Short Spacings and Polymorphic Forms of Natural and Commercial Solid Fats: A Review

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Short spacings refer to the cross sectional packing of the hydrocarbon chains. They are independent of chain length. Short spacings are widely used for characterizing the various polymorphic forms. Fats can crystallize into four polymorphic forms, i.e., sub-α, α, β' and β. These polymorphic forms differ in their chain packing and thermal stability. The β' form is also known to exhibit several intermediate polymorphic forms. The nomenclature for the polymorphic forms has generated a great deal of confusion over the years. Several researchers have reported on the polymorphic forms of pure triglycerides. Similar polymorphs have sometimes been described by different names. Currently, the nomenclature proposed by Larsson [Larsson, K., *Acta Chem. Scand. 20*:2256 (1966)] is being widely used. Much of the earlier work on polymorphism has been obtained by studying simple purified substances. The listing of short spacings for natural and commercial fats presented in this paper will be beneficial to researchers working in this field.

KEY WORDS: Crystal structure, crystallization, polymorphism, solid fat, short spacings.

Long chain compounds, such as fatty acids and their esters, may occur in different crystal forms, a phenomenon known as polymorphism. The polymorphic forms differ in a number of properties, including melting points and stability. It is widely acknowledged that the habit (size and shape) of crystals in a fat is related to the polymorphic state of the fat (1).

Most of the basic information on the polymorphism of long chain compounds has been obtained by studying simple purified substances. Natural fats often contain a wide variety of glycerides, differing in chain length and unsaturation of their component fatty acids. Commercial fats often obtained by partial hydrogenation of vegetable oils or animal fats or mixtures of these may be even more complex in composition. The polymorphic behavior of such complex mixtures is often not easily explained in terms of one or more of their major components.

The most widely used method for studying lipid polymorphism is X-ray diffraction. Other methods which have been useful in the study of polymorphism are low temperature infrared spectroscopy (2), differential scanning calorimetry (3), microscopy (4) and thermal analysis microscopy (5). Typical X-ray diffraction patterns of fats exhibit two groups of diffraction lines corresponding to the long and short spacings. The long spacings are observed around 1-15° 2θ, whereas the short spacings are observed around the 2θ region of 16-25° (6). The long spacings correspond to the planes formed by the methyl end groups and are dependent on the chain length and angle of tilt of the component fatty acids of the glyceride molecules. The short spacings refer to the cross sectional packing of the hydrocarbon chain and are independent of the chain length (7,8). The short spacings are used widely to characterize the various polymorphic forms. The chain packing of the α form is hexagonal, the β' form orthorhombic, and the β form triclinic. The β' form is usually associated with asymmetrical triglycerides, i.e., when the 1,2- or 2,3-positions are occupied by two saturated or two unsaturated fatty acids moieties (9). β Crystals are observed with symmetrical triglycerides, i.e., when the three positions are occupied by similar fatty acids or 1,3-position are occupied by similar fatty acids (9).

The nomenclature of different polymorphic forms has suffered from a great deal of confusion over the years. Differences in interpretation between the Malkin (10) and Lutton (11) groups were finally settled by the work of Chapman (12). A summary of the various designations found in the literature is presented in Table 1.

Lutton (11) introduced the term sub-α with short spacings at 4.14, 3.92 and 3.65 Å for 1-monoglycerides. The transformation between sub-α and α was reversible and occurred at low temperatures. Larsson (13) based his nomenclature on the arrangement of the zig-zag planes of the parallel hydrocarbon chains in the solid state. For instance, all the chains are parallel in the β form, whereas the β' exhibits perpendicular orientation.

Hoerr (14) investigated the polymorphic behavior of commercial fats using X-ray diffraction. He tried to correlate the X-ray diffraction results with the information obtained from the heating and cooling curves and visual observations by means of polarized light microscopy. He introduced the term "intermediate," which has a melting point between β' and β. Hoerr failed to mention the chain packing for the intermediate form. This suggests that the intermediate form might be actually a sub form of β.

Riiner (15) investigated the phase behavior of cruciferae seed oils by temperature programmed X-ray diffraction. He proposed the terms $\beta 2$ and $\beta 1$. Hernqvist and Larsson (16) were able to distinguish between $\beta' 2$ and $\beta' 1$ form of triundecanoin on the basis of short spacings. The difference between $\beta' 2$ and $\beta' 1$ is the orientation of the subcell chain packing in relation to the unit cell.

Among the different triglycerides, POP and SOS have been investigated by several researchers (6,17-20). POP and SOS are the prinicipal triglycerides in palm oil and cocoa butter, which are widely used in confectionary fats. The polymorphic forms and short spacings are given in Table 1. For the same triglyceride there is disagreement between researchers with respect to the number of polymorphs present. Much of this confusion is related to the purity of the material and the experimental conditions employed.

Malkin and Wilson (17) introduced the term β'' to their nomenclature. The new β'' form had a lower melting point than the β' form. Lutton and Jackson (18) added the term sub-β with short spacings similar to the β' form reported by Malkin and Wilson (17). Gibon *et al.* (6) introduced the

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TABLE 1

Polymorphic Forms of Triglycerides as Reported in the Literature

Compound	Polymorphic form and short spacing (Å)	Reference
SSS	Vitreous (γ) (4.15 d), α (4.15) β' (3.8, 4.2), β (4.6)	10
SSS	α (4.16), β' (3.8, 4.2), β (4.6)	11
1-Mono-glyceride	Sub α (4.14, 3.92, 3.75, 3.56) α (4.64, 4.18, 3.99, 3.81) β' (4.15, 3.87, 3.65, 3.30) β (4.55, 4.37, 3.86, 3.74)	11
Triglycerides	α (4.15) β' (4.2, 3.88 OR 4.27, 3.97, 3.71) β A form which does not satisfy the above criteria.	13
Commercial fats	α (4.15) β' (4.35, 4.2, 4.03, 3.80) Intermediate (4.62, 4.15, 3.75, 3.60) β (4.57, 4.22, 4.00, 3.85, 3.65, 3.50)	14
Cruciferae seed oils	α (4.15) β' (4.38, 3.90) β^1 (5.20, 4.80, 4.48, 4.10. 3.80, 3.62) β^2(4.60, 4.1-3.7)	15
Triundecanon	α (4.18) β'^2 (4.36, 4.22, 3.91) β'^1 (4.52, 4.32, 4.08, 3.96)	16
POP	α (4.22) Sub-β' (4.39, 4.23, 3.93) Mixture of L-2 & L-3 (5.30, 4.78, 4.50, 3.94, 3.63) Pseudo-β' (4.98, 4.56, 4.35, 4.20, 4.03) β (4.62, 4.10, 4.00, 3.86, 3.74)	6
POP	Vitreous (4.15) α (4.17) β' (5.22, 4.74, 4.47, 3.88, 3.58 β' (4.32, 4.11, 3.88) β (5.44, 4.58, 4.02, 3.84, 3.66)	17
POP	α-2 (4.14) Sub-β'-2 (4.34, 4.13, 3.84) β'-2 (4.27, 3.97) β-3 (5.42, 4.56, 4.04, 3.65)	18
POP	α-2 (4.19) β'' (5.22, 4.73, 4.50, 3.88, 3.59) β'-2 (4.13, 4.29, 3.95) β-3 (5.40, 4.56, 4.05, 3.73)	19
SOS	α-3 (4.19) β'-3 (4.59, 4.40, 4.21, 4.07, 3.76) Sub-β-3 (5.22, 4.74, 4.55, 4.23, 3.88, 3.60) β-3 (5.44, 4.62, 4.01, 3.86, 3.78, 3.64)	18
SOS	α-3 (4.22) Sub-β-3 (4.70, 3.88, 3.60) β-3 (4.56, 4.01, 3.78, 3.66)	19
SOS	α (4.21) γ (4.72, 3.88) Pseudo-β' (4.02, 3.70) β^2 (4.58, 3.67) β^1 (4.50, 3.65)	20
Erucic acid	α (4.46, 4.37, 4.30, 4.11,3.92, 3.74) γ (4.71, 4.26, 3.73, 4.04, 3.91, 3.68) α^1 (4.6, 4.4, 4.21, 4.04, 3.93, 3.73, 3.56, 3.40) γ^1 (4.55, 4.32, 4.18, 3.98, 3.77, 3.66, 3.48, 3.30)	21

term pseudo-β' because its short spacings were similar to β'. Recently, Sato (20) and Suzuki *et al.* (21) proposed the term γ. According to these authors, the α and γ forms undergo reversible transformation in the solid state at low temperatures. Lutton (11) designated this form as sub-α. Riiner (22) disagreed with the term sub-α because it would give a wrong impression that the low melting phases are structurally related to α. Instead he referred to it as β'2. The X-ray data for sub-α (4.14, 3.92, 3.75 and 3.56) and γ (4.72 and 3.88) are different because different compounds were investigated under different experimental conditions. The very fact that the transformation is reversible and occurs at low temperatures suggests that the term γ is actually sub-α or β'2.

Currently the nomenclature proposed by Larsson (13) is being widely used (Table 2). According to this nomenclature, α shows a single line near 4.15 Å. β' Exhibits two strong lines near 4.2 and 3.8 Å or three strong lines near 4.27, 3.97 and 3.71 Å. A form which does not satisfy the above criteria is called β. When two or more polymorphic forms have the same chain packings they are designated as β'1, β'2 and β'3, etc., in order of decreasing melting points.

TABLE 2

Nomenclature and Assignment of Polymorphs

Polymorph	X-ray short spacing characteristics	Reference
α	A single short spacing at ca. 4.15 Å.	9
β'	Usually two strong short spacings at ca. 3.80 and 4.20 Å or three short spacings at ca. 4.27, 3.97, and 3.71 Å.	
β	A form which does not satisfy the criteria for α or β', but also usually shows a very strong short spacing at ca. 4.60 Å	
Sub-forms		
β' (sub-α)	A β' form usually melting below an α form and with long spacings indicating an unusually large d spacing.	
sub β	A form which does not satisfy the criteria for α or β', but shows a strong short spacing at 4.74 Å and several medium strength spacings at ca. 4.50, 3.90 and 3.60 Å.	
γ	A form which melts below an α form and shows two strong short spacings at 4.72 and 3.88 Å	20
Pseudo-β'	A form which shows certain deviation from the ordinary β' form with a strong short spacing at 3.96, along with medium strength spacings at ca. 4.15, 4.27 and weak spacing at 4.40 Å	6

Among natural fats, cocoa butter has been studied extensively due to its economic importance. Cocoa butter is made up of three major fatty acids—oleic, stearic and palmitic, with minor amounts of linoleic and arachidonic acid. Different terminology has been used for describing the same polymorphic forms by different researchers (22-32) (Table 3). Some researchers (27,29-32) used Roman numerals, whereas others used (22-26,28) Greek letters to describe the different polymorphic forms in cocoa butter.

The short spacings for cocoa butter are shown in Table 4. Form I is obtained at low temperatures upon rapid cooling. It is the least stable form, with short spacings at 3.7 and 4.19 Å characteristic of the β'2 or sub-α structure. Polymorph II was obtained by cooling at 2°C upon solidification of the melt (27). It exhibited a strong line at 4.25 which, according to Lutton's nomenclature, is the α form.

Polymorph III was obtained by transformation of form II at 5°C upon solidification of the melt (27). Riiner (22) failed to observe polymorph III. According to him, polymorph III was a mixture of polymorph II and IV. Witzel and Becker (28) referred to it as β'1. The X-ray diffraction studies on form V reveal a very strong line at 4.6 Å characteristic of the β structure. However, form VI had similar short spacings as form V with lines of lesser intensity. Riiner (22) failed to observe form V because it formed very slowly from form IV, the transition taking more than 18 weeks at 21°C, presumably without change in chain packing.

The short spacings for unhydrogenated fats and oils that are solid or semisolid at room temperature are presented in Table 5. Among the animal fats, the polymorphic behavior of beef tallow and lard are widely studied because of their use in shortenings. Even though both of

TABLE 3

Classification of Cocoa Butter Crystalline Forms and Their Melting Points (°C)

	Vaeck (1951) (23)	Vaeck (1960) (24)	Giddey & Clerc (1961) (25)	Duck (1964) (26)	Willie & Lutton (1966) (27)	Witzel & Becker (1969) (28)	Riiner (1970) (15)	Chapman *et al.* (1971) (29)	Lovengren *et al.* (1976) (30)	Hicklin *et al.* (1985) (31)	Davis & Dimick (1986) (32)
Form	γ	γ		γ	I	α	β'2	I	VI	I	I
MP	18.0	17.0		18.0	17.3	—	—	—	13.0	17.9	17.60
Form	α	α	α	α	II	β'1	—	II	V	II	II
MP	23.5	21-24.0	—	23.5	23.3	—	—	—	20.0	24.4	19.9
Form	β''	β'	β'	β''	III	β'2	mix of α & β'	III	IV	III	III
MP	28.0	28.0	—	28.0	25.5	—	—	—	23.0	27.7	24.5
Form	β	β	β	β'	IV	pre β	β'	IV	III	IV	IV
MP	34.5	34-35.0	—	33.0	27.3	34.5	—	25.6	25.0	28.4	27.90
Form				β	V	β	β	V	II	V	V
MP				34.0	33.8	36.2	—	30.8	30.0	33.0	34.4
Form					VI			VI	I	VI	VI
MP					36.3			32.2	33.5	34.6	34.1

TABLE 4

X-Ray Diffraction Data for Cocoa Butter

Willie & Lutton (1966) (27)		Witzel & Becker (1969) (28)		Riiner (1970) (15)		Chapman *et al.* (1971) (29)		Hicklin *et al.* (1985) (31)	
Short spacing	Polymorph	Short spacing	Polymorph	Short spacing	Polymorph	Short spacing	Polymorph	Short spacing	Polymorph
4.19 VS, 3.70 S	I	—	—	4.19 VS, 3.72 M	$\beta'2$	4.17 S, 3.87 M	I	4.19 VS, 3.70 S	I
4.24 VS	II	4.21	α	4.25 (d) S	α	4.24 VS	II	4.25 S	II
4.92 VW, 4.62 W 4.25 VS, 3.86 S	III	4.66, 4.33, 4.22 3.86	$\beta'1$	—	—	4.20 VS, 3.87 W	III	4.63 M, 4.25 S 3.87 M	III
4.35 VS, 4.15 W 3.97 M, 3.81 M	IV	4.58, 4.33 4.16	$\beta'2$	4.61 S, 3.90 W 3.77 W	$\beta'1$	4.32 S, 4.13 S 3.88 W, 3.75 M	IV	4.35 VS, 4.17 W	IV
5.40 M, 5.15 W 4.58 VS, 4.23 VW 3.87 M, 3.75 W 3.67 W, 3.39 VW	V	5.42, 4.59, 3.98, 3.85 3.76, 3.67	pre β	4.61 S, 3.90 W 3.77 W	β	4.58 VS, 4.22 W 3.98 S, 3.87 M 3.73 M, 3.65 S	V	5.43 M, 4.60 VS 3.99 M, 3.88 W 3.76 M, 3.68 W	V
5.43 M, 5.15 W 4.59 VS, 4.27 VW 4.04 W, 3.86 M 3.70 S, 3.36 VW	VI	5.44, 4.59, 4.00, 3.86 3.70	β			4.53 VS, 4.21 W 4.01 W, 3.84 M 3.67 S	VI	5.47 M, 5.16 W 4.60 VS, 4.28 W 4.04 M, 3.88 S 3.71 S	VI

TABLE 5

X-Ray Diffraction Pattern of Natural Fats and Oils

Product	Temperature (°C)	Short spacings (R)													Polymorphic form	Reference
		5.3	5.2	4.6	4.5	4.4	4.3	4.2	4.1	4.0	3.9	3.8	3.7	3.6		
Beef tallow	22			4.58 W			4.30 (d)S					3.84 S			$\beta' > \beta$	22
Beef tallow	5			4.60 VW				4.25 S				3.84 S			$\beta' > \beta$	33
Lard	22			4.62 S	4.55 S	4.45 M		4.20 (d)M			3.89 M	3.79 S	3.70 W		$\beta' > \beta$	22
Lard	24	5.32 W		4.60 VS				4.20 W			3.90 M	3.87 M	3.69 M		$\beta' > \beta$	36
Milk fat	5			4.60 W				4.19 S				3.81 M			$\beta' > \beta$	33
Milk fat	5			4.60					4.17			3.78			$\beta' > \beta$	37
Coconut oil	22				4.51 W		4.33 M	4.23 M	4.12 M			3.84 S			$\beta' > \beta$	22
Corn	-15 to -7			4.60		4.42		4.18			3.91		3.71		$\beta' > \beta$	22
Cottonseed	-19 to +6					4.45		4.17			3.91		3.71		β'	22
Palm kernel	22					4.44 M	4.25 S			4.04 M		3.84 S			β'	22
Palm oil	22						4.35 (d)M	4.20 S				3.87 S			β'	22
Palm oil	-5 to -10							4.18 S					3.73 M		$\beta'2$	39
							4.35 M	4.20 S			3.90 M				$\beta'1$	
Palm oil	23						4.35 S	4.19 S				3.88 M			β'	40
Palm oil[a]	5			4..56 VW			4.34 S	4.20 S			3.89 S				$\beta' > \beta$	40
Palm oil[b]	5 to 20			4.56 W			4.35 M	4.19 M		4.00 VW					$\beta' > \beta$	40
Peanut oil	-8					4.40			4.15		3.90		3.70		β'	22
Safflower seed	-10			4.60					4.13				3.70		$\beta' + \beta$	22
Sheanut oil	22			4.55 S						4.03 M	3.97 M		3.73 M	3.68 M	β	22
Soybean	-7			4.61		4.44			4.15		3.90			3.68	$\beta' + \beta$	22
Sunflower	-9		5.25	4.60		4.40			4.13			3.84		3.63	$\beta' + \beta$	22

[a] Stored for 36 days at 5°C.

[b] Temperature cycled between 5 and 20°C.

these fats are of animal origin, beef tallow crystallizes in the β' form and lard in the β form. The β' form of beef tallow is due to the presence of PSP and PSS, whereas the β form is attributed to the POP/PPO compound (33). Lard crystallizes in the β form. This is because lard contains about 25% palmitic acid which is on the second carbon of the glycerol molecule (34). According to Quimby *et al.* (35), 2-palmityl glycerides normally crystallize in the β form. Lard exhibits spacings at 3.7, 3.9, 4.6 and 5.3 Å, which are characteristics of the β form (36).

Diffraction data indicate that milkfat occurs mainly in the β' form with traces of the β polymorph. The presence of β characteristics is attributed to the presence of a small amount of high melting trisaturated triglycerides (33). Woodrow and deMan (37) investigated the polymorphic behavior of milkfat after slow and rapid cooling. Slow cooling resulted in a mixture of β' and β crystals. Rapid cooling of milkfat resulted in the formation of α form, which eventually transformed to β' and β upon holding the sample at 5°C.

Among the vegetable oils, palm oil is gaining a lot of importance because of its use in products such as cooking oil, margarine, shortenings and confectionary fats. Palm oil is primarily made up of palmitic (44%) and oleic (37%) acids. It has been reported that addition of palm oil has a beneficial effect on the polymorphic stability on products such as margarine and shortening, i.e., it delays or prevents the crystallization into the β form (38). This stabilizing effect may be due to the increased chain length diversity of the fatty acids in these blends. Persmark *et al.* (39) investigated the solidification and polymorphic properties of palm oil by X-ray diffraction, dilatometric and cooling curves. Three polymorphs—$\beta'2$, $\beta'1$ and α—were observed for palm oil. These researchers also studied the polymorphic behavior of a palm oil fraction obtained from acetone. They concluded that the fractionated samples exhibited a very complex polymorphic behavior as compared to the original palm oil. This is partly due to the fractionation process which results in solid phases that simply do not exist in the original oil. Recently, Yap *et al.* (40) investigated the polymorphic behavior of palm oil in a constant temperature-time study and by temperature cycling. Palm oil exhibited a weak line at 4.56 Å after 36 days of storage at 5°C, it was observed that after the fourth cycle a weak band appeared at 4.6 Å indicating a partial transformation of the β form.

Among the lauric fats, coconut and palm kernel oil are the most important. These fats contain about 50% lauric acid. Their characteristic short spacings are shown in Table 5. Riiner (22) obtained an α polymorph on rapid cooling, which subsequently transformed to the stable β' form.

In margarines and shortenings the solids should consist of β' crystals, which are responsible for a smooth texture. On the other hand, β crystals are large in size and therefore cause graininess in margarines and shortenings, although they are useful in pastry fats. Fats can be suitably modified by hydrogenation or interesterification. Unfortunately not all hydrogenated fats tend to crystallize in the β' form because they differ in their triglyceride composition, chain length, degree of unsaturation, *trans* content and trisaturates such as SSS and PSS.

The iodine values (IV) and short spacings for hydrogenated fats and oils are shown in Table 6. Fats such as beef tallow contain about 25% palmitic acid, 12% of which is located in the 2-position. Upon hydrogenation PPS and PSP are present in equal amounts (41). Oils such as palm, cotton and soybean consists mainly of 16 and 18 carbon fatty acids, and it can be concluded that triglycerides of 48 and 54 carbons consist mainly of tripalmitin and tristearin. Palm oil contains high percentage of POP (9) which, upon hydrogenation, is converted to PSP. Cottonseed consists mainly of SPP (42). Lutton (11) investigated the polymorphism of saturated C16-C18 mixed triglycerides. According to the author, PSP exists only in the β' form, whereas SPP and PSS exhibits both β' and β characteristics. deMan *et al.* (43) have shown that hydrogenated cottonseed oil exhibits a mixture of α, β' and β forms. The diffuse band between 4.13-4.25 makes it difficult to distinguish between α and β'. If β' crystals are present it will show a short spacing at approximately 3.8 Å.

Hydrogenated soybean oil exhibits the major polymorphic forms as well as several intermediate forms (43). The significance of these additional short spacings is hard to explain. According to Moran (44), these intermediate short spacings may be due to the superimposition of the

TABLE 6

X-Ray Diffraction Data For Hydrogenated Fats and Oils

Product	Iodine value	Short spacings (R)													Polymorphic form	Reference
		5.30	5.10	5.00	4.60	4.50	4.40	4.30	4.20	4.10	4.00	3.90	3.80	3.70		
Beef tallow	4.2								4.20 (d) S				3.80 S		β'	22
Beef tallow	–									4.13-4.11 VS			3.80 VW		$\alpha + \beta'$	43
Canola (selective)	66.61			5.05 VW		4.55 VW	4.40 M		4.25 S				3.84 S		$\beta' > \beta$	46
Canola (nonselective)	72.01							4.37 M	4.20 S		4.07 W		3.84 S		β'	46
Coconut oil	2.2							4.34 M	4.23 S				3.82 S		β'	22
Cottonseed	67.80							4.37 M	4.23 S				3.86 S		β'	22
Cottonseed	3.5								4.20 (d) S				3.80 S		β'	22
Cottonseed	–					4.57 W			4.25-4.16 (d) S				3.81 S		β	43
Herring oil	74.80								4.25 (d) S				3.84 S		β'	22
Herring oil	58.30								4.23 (d) S				3.82 S		β'	22
Palm oil	27.50							4.36 M	4.22 S		4.06 W		3.86 S		β'	39
Palm kernel	5.1						4.43 W		4.21 S				3.81 S		β'	22
Palm olein	28.0							4.34 S		4.19 VS	4.04 M		3.85 M		β'	46
Palm stearin	31.3					4.56 W		4.35 S	4.20 W		4.05 W		3.87 S		$\beta' + \beta$	46
Peanut oil	67.7								4.25 (d) S				3.84 S		β'	22
Peanut oil	62.70					4.57 W			4.25 (d) S				3.84 S		$\beta + \beta'$	22
Rapeseed oil	70.20							4.36 S	4.23 S		4.07 W		3.86 S		β'	22
Rapeseed oil	64.2					4.57 W		4.34 S	4.21 S		4.07 W		3.87 S		$\beta + \beta'$	22
Soybean	70.0					4.58 W		4.37 M	4.24 S		4.08 W		3.86 S		$\beta + \beta'$	22
Soybean	–	5.30 W	5.15 W	4.79 VW		4.53 VS		4.33 VW	4.20 VW			3.97 M			β	43
Soybean	74.0	5.30 W					4.49 VS			4.18 W				3.76 M	β	45
Sunflower	80.00				4.65 S							3.95 M	3.84 M	3.73 W	β	22
					4.60 W							3.90 M				

double chain length on an existing triple chain length structure. Riiner (22) and Merker (45) failed to observe these intermediate spacings because they used partially hydrogenated soybean oil.

Recent studies carried out by Yap (46) showed that selectively hydrogenated canola oil contained a mixture of β′ and β forms upon temperature cycling, whereas nonselective hydrogenation resulted in β form crystals using the same temperature cycling conditions. Riiner (22) hydrogenated rapeseed oil to iodine values of 70.2 and 64.2, and investigated their polymorphic behavior. Both samples showed similar short spacings. An additional weak short spacing at 4.58 Å was observed for the sample hydrogenated to an iodine value of 64.2. This could be attributed to the small amount of high melting trisaturated triglycerides formed during hydrogenation.

Interesterification involves rearrangement of fatty acids within and between triglycerides. This results in the formation of new triglycerides which do not exist in the original fat. Interesterified fats sometimes exhibit simpler melting curves.

X-ray diffraction data for interesterified fats are shown in Table 7. Both milk fat and beef tallow demonstrate β′ characteristics. Wiedermann *et al.* (36) compared the polymorphic behavior of lard modified to different degrees of interesterification. He was able to obtain a crystal modified lard that was stable in the β′ form. Directed interesterified lard was in the β form, which he attributed to the formation of trisaturates.

When two or more fats are mixed the system becomes more complex. Prior to interesterification a mixture of β′ and β crystals was observed for blends of milkfat and beef tallow (Table 7). As the beef tallow percentage increased, the β crystallinity increased, except for 100% beef tallow. Upon interesterification of these blends the β crystals disappeared, except for 100% beef tallow. The presence of β form in beef tallow could be attributed to the presence of POP and PPO (33).

One of the undesirable attributes of chocolate is the formation of fat bloom. Several theories have been proposed for the cause of fat bloom. According to Willie and Lutton (27), form VI may be responsible for fat bloom. This problem can be delayed by the addition of bloom inhibitors such as cocoa butter substitutes, cocoa butter equivalents, milk fat and hydrogenated vegetable fats. Chapman *et al.* (29) investigated the effect of milk fat on the polymorphic behavior of cocoa butter (Table 8). They concluded that addition of milk fat lowered the melting points of all phases as compared to pure cocoa butter. The transformation from form V to VI was very slow. This suggests that milk fat may be responsible for the slow transformation.

Hicklin *et al.* (31) studied the effect of hydrogenated vegetable fat on the polymorphic and morphological behavior of cocoa butter. According to these researchers, addition of 10 and 20% of hydrogenated vegetable fat had very little effect on the morphology of form V. X-ray studies revealed short spacings characteristic of the β form. As the percentage of vegetable fat increased the crystal size decreased. X-ray data showed the suppression of β structure and domination of the β′ form. However, upon temperature cycling a strong line was noticed at 4.6 Å with the loss of lines at 4.08 and 4.39 Å.

Merker and co-workers (45) incorporated different levels of hydrogenated cottonseed oil in soybean oil and studied the relationship of polymorphism to the texture of margarines. Hydrogenated soybean oil exhibited β crystals. Mixed β and β′ polymorphs were observed for samples containing 10% hydrogenated cottonseed oil. As the percentage of hydrogenated cottonseed oil increased, only β′ crystals were observed (Table 8). Recently deMan *et al.* (43) reported the polymorphic behavior of a variety

TABLE 7

X-Ray Diffraction Pattern of Interesterified Fats

Product		Short spacing Å			Polymorphic form	Reference
Beef tallow		3.86 M	4.21 S	4.60 S	β′ + β	33
Lard		3.86 M	4.21 S	4.67 VS	β > β′	35
Milk fat		3.79 M	4.16 S		β′	33
Before interesterification						
Milk fat (%)	Beef tallow (%)					
100	0	3.80 M	4.18 S	4.60 VW	β′ > β	33
80	20	3.80 M	4.16 S	4.56 VW	β′ > β	33
60	40	3.81 M	4.17 S	4.58 W	β′ > β	33
40	60	3.80 W	4.16 S	4.56 M	β′ + β	33
20	80	3.80 W	4.20 S	4.56 M	β′ + β	33
0	100	3.86 M	4.25 S	4.60 VW	β′ > β	33
After interestification						
100	0	3.79 M	4.16 S		β′	33
80	20	3.82 M	4.19 S		β′	33
60	40	3.82 M	4.19 S		β′	33
40	60	3.83 M	4.15 S		β′	33
20	80	3.82 M	4.18 S		β′	33
0	100	3.86 M	4.21 S	4.60 VW	β′ > β	33

TABLE 8

X-Raya Diffraction Pattern of Various Blends of Fats

Product	Short spacings (Å)																Poly orphic form	Refer-ence
	5.3	5.2	5.1	5.0	4.9	4.6	4.5	4.4	4.3	4.2	4.1	4.0	3.9	3.8	3.7	3.6		
Cocoa butter + milk fat											4.18 VS			3.80 M			I	29
Cocoa butter + milk fat										4.21 VS							II	29
Cocoa butter + milk fat						4.61 VW				4.23 VS				3.86 W			III	29
Cocoa butter + milk fat									4.34 S		4.12 S			3.83 W			IV	29
Cocoa butter + milk fat						4.61 VS				4.23 VW			3.99 M	3.86 M	3.75 M	3.68 M	V	29
Cocoa butter + milk fat					4.88 VW	4.60 VS				4.25 VW		4.02 W		3.87 M		3.68 S	VI	29
Vegetable fat 10% + cocoa butter 90%	5.45 M									4.24 S		4.00 M		3.89 W	3.75 M	3.68 W	β′	31
Vegetable fat 50% + cocoa butter 50% (uncycled)									4.39 M	4.24 S		4.08 M		3.87 S			β′	31
Vegetable fat 50% + cocoa butter 50% (cycled)						4.60 S				4.25 S				3.89 M			β>β′	31
Soybean oil 100% + cottonseed oil 0%	5.3 W							4.49 VS			4.18 W				3.76 M		β	45
Soybean 90% + hydrogenated cottonseed oil 10%								4.49 M			4.18 VS			3.80 M			β	45
Soybean oil 80% + hydrogenated cottonseed oil 20%											4.16 S			3.80 M			β′	45
Soybean oil 70% + hydrogenated cottonseed											4.15 VS				3.76 M		β′	45
Hydrogenated soybean canola oil 20% (23°C)													3.97 W	3.83 M		3.67 M	β	43
Hydrogenated palm + canola oil 20% (23°C)							4.55 M		4.30 W		4.17 S				3.78 S		β′>β	43
Hydrogenated soybean canola oil 50% (23°C)	5.36 M	5.26 W				4.57 VS		4.47 W					3.98 M	3.85 S	3.70 S		β	43
Hydrogenated palm + canola oil 50% (23°C)						4.57 M			4.33 M		4.18 S	4.02 W			3.79 S		β′>β	43
Hydrogenated soybean canola oil 80% (4°C)	5.36 VW						4.55 VS						3.98 VW	3.84 M		3.67 M	β	43
Hydrogenated palm + canola oil 80% (4°C)									4.29 W		4.18 S	4.03 W			3.75 S		β′	43

of hard fats dissolved in canola oil at levels of 20, 50 and 80%. All of the hard fat mixtures were present in the β form except palm, which showed β′ crystallinity. The β′ characteristics of palm oil may be due to its unique triglyceride composition, which is very diverse. Palm oil contains about 44% of palmitic acid which is distributed mainly between the 1,3-positions of the triglyceride molecule.

A review of literature reveals no short spacings for commercial margarines, shortenings and frying fats. However, for the past few years deMan and co-workers (deMan, L., and J.M. deMan, unpublished data) have done extensive study on the polymorphic forms of these products using X-ray diffraction and differential scanning calorimetry (DSC).

Canola margarines can be distinguished from soybean and corn margarines by their palmitic acid content. Canola contains 5% of 16:0 (47), whereas soybean contains about 11% (34). Short spacings for commercial margarines are tabulated in Table 9. Canola margarines tend to crystallize in the β form because of their low diversity in fatty acid content. Palm oil is incorporated into canola margarines to increase the diversity of fatty acid chain length and thereby delay or prevent the formation of β crystals (48). According to Hernqvist (49), diglycerides stabilize β′ crystals in margarines and fats. Addition of palm oil to products H and I (Table 9) did not prevent the polymorphic transition of β′ to β. Processing and/or storage conditions may have caused the β crystal formation. Yap (46) has demonstrated that palm oil in the unhydrogenated form is less effective in delaying the β transition than hydrogenated palm oil. Margarines made from soybean showed β′ crystallinity. Products T and U showed a mixture of β′ and β crystals. The β′ crystals in fractionated tallow may be attributed to the presence of PSP and PSS (9).

TABLE 9

X-Ray Diffraction Pattern for Commercial Margarines

Product ingredients	Short spacings (Å)												Polymorphic form	Reference
	5.3	5.2	5.1	4.6	4.5	4.4	4.3	4.2	4.0	3.9	3.8	3.7		
A Canola	5.38 W	5.28 W	5.09 VW	4.60 S	4.53 M	4.45 M				3.92 S	3.82 M	3.70 M	β	48
B Canola	5.33 VW	5.20 VW		4.60 S	4.51 W	4.42 W				3.89 S	3.80 M	3.68 M	β	48
C Canola				4.57 S	4.54 W	4.44 W				3.88 S	3.77 W		β	48
D Canola				4.57 S						3.90 M	3.78 W		β	48
E Canola-palm								4.23 S			3.83 S		β'	48
F Canola-palm								4.24 S			3.83 S		β'	48
G Canola-palm							4.33 W	4.21 S	4.06 W		3.84 S		β'	48
H Canola-palm				4.58 W			4.37 M	4.24 S	4.07 W		3.86 S		β' > β	48
I Canola-palm				4.56 W			4.36 M	4.23 S	4.07 W		3.85 S		β' > β	48
J Canola-palm							4.36 W	4.22 S	4.06 W		3.84 S		β'	48
K Canola-palm							4.35 W	4.21 M			3.83 S		β'	48
L Canola-palm							4.36 W	4.22 M			3.84 S		β'	48
M Canola-palm								4.23 S			3.84 S		β'	48
N Canola-palm								4.22 S			3.85 S		β'	48
O Corn								4.29 S			3.82 S		β'	48
P Soybean							4.35 W	4.20 S	4.06 W		3.83 S		β'	48
Q Soybean							4.36 W	4.24 S	4.06 W		3.85 S		β'	48
R Soybean							4.37 W	4.21 S			3.83 S		β'	48
S Soybean							4.33 W	4.20 S			3.83 S		β'	48
T Tallow fractionated				4.54 S		4.39 W		4.19 M			3.82 S		β' + β	48
U Tallow fractionated				4.58 W		4.35 W		4.21 M		3.86 S			β' > β	48

TABLE 10

X-Ray Diffraction Pattern for Commercial Shortenings

Product ingredients	Short spacings (Å)									Polymorphic form	Reference
	5.3	5.2	4.6	4.4	4.3	4.2	4.0	3.8	3.7		
A Canola	5.34 M 5.30 M	5.03 W	4.56 S	4.44 M		4.19 W		3.85 S	3.77 M 3.71 M	β	48
B Soybean-palm			4.50 W		4.32 M	4.18 S		3.78 S		β'	48
C Soybean-palm					4.33 W	4.21 M		3.79 S		β'	48
D Soybean-palm					4.32 W	4.17 M		3.76 M		β'	48
E Soybean-palm					4.36 W	4.21 S		3.80 S		β'	48
F Soybean-palm					4.35 W	4.20 S	4.04 W	3.90 S		β'	48
G Soybean-canola-palm					4.32 W	4.20 M		3.80 M		β'	48
H Vegetable					4.30 M	4.19 S	4.03 M	3.82 S		β'	48
I Vegetable interesterified			4.55 M		4.34 M	4.18 S	4.00 M	3.85 S		β' > β	48
J Tallow + vegetable			4.57 S					3.84 W	3.69 W	β	48
K Animal						4.20 S		3.80 S		β'	48
L Lard			4.58 S 4.56 S	4.46 W				3.88 W	3.76 W	β	48

TABLE 11

X-Ray Diffraction Pattern for Commercial Solid Frying Shortenings

Product ingredients	Short spacings (Å)										Polymorphic form	Reference
	5.3	5.2	4.6	4.4	4.3	4.2	4.0	3.8	3.7	3.6		
A Corn					4.36 W	4.21 S	4.05 W	3.85 S	3.79 W		β'	48
B Canola	5.34 W	5.21 W	4.57 S 4.51 W	4.44 M				3.87 S	3.76 M	3.64 W	β	48
C Soybean (pourable)			4.57 S					3.84 M	3.68 M		β	48
D Vegetable					4.33 W	4.19 S	4.01 M	3.83 S			β'	48
E Vegetable containing coconut					4.33 W	4.20 S		3.81 S			β'	48
F Animal + vegetable						4.21 S		3.82 S			β'	48
G Tallow + vegetable						4.19 S		3.80 S			β'	48
H Tallow						4.24 S		3.80 S			β'	48

X-ray diffraction data for commercial shortenings are listed in Table 10. Shortenings made exclusively from canola (product A) showed β crystals, whereas blends of canola with soy and palm (product G) resulted in β' This is due to the greater diversity of fatty acids in the blends. Product H was made from vegetable fat and exhibited β' crystals as compared to product I, which was made from interesterified vegetable fat and showed the presence of both β' and β crystals. The β crystals may be due to the rearrangement of the fatty acid on the glycerol molecule. Most of the commercial frying fats exhibited β' crystallinity (Table 11) except products B and C, which had β crystals. B contained canola and C a lightly hydrogenated soybean oil with added soybean hard fat.

The information presented in this review demonstrates that our information on the polymorphic behavior of complex fat is far from complete. It is hoped that the compilation of short spacings of these fats will be helpful to scientists working in this area.

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