolate. Two procedures have been employed to promote the formation of this particular crystalline form. The most extensively used is tempering (*i.e.* putting molten chocolate through a series of cooling and heating processes). This optimises the production of the appropriate polymorph. An alternative procedure requires seeding of the molten chocolate with cocoa butter already prepared in form V ( $\beta_2$ ) or VI ( $\beta_1$ ) but this method is restricted by the difficulty of obtaining adequate supplies of these crystalline forms.

The synthetic glycerol ester 2-oleo-1,3-dibehenin (BOB, O = 18:1, B = 22:0) may be added to cocoa butter to prevent bloom formation by keeping it in its form V at temperatures above 30°C (Section 8.7).

Oils rich in saturated acids contain high-melting triacylglycerols that may crystallise from the oil when stored. When this is considered to be undesirable the oil is subjected to winterisation. The oil is chilled gradually and kept at around 5° for several hours before being filtered. The liquid fraction should then remain clear at ambient temperature. This process is applied to cottonseed oil and to partially hydrogenated soybean oil.

Timms (1978) reviewed and significantly extended information on the heats of fusion of glycerides. He derived an equation for the heat of fusion of mono acid glycerides in the  $\beta$  polymorph form and showed how this could be adapted to calculate the heat of fusion of most glycerides of commercial interest.

## 5.4 Ultraviolet spectroscopy

The use of ultraviolet (UV) spectroscopy in the study of lipids is confined to systems containing or generating conjugated unsaturation. It is therefore of value in the study of the rare natural acids with conjugated unsaturation. Conjugated dienes such as CLA have a UV maximum around 230–240 nm and trienes show triple peaks around 261, 271, and 281 nm. The more common methylene-interrupted polyenes do not show any interesting UV absorption until double bonds migrate to form conjugated systems. This happens during autoxidation (Section 6.2), alkali isomerisation, and other reactions involving doubly allylic methylene groups. UV spectroscopy is also used in the study of carotenoids with extended conjugated systems (Young and Hamilton in Hamilton and Cast, 1999; Angioni *et al.*, in Dobson, 2002).

## 5.5 IR and Raman spectroscopy

IR spectroscopy has been applied to solid lipids to provide information about polymorphism, crystal structure, conformation, and chain length but the commonest use of traditional IR spectroscopy has been the recognition and measurement of *trans* unsaturation in acids and esters where unsaturation is normally predominantly *cis*, using neat liquids or solutions. One *trans* double bond absorbs at  $968\text{ cm}^{-1}$ . Additional *trans* centres increase the intensity but do not change the frequency unless they are conjugated when small changes are reported.

There is no similar diagnostic absorption for a *cis* olefin but Raman spectra show strong absorption bands at  $1665 \pm 1\text{ cm}^{-1}$  (*cis* olefin),  $1670 \pm 1\text{ cm}^{-1}$  (*trans* olefin), and  $2230 \pm 1\text{ cm}^{-1}$  and  $2291 \pm 2\text{ cm}^{-1}$  (acetylenes). Carbonyl compounds have a strong absorption band in the region  $1650\text{--}1750\text{ cm}^{-1}$ . This wavelength varies slightly with the nature of the carbonyl compound as in the following saturated and  $\alpha\beta$ -unsaturated compounds, respectively: aldehydes ( $1740\text{--}1720$  and  $1705\text{--}1680\text{ cm}^{-1}$ ), ketones ( $1725\text{--}1705$  and  $1685\text{--}1665\text{ cm}^{-1}$ ), acids ( $1725\text{--}1700$  and  $1715\text{--}1690\text{ cm}^{-1}$ ), and esters ( $1750\text{--}1730$  and  $1730\text{--}1715\text{ cm}^{-1}$ ).

The analytical uses of FTIR and of NIR have been discussed in Section 4.8.

## 5.6 Nuclear magnetic resonance spectroscopy

See Sections 4.9 and 4.10.

## 5.7 Mass spectrometry

See Sections 4.11.

## 5.8 Density

Density may not seem an exciting physical property to many technologists but it is very important in the trading of oils since shipments



are sold on a weight basis but measured on a volume basis. These two values are related by density so it is important to have correct and agreed values for this unit. This is not the same for all oils. It depends on fatty acid composition and minor components as well as on the temperature. Pantzaris has derived an equation taking these variables into account. It is based on iodine value, saponification value, and temperature.

$$d = 0.8543 + 0.000308(\text{SV}) + 0.000157(\text{IV}) - 0.00068t$$

Where  $d$  = apparent density (g/ml or kg/l), SV = saponification value, IV = iodine value, and  $t$  = temperature ( $^{\circ}\text{C}$ ).

Density can be defined in various ways and the correct form must be used when relating volume to weight.

- Density (absolute density or density in vacuum) is: *Mass in vacuum of a volume of oil at  $t^{\circ}\text{C}$   $\div$  volume of the oil at the same temperature expressed in g/ml or kg/l.*
- Apparent density (density in air, weight-by-volume, or litre-mass) is: *Mass in air of a volume of oil at  $t^{\circ}\text{C}$   $\div$  volume of the oil at the same temperature expressed in g/ml or kg/l.*
- Relative density (specific gravity, density in relation to water) is: *Mass in air of a given volume of oil at  $t_1^{\circ}\text{C}$   $\div$  mass in air of same volume of water at  $t_2^{\circ}\text{C}$ .* This is a ratio without units. It is important to note that two temperatures are involved and the value is meaningless unless both figures are cited. This is the value most usually employed and equations exist to connect these three expressions.

Further information is given by Gunstone in Hamm and Hamilton (2000).

## 5.9 Viscosity

Viscosity can be reported as kinematic viscosity or dynamic viscosity with the two values being related through density. The viscosity of a vegetable oil depends on its chemical composition (summarised in the IV and SV) and the temperature of measurement. Equations have been derived which permit calculation of viscosity from knowledge of the other parameters. These have been developed empirically from observations with a range of oils at different temperatures. Viscosity has been correlated with density, refraction, surface tension, and

other physical properties and the relation between temperature and viscosity for selected oils has been described. Detailed references for these matters can be found in Gunstone (2004).

## 5.10 Refractive index

The refractive index is easily measured on small amounts of material. Refractive index increases with chain length (though not in a linear fashion) and with increasing unsaturation. Geometric isomers differ from one another and methylene-interrupted polyenes differ from those with conjugated unsaturation. Triacylglycerols have higher values than free acids. Values for commercial oils are cited in Table 5.4.

## 5.11 Solubility of gases in oils

A discussion (Hilder in Gunstone and Padley, 1997) on the solubility of gases in oils includes the data presented in Tables 5.5 and 5.6 for oxygen, nitrogen, and air. When an oil is in contact with air the dissolved gases will depend on their individual solubility as well as their concentration in air. The high solubility of the monatomic argon enhances its concentration so that 1% in air becomes 3% of the gases in the oil. The solubility of hydrogen in oils and fats is discussed in Section 6.2.

## 5.12 Other physical properties

Gross heats of combustion (HG) for saturated and unsaturated triacylglycerols can be related to the number of valence electrons (EN). The following equations have been derived:

$$\text{HG} = -109.20 + 26.39 \text{ EN} \quad \text{saturated triacylglycerols}$$

$$\text{HG} = 115.87 + 25.88 \text{ EN} \quad \text{unsaturated triacylglycerols}$$

$$\text{HG} = 1,896,000/\text{SN} - 0.6 \text{ IV} - 1600$$

**Table 5.4** Physical and chemical properties of selected commodity oils and fats

	Specific gravity (temperature °C)	Refractive index (40°C)	Refractive index (25°C)	IV	SV	Titre (°C)	Unsaponifiable (%)	MP (°C)
Cocoa butter	0.973–0.980 (25/25)	1.456–1.458	–	32–40	192–200	45–50	0.2–1.0	31–35
Coconut	0.908–0.921 (40/20)	1.448–1.450	–	6–11	248–265	–	<1.5	23–26
Corn	0.917–0.925 (20/20)	1.465–1.468	1.470–1.473	107–128	187–195	–	1–3	–
Cottonseed	0.918–0.926 (20/20)	1.458–1.466	–	100–115	189–198	–	<2	–
Linseed	0.930–0.936 (15.5/15.5) <sup>d</sup>	1.472–1.475	1.477–1.482	170–203	188–196	19–21	0.1–2.0	–
Olive	0.910–0.916 (20/20)	–	1.468–1.471	75–94	184–196	–	1.5	–3–0
Palm kernel	0.899–0.914 (40/20)	1.452–1.488	–	14–21	230–254	–	<1.1	24–26
Palm	0.891–0.899 (50/20)	1.449–1.455 <sup>e</sup>	–	50–55	190–209	–	<1.4	33–40
Palm olein	0.899–0.920 (40/20)	1.459–1.459	–	>55	194–202	–	<1.4	–
Palm stearin	0.881–0.891 (60/20)	1.447–1.451	–	<49	193–205	–	<1.0	–
Peanut	0.914–0.917 (20/20)	1.460–1.465	–	86–107	187–196	–	<1.1	–
Rape <sup>a</sup>	0.910–0.920 (20/20)	1.465–1.469	–	94–120	168–181	–	<0.21 <sup>f</sup>	–
Rape <sup>b</sup>	0.914–0.920 (20/20)	1.465–1.467	–	110–126	182–193	–	<0.21 <sup>f</sup>	–
Sesame	0.915–0.923 (20/20)	1.465–1.469	–	104–120	187–195	–	<2.1	–
Soybean	0.919–0.925 (20/20)	1.466–1.470	–	124–139	189–195	–	<1.6	–
Sunflower	0.918–0.923 (20/20)	1.467–1.469	1.472–1.476	118–145	188–194	–	<1.6 (max 2.0)	–
Sunflower <sup>c</sup>	0.915–0.920 (20/20)	–	1.467–1.469	75–90	–	–	0.8–1.0 (max 2.0)	–

Notes

- <sup>a</sup>High-erucic rape seed oil.
- <sup>b</sup>Low-erucic rape seed oil.
- <sup>c</sup>High oleic sunflower seed oil.
- <sup>d</sup>Also 0.924–0.930 (25/25).
- <sup>e</sup>50°C.
- <sup>f</sup>These values are correctly copied from the source but they are in error. Better values are 0.5–1.2%.

Source: Physical and Chemical Characteristics of Oils, Fats, and Waxes (Firestone, 1999).

**Table 5.5** Solubility of oxygen and nitrogen (ppm, 1 bar) in oils

Temperature (°C)	Oxygen	Nitrogen
0	170	80
25	180	85
50	185	90
75	190	95
100	200	105
125	*	110
150	*	115

Source: Hilder in Gunstone and Padley (1997).

\*Oxygen solubilities at higher temperatures are not reliable because oxidation occurs.

**Table 5.6** Gas content of oil saturated with air

	Solubility (ppm)	Air dissolved in oil (ppm)
Oxygen	180	38
Nitrogen	85	66
Argon	270	3

Source: Hilder in Gunstone and Padley (1997).

In a useful paper Coupland and McClements (1997) reported several physical properties (density, viscosity, adiabatic expansion coefficient, thermal conductivity, specific heat, ultrasonic velocity, and ultrasonic attenuation coefficient) for a number of liquid oils. Chumpitaz *et al.* (1999) recently reported the surface tension of several fatty acids and triacylglycerols.

These data are important for processes involving gas–liquid contact such as distillation and stripping columns, deodorisers, reactors, and equipment for physical refining.

Useful data taken from the AOCS publication ‘Physical and Chemical Characteristics of Oils, Fats, and Waxes’ is given in Table 5.5.