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SOME EFFECTS OF LIPIDS ON THE STRUCTURE OF FOODS

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Abstract

The functional properties of different lipids in foods are demonstrated and related to the structure of lipid or lipid-water phases. On the basis of new X-ray data on the crystal structure of the β' -form and the $\alpha \rightarrow \beta'$ transition in fats, the polymorphic transitions are considered as different lateral arrangements of triglyceride dimers. The physical properties of fat crystals can be explained from the structures, as well as possibilities to influence the polymorphic transitions.

Molecular interaction between polar lipids and proteins or starch is discussed, and the effect of the amylose-lipid inclusion complex on gelatinization temperature and water penetration of starch is demonstrated.

Aqueous phases of polar lipids can form different structures, and the lamellar liquid-crystalline phase is the most important one with regard to functionality in foods. The role of this phase in emulsification and in foam stabilization is considered. The effect of lipids in the bread-making process can be fully explained on the basis of foam stabilization by lipid monolayers provided by a dispersed lipid-water phase. A cubic phase, which can solubilize large amounts of proteins, is finally described.

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KEY WORDS: lipid phase transitions, lipid-water phases, lipid-water interaction, fat polymorphism, fat crystal structure, starch-lipid interaction, microemulsions, cereal lipids, lipids in baking, bread staling.

Introduction

Even if lipids are present only in minor amounts in foods, they can still have profound effects on the structure and physical properties. This is due to the fact that most foods are colloidal systems, in which polar lipids, due to their surface-active nature, accumulate at interfaces. In this paper some recent results from our laboratory and the related published literature on the functional properties of lipids are summarized.

Results and Discussion

From a physico-chemical point of view it is natural to divide lipids into polar and non-polar ones. Polar lipids, contrary to non-polar, interact with water, giving liquid-crystalline phases, and their use as functional additives in foods is usually related to their aqueous interaction.

The structural results given here are based mainly on X-ray diffraction studies; some surface balance measurements are also included [2].

Fat crystals - Structure and functionality

The rheological properties of plastic fats are, beside the solid/liquid ratio, related to the morphology and size distribution of the crystals. The polymorphic crystal forms are different in this respect, and it is therefore important to be able to control the polymorphic transitions. Information on the molecular packing in the crystals provides a tool to influence the phase behaviour, as will be demonstrated below. A short description of fat crystal structures will first be given.

When a simple fatty acid triglyceride in the liquid state is cooled, an α -form is obtained, which later can be transformed into the metastable β' -form, and finally the stable β -form is formed [5,12].

Some X-ray data on the β' -form have earlier been reported [12]. Using triundecanoin, which can be crystallized in the β' -form from solvents, we have now obtained complete unit cell data. The dimensions of the monoclinic unit cell are $a = 23.6 \pm 0.2$ Å, $b = 5.69 \pm 0.05$ Å and $c = 58.8 \pm 0.5$ Å and $\beta = 90^\circ \pm 0.5^\circ$. The cell contains eight molecules, and the space group is $P2_1/c$. As the hydrocarbon chain packing geometry

(orthorhombic chain packing subcell, 01) and the tilt of the chains within the unit cell are known, it is possible to derive the positions of the chains. It can then be concluded that the space available for the glycerol groups, as well as the relative position of the ester bonds, are the same or nearly the same in the β' -form as in the earlier known β -form. Furthermore we have recorded the X-ray diffraction pattern versus temperature for the transition $\alpha \rightarrow \beta'$ in triundecanoin after different thermal pre-treatment, in order to get the transition as slow as possible. An intermediate form or a kind of transition state could then be seen, in which the hydrocarbon chain packing changes continuously from the hexagonal arrangement with rotational disorder in the α -form to the orthorhombic chain packing, 01. This observation indicates that the glycerol group structure is similar also in the α - and β' -forms. With this background the phase transitions can be rationalized as different lateral arrangements of dimeric units.

In the melt of fats there is, according to low-angle X-ray scattering, a considerable degree of order [13]. The molecules should be expected to be preferably arranged in dimers resulting in space-filling units. By lateral packing of such units a mainly bilayer type of structure is obtained, and the proposed structure is shown in Fig. 1. An estimation from X-ray line-broadening near the melting point results in an average bilayer diameter of about 200 Å. The bilayers must be highly curved to give an over-all isotropic structure with Newtonian flow properties. Although the structure is highly dynamic with rapid exchange of molecules, there is a 'memory' for a considerable time in the melt of the crystal structure from which it was formed. Different crystallization behaviour can thus be observed,

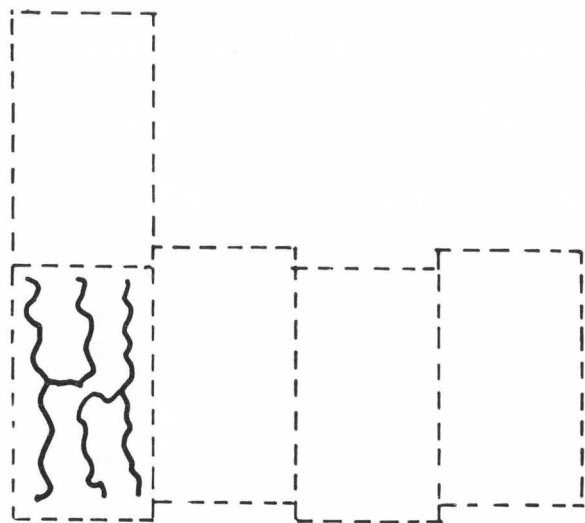


Fig. 1. Illustration of the tendency for molecular dimer formation and lateral arrangement in bilayer units in the liquid state of triglycerides.

depending upon which crystal forms occurred in the fat before it was melted. To get a statistical molecular disorder after melting of a complex fat, it is known from experience that about 0.1 - 1 h at 20 - 40°C above the melting point is needed [11].

The α -crystal form, which is obtained when the melt is cooled, is to some degree disordered. Van den Tempel has discussed similarities between the α -form and a smectic liquid crystal [24]. In a way similar to the formation of liquid crystals without a nucleation step and therefore with no supercooling, the α -form is formed from the melt without supercooling. The hydrocarbon chains, as shown in Fig. 2, are vertically oriented in the layers, i.e. the chains keep the average chain direction in the melt. The molecules in the α -form are not close-packed in an efficient way. Within the bilayer the hydrocarbon chain arrangement, allowing rotational disorder, means a cross-section area per chain of about 19.5 Å², compared to about 18.2 Å² in the β' - and β -forms. Furthermore the appearance of the methyl end group planes of the bilayers complicates the packing of one bilayer in relation to adjacent layers. Ideally all methyl end groups from a chain layer should be located in one plane, as the stacking of the bimolecular layers to form the crystal is complicated if the chains from one bilayer have to penetrate into neighbouring bilayers (cf. Figs. 2 and 4).

In the transition $\alpha \rightarrow \beta'$ (see Fig. 3) a closer chain-packing is adopted, and also the chain penetration between adjacent bilayers is reduced. The tilt of the chains in the bilayers can adopt only certain discrete values, as the chain packing subcell must fit the crystal lattice, and when orthorhombic chain packing is adopted in the β' -form, there is still some degree of chain

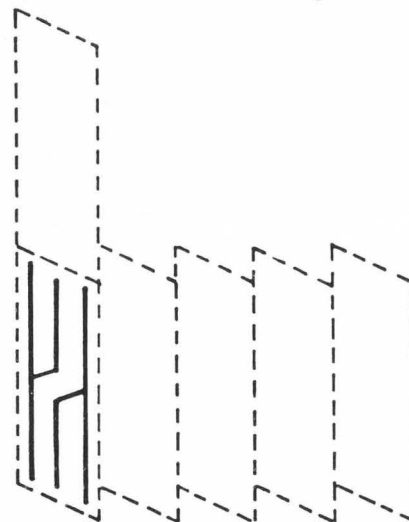


Fig. 2. Proposed structure of the α -form of triglycerides. The lateral arrangement of the structure units results in bimolecular layers. Due to the shape of the end group surfaces of the bilayer there is a considerable penetration of hydrocarbon chains between adjacent bilayers. The molecular arrangement in the structure unit as in Fig. 4.

penetration. The final transition $\beta' \rightarrow \beta$, however, means that the chain penetration of the β' -form is almost eliminated. The adoption of the triclinic close-packing arrangement of the hydrocarbon chains in the β -form allows a chain tilt which is in agreement with the tilt angle of the dimeric structure unit, as shown in Fig. 4.

The crystal morphology can be related to the crystal structures. The α -form forms very thin plates. Due to the chain penetration discussed above the growth perpendicular to the layers is extremely slow. Also the β -form forms plates parallel to the molecular bilayers, but they are much thicker. The β' -form, on the other side, forms long needles. The reason for this is that crystal growth is slow perpendicular to the bilayers, due to the chain penetration discussed

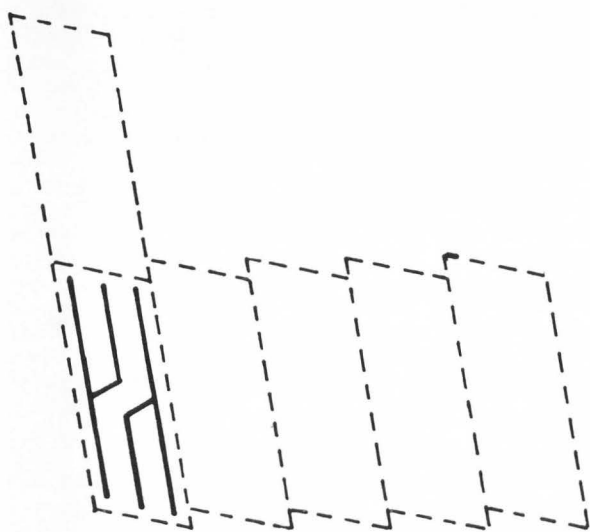


Fig. 3. Main features of the structure of the β' -form of triglycerides, illustrated in analogy with the α - and β -forms. (The true unit cell consists of four of the indicated structure units).

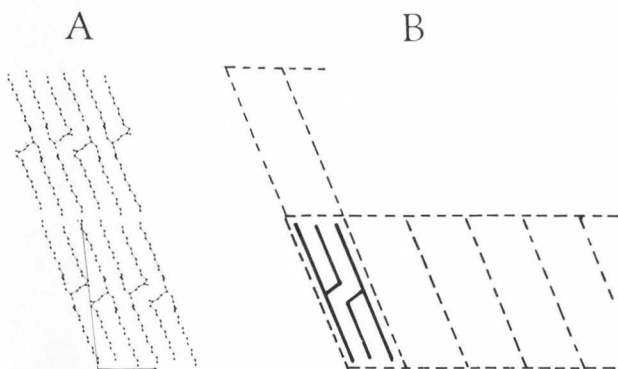


Fig. 4. Structure of the β -form of triglycerides. The true crystal structure is shown to the left and the simplified illustration of lateral arrangement of the bimolecular structure units to the right.

above, but also in one of the directions within the bilayer. The growth along the short unit cell axis ($b = 5.69 \text{ \AA}$) is rapid, whereas the molecules have to adopt a much more complicated arrangement for the repetition in the long axis direction ($a = 23.6 \text{ \AA}$), and therefore the growth is slow.

Knowledge of the crystal structures is useful for understanding relations between the chemical composition of fats and crystallization properties. The following example illustrates how crystal structure information can be used to solve a technical problem.

For nutritional reasons the erucic acid content of rapeseed oil has been reduced during recent years by plant breeding. In Sweden this reduction from about 50% erucic acid to about 1% has resulted in an oil which cannot be used for production of margarine. The solid fat in a margarine should stay in the β' -form, as transition into the β -form results in crystals, which are too large, giving a 'sandy' feeling in the mouth. It is probably the homogeneous fatty acid pattern in the new rapeseed oil which is causing the rapid $\beta' \rightarrow \beta$ phase transition. About 90% of the acyl groups consist of C18 acids. We have in different ways tried to inhibit this phase transition on the basis of crystal structure information. One successful approach has been to use lipid additives, which can co-crystallize with the triglyceride and which furthermore have a stable crystal form with the same chain packing (01) as the triglyceride β' -form [13]. Thus the addition of diglycerides has been shown to delay the $\beta' \rightarrow \beta$ transition, and tests in pilot plant scale have shown that the addition of a few percent of a rapeseed oil diglyceride can give an acceptable rapeseed oil margarine. All triglycerides form diglycerides when they are digested in the intestine, and therefore the use of diglycerides as additives is a solution which hardly can be questioned from a nutritional point of view.

Molecular interaction between polar lipids and other food components

The principles for formation of molecular association structures between lipids and proteins have been extensively discussed by Tanford [23] on the basis of hydrophobic interaction. It is well-known that lipids, which form micellar solutions, are able to unfold and solubilize proteins. Such lipids can also, however, give the opposite effect, and stabilize the native protein structure. Dr. Hegg in our Laboratory has shown how alkyl sulphates and fatty acids can stabilize ovalbumin and bovine serum albumin against thermal denaturation [9,10]. Pasteurization without denaturation of egg white or blood plasma might be practical applications of these phenomena. An alternative way to protect the native protein structure in a cubic lipid matrix will be discussed in the next paragraph.

A very important example of molecular interaction in foods is the complex between mono-acyl lipids and amylose. The formation of this inclusion complex, with the lipid hydrocarbon chain surrounded by the helical V-amylose, has been known for a long time. A proposed model of the

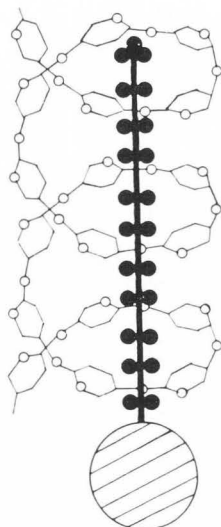


Fig. 5. Structure of helical inclusion complex between the monoglyceride of stearic acid and amylose according to a Raman spectroscopy study [4].

structure, according to Raman spectroscopy studies [4] is shown in Fig. 5. In order to understand the effects of lipids on starch products, a recent study on the mechanism of starch gelatinization provides a good basis. According to this work [19], gelatinization can only take place if amylose molecules can leach out from the starch granules to the water phase. The lipid-amylose complex can be insoluble. From this one should expect that if lipid monomers are supplied to the surface of the granules so that an insoluble surface film is formed, gelatinization should be inhibited. This was also verified experimentally, using a liposomal dispersion of monolaurin [14]. Thus surface coating by lipids offers a possibility to increase the gelatinization temperature, and to reduce the water uptake. Such effects on potato starch by monoglycerides are demonstrated in Fig. 6.

The well-known ability of polar lipids to reduce stickiness of starch foods, such as pasta products, is probably due to reduction of free amylose in the continuous phase by formation of an insoluble lipid-amylose complex. Staling of bread involves water transport, by which water moves from the continuous gluten phase to the starch granules [7]. The anti-staling effect of polar lipids is probably due to formation of an insoluble complex at the surface of the starch granules, and this surface film should be expected to act as a barrier against water transport.

Cereal starch contains about 1% (w/w) of lipids, mainly lysolecithin. Different functions of the lipids in the biosynthesis of starch have been proposed, such as conformation effects which will determine the amylose/amylopectin ratio [1]. From studies of degradation by pancreatic α -amylase we have proposed that the lipid-amylose complex can contribute to dietary fiber [15].

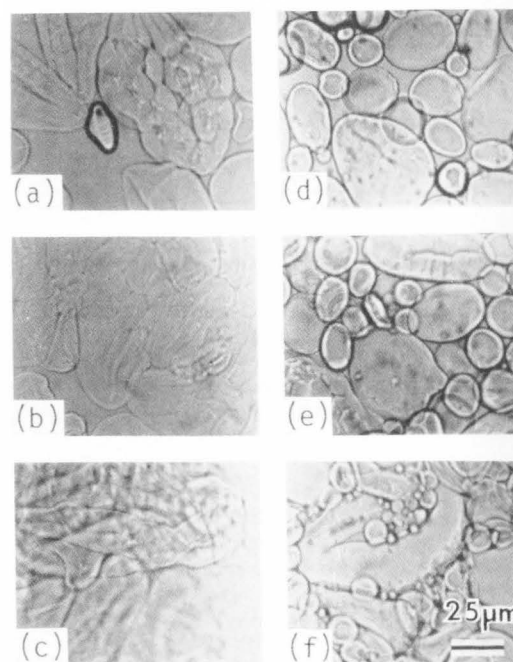


Fig. 6. Effect of a lipid surface coating on the gelatinization of potato starch viewed in the optical microscope. The temperatures are: 60° in (a) and (d), 65° in (b) and (e), and 70°C in (c) and (f) respectively. (d), (e), and (f) show lipid coated granules corresponding to the uncoated granules in (a), (b), and (c) respectively. The lipids used were monoglycerides, 2.8 weight per cent calculated on starch weight [6, 23].

Functional properties of lipid-water phases

Polar lipids in foods, such as monoglycerides and phospholipids, are able to form liquid-crystalline phases with water. The formation of the lamellar liquid-crystalline phase from lipid crystals is shown in Fig. 7. When crystals of, for example, monoglycerides are heated, the thermal movement of the chains in the lattice increases successively. Due to the strong intermolecular bonds in the polar sheets compared to the weak van der Waals interaction between neighbouring hydrocarbon chains, it is possible that the chains can 'melt' although the polar sheets keep the overall structure (lipid bilayers). The same type of structure can also be formed in the presence of water, when water penetrates the polar sheets at the transition, so that a structure of lipid bilayers separated by water layers is formed. This is the most important lipid-water phase from a functional point of view with regard to foods. The phase can form surfaces from either hydrophilic (polar heads) or hydrophobic (methyl end groups) groups. Therefore the phase as a whole is very effective in forming films between oil and water phases. The significance of this liquid crystalline phase in emulsions was first demonstrated by Friberg and co-workers (cf. Ref.

[8]). The emulsion stability due to such films can in fact be further increased by crystallization of the chains of the lamellar liquid-crystalline phase, after such an emulsion has been formed [17]. This increased stability is not surprising as crystalline bilayers in the interface result in mechanical properties similar to a solid 'skin'.

True emulsions of the water-in-oil type are rare in foods. Although butter or margarine often are classified as water-in-oil emulsions, they are not emulsions in strict meaning, as the oil phase is partly crystalline. (The emulsion is destroyed if the crystals are melted). There is, however, a liquid lipid-water phase, termed L2-phase, which can be relevant to food emulsions. The L2-phase can be formed in ternary systems consisting of polar lipids/fats/water, and it consists of water aggregates in a continuous hydrocarbon chain matrix [22]. It might therefore also be described as a water-in-oil microemulsion. Such a ternary system is shown in Fig. 8. In the large three-phase area of this diagram, consisting of the triglyceride oil phase, the L2-phase and water, the interfacial tension between this L2-phase and water is about 1.5 mN/m, and the L2-phase/oil interfacial tension is even lower [22]. It is therefore easy to disperse the L2-phase in an oil. If a small amount of water is stirred into this dispersion, it is possible to see in the microscope how water droplets can be surrounded by the L2-phase, which in turn is dispersed in the oil phase. Such a three-phase emulsion has very low kinetic stability, but might still be relevant in food emulsification processes. In the production of margarine, for example, monoglycerides are frequently used as emulsifiers, and before cooling the phase equilibria can be represented by the ternary diagram of Fig. 8.

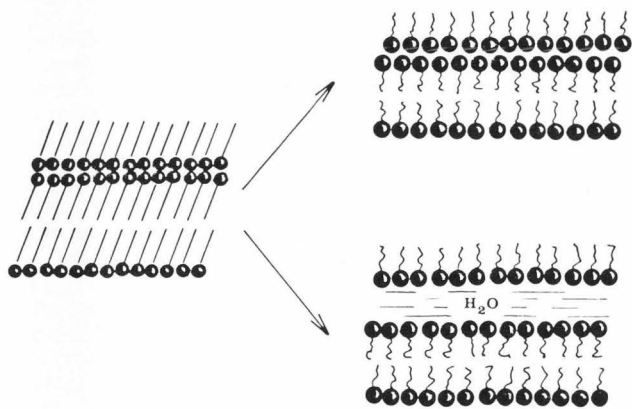


Fig. 7. Formation of lamellar liquid-crystalline phase from the crystalline state of a polar lipid. The formation of this phase by heating only, giving a thermotropic liquid crystal, is shown above and the formation of a lyotropic liquid-crystalline phase in the presence of water is illustrated below.

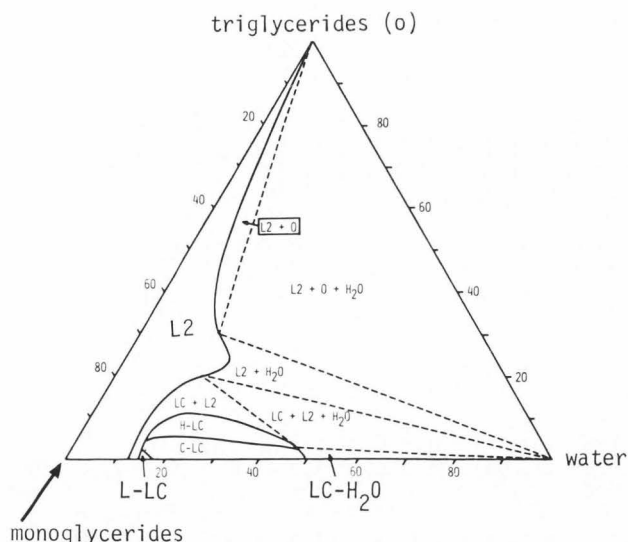


Fig. 8. Phase equilibria in a ternary system of sunflower oil monoglycerides/water/soybean oil at 40°C. L-LC, C-LC and H-LC are liquid-crystalline phases (lamellar, cubic and reverse hexagonal, respectively), and O corresponds to the triglyceride oil phase. The three-phase region L2/O/H₂O is proposed to be relevant in the formation of a water-in-oil emulsion, such as margarine.

Lipid-water phases are also able to stabilize foam structures in foods. The role of polar lipids in breadmaking will be used to illustrate such a mechanism. The unique baking properties of wheat flour can be attributed to the gas-holding capacity and rheological properties of the gluten gel. When wheat flour is worked with water to a dough, which is a dispersion of starch granules and air bubbles in a continuous gluten phase, the following lipid changes can be observed. The polar lipids, mainly digalactodiglycerides, monogalactodiglycerides and phospholipids, form liquid-crystalline phases with water, and the non-polar lipids, mainly triglycerides, are emulsified (using parts of the polar lipids as emulsifiers) [3]. Of approximately 1% (w/w) of lipids (calculated on dry weight of the flour) about half is polar and the other half non-polar. The polar lipids have also a tendency to form a monomolecular film at the air/water interface in the dough, as evident from surface balance measurements [2]. When wheat flour is spread on the water surface of a conventional surface balance, an equilibrium pressure of about 20 mN/m is obtained within a second. This value is characteristic for proteins. After some minutes an equilibrium spreading pressure of about 40 mN/m is successively reached. This value of the film pressure is characteristic for polar lipids, and it is therefore proposed that the change reflects how the protein molecules are squeezed out from the monolayer by lipid molecules.

When gas is produced by the yeast fermentation and amylase degradation of starch, the dough is changed to a foam structure. The polar lipids have a crucial role in the gas-holding capacity of the dough, and it has been possible to correlate the baking properties with wheat lipid-water interaction and phase equilibria. Thus the formation of a lamellar liquid-crystalline phase when cereal lipids interact with water is observed for cereal flour with good baking performance. Moreover it has been possible to obtain the X-ray diffraction pattern characteristic for this lipid-water phase from such a gluten gel [16]. The lamellar liquid-crystalline phase forms small aggregates, so-called liposomes, in an excess of water type of environment. These small particles are ideal to stabilize an expanding gas/water interface. A demonstration of the ability of polar lipid to increase bread volume is given in Fig. 9.

Among other lipid-water phases of interest in foods a cubic phase formed by monoglycerides and water [18] should be mentioned. This phase can be formed in the intestine during fat digestion, and it may have a role in fat absorption [20,21]. We have recently found that large amounts of protein, for example lysozyme, can be solubilized in this phase, and this lipid-protein phase can be an alternative to the lipid-water molecular complexes, earlier discussed, in order to stabilize or protect the native protein structure.

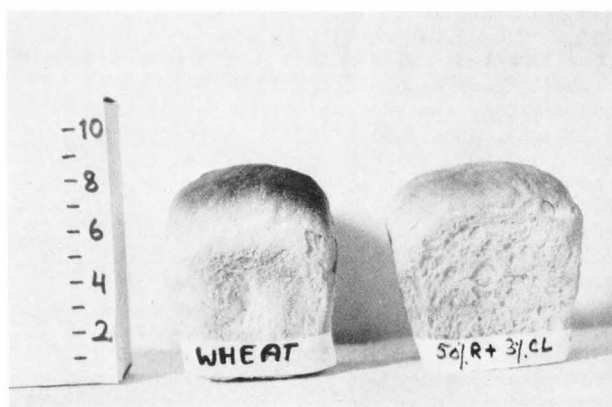


Fig. 9. Bread baked on a mixture of rice flour and wheat flour 1:1 in weight ratio, using 3% (w/w) lecithin (calculated on the bread weight) in the liposomal state. A bread baked only on the wheat flour without the addition of lipids is shown for comparison (baking conditions described in [2]). The numbers on the scale are in cm.

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Discussion with Reviewers

P. Walstra: To me the results on the β' unit cell suggest an orthorhombic rather than monoclinic crystal system.

Author: Although the unit cell dimensions correspond to the orthorhombic system, the true symmetry is monoclinic. This is a cause of 'perfect' crystal twinning, and earlier data on β' have suffered from this twinning effect.

P. Walstra: The rheological properties of a fat strongly depend on the formation of a network of crystals and on the attractive forces between crystals in the network. If there is no crystallization equilibrium, additional crystallization or recrystallization (dissolution of some crystal regions and growth of others) may occur. This may cause sintering of adjoining crystals, greatly increasing the strength of the network. On the other hand, very slow recrystallization may cause the formation of very large crystals (often spherulites), which form at most a weak network. Do you consider polymorphic transitions to be of importance for the mentioned changes in rheological properties?

Author: I do think that polymorphic transitions can influence the mentioned rheological changes, and this might take place in the following way. At a polymorphic transition new crystal surfaces are formed, and there will always be a tendency to reduce the size of the crystal/oil interface. Formation of 'joints' between neighbouring crystals

should thus be favoured.

P. Walstra: Your discussion in the text implies that polymorphic transitions occur in the solid state. It is often assumed that such transitions primarily occur via the liquid state. Anyhow, it has been observed that polymorphic transitions are greatly slowed down if very little liquid fat is present. What is your opinion about these aspects?

Author: My view of the state of order during fat crystal phase transitions is related to the structure and dynamics of liquid crystals. It is thus obvious that the molecular rearrangement requires a mobility similar to that of a liquid. On the other hand the main structural features should be expected to be kept, such as the chain axis directions within the dimeric units.

J.M. deMan: There is no doubt that there is some relationship between crystal morphology and polymorphic form of the crystals. However, I do not think the relationship is as simple as is indicated by some authors. I have seen different types of crystal growth patterns in hydrogenated Canola oil, which do not fit into a simple scheme. I feel that more critical examination of this relationship in different fats is necessary. Do you agree?

Author: I agree, my own discussion concerns simple triglycerides only. The differences in end group planes are in my view the most important factor for morphology

J.M. deMan: It is mentioned that diglycerides can prevent the transition $\beta' \rightarrow \beta$. How is this done in practice? Diglycerides are not commercial products but occur in all technical monoglycerides as contaminants. Would technical monoglycerides have the same effect?

Author: Diglycerides (about 90%) can be obtained as a by-product in the production of distilled monoglycerides and are therefore already today commercially available. An addition of the order of magnitude 1% (w/w) can give the β' -stabilizing effects described in the paper.

D.N. Holcomb: You refer to α -form as that formed directly from the triglyceride melt. Is this always the case? Are the β' and β -forms never formed directly?

Author: As far as I know the α -form must always be formed first. In some cases, such as very pure saturated monoacidtriglycerides (like tristearin) it has a very short time of existence, but it can always be detected in the microscope.

D.N. Holcomb: How "long-range" is the lateral arrangement depicted in Figure 1 for the liquid state of triglycerides? I would think such ordering must be fairly "short-range" since the viscosity of a melted triglyceride does not seem to be extremely high.

Author: An estimate of the size of the ordered units based on X-ray line-broadening indicates that the order of magnitude is 100 Å.

R. Perron: For usual even saturated monoacids triglycerides, it was recently founded by calorimetric measurements, that β' forms would have a less compacity at the end groups level (M. Ollivon and R. Perron, *Thermochimica Acta*, 53 (1982) 183-194), and two β' forms are probably to be considered (J.W. HAGEMANN and W.H. TALLENT, *JAACS*, 49 (1972)118), (M. OLLIVON and R. PERRON, *Chem. Phys. Lipids*, in press). In this last paper, it is also shown that the liquid α is structurally different (at the end groups level) from the super-cooled liquid. This difference is induced during the crystallization of the α form. Independently, β' and β nuclei are formed in these two liquids, and induce β' or β forms.

Author: We have also observed two different β' -forms in odd-membered triglycerides, and they differ by a few degrees in the angle of tilt of the chains. In even ones, however, we have not been able to observe more than one.

Since I do not have access to your paper in press, I am unable to offer detailed comments.

A.C.M. van Hooydonk: The stability of an oil-in-water emulsion depends, among other factors, on the presence of fat crystals in the oil droplets. It was found that the rate of coalescence could, for instance, be six orders of magnitude greater if part of the fat in the droplets is crystallized.

The crystal habit in the droplet was found to be important for the stability. The most unstable systems were characterized by a preferential orientation of the crystals near the oil-water interface. This phenomenon seems to be related to the type and concentration of the emulsifier. It might well be that the formation of a liquid-crystalline phase, as described in this paper, causes orientation of neighbour triglyceride molecules and therefore promote crystallization at the oil-water interface when the emulsion is cooled below the melting point of the fat. In this case the crystalline bilayer of the surfactant results in a more unstable emulsion.

What is your opinion about this?

Author: It seems probable also to me that a lamellar liquid-crystalline phase or gel phase, formed by the emulsifier at the triglyceride /water interface, will induce an increased degree of order of the triglyceride molecules, and in this way promote crystallization.

O. Johari: Can you please detail your materials and methods?

Author: Since the paper concerns discussion and interpretation of already published data, an experimental section was not included. All the details can be found in the papers being referred.