Sintering of Fat Crystal Networks in Oil During Post-Crystallization Processes

Dorota Johansson[1] **and Björn Bergenståhl***
Institute for Surface Chemistry, S-114 86 Stockholm, Sweden

ABSTRACT: Several foods contain semi-solid fats that consist of solid crystals dispersed in a liquid oil. In oil-continuous margarine, butter, and chocolate, fat crystals determine properties such as consistency, stability against oiling-out, and emulsion stability. Trends toward foods with less fat and/or less saturated fat create a need for understanding and controlling the properties of fat crystal dispersions. Fat crystals form a network in oil due to mutual adhesion. One source of strong adhesion is formation of solid bridges (sintering), which has been studied in this work through sedimentation and rheological experiments. Results indicate that sintering may be created by crystallization of a fat phase with a melting point between that of the oil and the crystal. Generally speaking, β′ crystals were sintered by β′ fat bridges, favored by rapid cooling, and β crystals by β fat bridges, favored by slow cooling. The existence of the same polymorphic form of the crystal and bridge indicated that solid bridges, rather than bridges formed by small crystal nuclei, were formed. A maximum in sintering ability for an optimal sintering fat concentration occurred due to competition between bridge formation and other crystallization processes. Some emulsifiers influenced the sintering process. For example, monooolein made it more pronounced, while technical lecithin had the opposite effect.

JAOCS 72, 911–920 (1995).

KEY WORDS: Adhesion, dispersions, fat crystals, food, post-crystallization, rheology, stability, sedimentation, sintering, solid bridge.

Fat crystals in semi-solid food products, such as margarine, butter, or chocolate, are formed during production (1–4). Bulk crystallization processes are sensitive to technological parameters such as temperature, shear forces, and composition of the fat phase (3,5,6). Fat composition may vary with geographic origin of the fat source or with the season. For example, butter is usually hardest during winter when milk fat contains alot of high-melting triglycerides, reflecting the composition of the cow's winter diet (7,8). It is rather complicated to adjust the tempering procedure for products, such as chocolate, to achieve the form, size, and structure of fat crystals that produce a desirable texture and melting sensation (4,9,10).

After production, different crystallization processes proceed in the products mentioned in the previous paragraph. These post-crystallization processes include nucleation of new crystals and crystal growth, Ostwald ripening (dissolution of small crystals and growth of big ones), polymorphic transformation, migration of oil, and migration of small crystals. Post-crystallization is sometimes desired to produce a harder consistency of low-fat products. In most other cases, post-crystallization processes are undesirable. For example, Ostwald ripening may cause loss in consistency because larger crystals give looser networks. Polymorphic changes may lead to a grainy structure in margarine (β crystals) or chocolate (form VI) (9,11–14). Fat bloom in chocolate is usually connected to polymorphic transition of form V to form VI, but it has been shown that the polymorphic transition may occur without fat bloom (9). Fat migration is the most likely reason for fat bloom.

Crystal growth during post-crystallization may sometimes lead to formation of solid bridges (sintering) in narrow gaps of fat crystal networks. Such sintering has been mentioned in the literature (2,15), but it never has been studied extensively. Generally speaking, fat crystal bonds in semi-solid foods are divided into primary bonds (solid bridges), which are very strong and dissociate up on mechanical work, and secondary bonds, which are much weaker and exist even after mechanical softening (16–18). In this work, the formation of bridges is considered as an additional adhesion force in fat dispersions, similar to water bridges in air. Fat crystals flocculate and form a network due to mutual adhesion. Van der Waals forces alone are too weak to produce the network strength observed experimentally by rheology studies (19,20). Other forces also exist due to the presence of emulsifiers (steric, Coulombic) (19,21,22). Water bridges likely exist (19,23), and solid bridges also have been mentioned in the literature (2,15,16).

Fat crystal adhesion is important because it determines the structures formed and, consequently, the texture and consistency of the resulting products. Thus, knowledge of adhesion sources provides a tool to adapt these parameters. The structures of fat crystal networks are not well described. Some older theories simplify the network as an arrangement of

---

[1] Present address: Pharmacia AB, S-112 87, Stockholm, Sweden.

*To whom correspondence should be addressed at Institute for Surface Chemistry, Box 5607, S-114 86 Stockholm, Sweden.

straight chains of flocculated fat crystals in three perpendicular directions through the sample (16). Further development of this simple network theory into a so-called transient network model (24) introduced conglomerates of fat particles that are interconnected by straight crystal chains. During the last few years, some attempts have been made to apply fractal models to fat crystal structures in oils (25). Microstructural information also has been provided by SEM (scanning electron microscopy) and CSLM (confocal scanning laser microscopy) as, for example, the existence of milk fat globules in butter, the existence of crystalline shells around water droplets in margarine, or the existence of solid bridges between fat crystal aggregates, which may be either sheet-like or bulky (15,26–32).

The aim of this project (33) was to control formation of solid bridges between fat crystals during post-crystallization processes. Because a crystallization process is involved, the polymorphism of fat components is important to consider, as well as crystallization phenomena such as nucleation and crystal growth. In addition to those areas of study, we modelled structures of solid bridges formed.

EXPERIMENTAL PROCEDURES

High-melting fat crystals. Two different types of crystals were studied—a pure tristearin from Fluka (Buchs, Switzerland) and a totally hydrogenated palm oil (palm stearin) from Karlshamns AB (Karlshamn, Sweden). The tristearin purity was ≥99%, density 1.0577 g/mL, mole mass 892 g/mol, and iodine value very low (totally saturated fat) (34). Tristearin is stable in the β polymorphic form, which has a melting point of 72°C (35). The α form (in rapidly cooled fat) has a melting point of 53°C (35).

Palm stearin has a mole mass of 756 g/mol and an iodine value of 2.6. It is stable in the β′ polymorphic form, which has a melting point of 57–59°C. The β′ form is stable and also occurs in palm stearin that is crystallized from organic solvents, such as acetone. The α-form in the rapidly cooled palm stearin has a melting point of 46°C. The fatty acid composition of palm stearin is: 53% C16:0, 42% C18:0, 2% C18:1, 3% others. The triglyceride composition is presented in Table 1, and some properties of these triglycerides are presented in Table 2. The compositional data were obtained from the supplier.

Intermediate-melting sintering fats. Fats with a melting range between that of the oil and the high-melting fat crystals were used to form solid bridges in existing networks during post-crystallization processes. Two fats were studied—totally hydrogenated palm kernel oil (palm kernel fat) and partially hydrogenated low-erucic acid rapeseed oil (Lobra 34). Both fats were delivered and characterized [differential scanning calorimetry (DSC), X-ray, and high-performance liquid chro-

TABLE 1
Triglyceride Composition (%) of Examined Fats[a]

	Composition of			
Triglyceride[b]	Soybean oil	Palm stearin	Palm kernel	Lobra 34
8-12-12			3.0	
10-12-12/8-12-14			6.0	
12-12-12/10-12-14			27.0	
12-12-14			25.0	
12-14-14/12-12-16	15.0			
14-14-14			9.0	
12-16-18/14-16-16/14-14-18		3.0	3.0	
14-16-18			3.0	
16-16-16		23.0		
16-16-18		37.0	1.0	
16-18-18		26.0	1.0	
18-18-18		11.0	1.0	0.5
16-O-O	3.0			1.7
16-O-18	0.5			3.7
18-O-18				2.3
18-O-O	0.5			
16-O-16	0.7			7.4
16-Le-16	2.6			0.6
16-O-Le	7.7			
16-Le-Le	13.0			
16-Le-Ln	1.3			
O-O-O	2.6			7.5
O-O-Le	11.6			
O-Le-Le	31.2			
Le-Le-Le	23.7			
Le-Le-Ln	1.5			
Total	99.9%	100%	94%	21.4%

[a] Data and triglycerides from Karlshamns AB (Karlshamn, Sweden).
[b] Total amount of analytically determined triglycerides in samples (unlisted are not known).

TABLE 2
Some Physical Data for the β′ Form of Triglycerides Occurring in Examined Fats[a]

	T_m	ΔH_m	X_M • 100		
Triglyceride	(°C)	(kJ/mol)	10°C	22°C	35°C
8-12-12	~26	~70	20.3	68	100
10-12-12/8-12-14	31.0	~80	9.5	38	100
12-12-12/10-12-14	34.5	81.2	6.4	26.0	100
12-12-14	39.0	116.5	1.0	7.5	56
12-14-14/12-12-16	~43	~110	0.8	5.1	34
14-14-14	45.5	100.5	0.9	4.8	27
12-16-18/14-16-16/14-14-18	52.0	~120	0.1	1.1	8.6
14-16-18	55.0	~125	0.07	0.6	5.1
16-16-16	55.5	131.5	0.04	0.4	4.1
16-16-18	59.0	~135	0.02	0.2	2.2
16-18-18	61.0	~140	0.01	0.1	1.4
18-18-18	62.7	142.8	0.007	0.09	1
16-O-O	2.5	91.5	100	100	100
16-O-18	~30	~90	8.0	38	100
18-O-O	8.6	109.6	100	100	100
16-O-16	~32	~90	6.3	30	100
16-Le-16	~25	~90	14.6	69	100
16-O-Le					
16-Le-Le					
16-Le-Ln					
O-O-O	−5.0	~80	100	100	100
O-O-Le					
O-Le-Le					
Le-Le-Le	−21.0	~70	100	100	100
Le-Le-Ln					

[a] T_m, melting point; ΔH_m, heat of fusion (melting enthalpy, J/mol); M, mole mass (g/mol); and X_M, solubility in oil (mole fraction) at 10, 22, and 35°C. X_M was calculated as: $X_M = \exp\,[-(\Delta H_m/R) \bullet (1/T - 1/T_m)]$ [Atkins, P.W., *Physical Chemistry*, Oxford University Press, Oxford, 1982], where R, [the gas constant 8.3143 (J/mol • K)]; and T, the actual temperature (K). Numbers (6, 8, etc.) refer to the length of saturated fatty acids in triglycerides, and letters refer to unsaturated fatty acids (O = 18:1, Le = 18:2 and Ln = 18:3). Abbreviations as in Table 1. From Hagemann, J.W., in *Crystallization and Polymorphism of Fats and Fatty Acids*, edited by N. Garti and K. Sato, Marcel Dekker, Inc., New York, 1988, p. 9; and Gunstone, F.D., J.L. Harwood and F.B. Padley (ed.), *The Lipid Handbook*, Chapman and Hall, London and New York, 1986. "~" stands for the estimated values. M was calculated from the atomic mole masses (H = 1.0079, C = 12.011, O = 15.999).

matography (HPLC)] by Karlshamns AB. Their triglyceride compositions are presented in Table 1, and melting temperatures, heats of fusion and solubilities of the β′ forms of these triglycerides are presented in Table 2.

Palm kernel fat is stable in the β′ form; it crystallizes in the α form but is unstable and converts to the β′ form in less than 20 min at 0°C (the conversion is faster at higher temperatures). The β′ form is stable for weeks (stability experiments have not been performed for longer periods). Palm kernel fat has a mole mass of ~680 g/mol.

Lobra 34 is stable in the β form. It usually crystallizes in the α form and converts to the β form *via* the β′ form. This transformation can take some hours (up to days) depending on the temperature. The mole mass of Lobra 34 is ~880 g/mol.

Melting of palm kernel and Lobra 34 fats was characterized by the differential thermal analysis technique (results are schematically presented in Fig. 1). Palm kernel fat has a narrow melting range with a peak at about 30°C. All fat is melted at 36°C. Lobra 34 has a broad melting range and no distinct peak value. Most is crystallized at 10°C, and there is some solid fat left at 50°C.

Oil. A refined soybean oil from Karlshamns AB was used in all experiments. The interfacial tension between this oil and distilled water was slightly above 30 mN/m. This high value indicates that the oil was pure with respect to surface-active components. The oil has an iodine value of 130 and a melting point of −20°C. The fatty acid composition is: 10.6% C16:0 (palmitic acid), 3.6% C18:0 (stearic acid), 18.2% C18:1 (oleic acid), 56.7% C18:2 (linoleic acid), 9.5% C18:3 (linolenic acid), 0.3% C20:0 (arachidic acid), 0.4% C22:0 (behenic acid), and 0.7% others. The triglyceride composition is presented in Table 1. The oil was not further purified. The density of the oil was 0.92 g/mL at room temperature and 0.91 g/mL at 35°C.

Emulsifiers. The effect of the following nonionic emulsifiers on the sintering processes was studied: pure monoolein, sorbitan tristearate (Famodan TS), and sorbitan monostearate (Famodan MS) from Grindsted A/S (Brabrand, Denmark); the ethoxylated emulsifiers polyoxyethylene [20 = number of EO groups in molecule] sorbitan monostearate (Tween 60, ethoxylated sorbitan monostearate) from ICI Surfactants (Everberg, Belgium), penta-ethyleneglycol mono-*n*-dode-

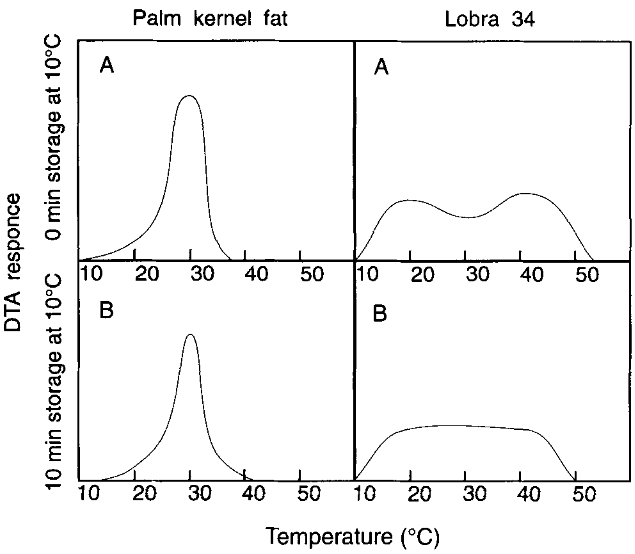

FIG. 1. A schematic picture of DTA (differential thermal analysis) response for Lobra 34 (Karlshamns AB, Karlshamn, Sweden) and palm kernel fats in the temperature interval of 10 to 50°C. The samples where stored at room temperature prior to measurement, and performed immediately (0 min storage, A) and after 10 min storage (B) in the apparatus at 10°C. The gradient rate was 5°C/min.

cylether (Nikkol BL5SY, ethoxylated alkyl ether) from Nikkol Chemicals (Tokyo, Japan), polyoxyethylene [12 = number of EO groups in molecule] castor oil [Bredol 691, ethoxylated (12 = number of EO groups in molecule) castor oil] and polyoxyethylene [20 = number of EO groups in molecule] castor oil [Bredol 697, ethoxylated (20 = number of EO groups in molecule) castor oil] from Akzo Nobel (Stenungsund, Sweden). We also have examined a technical soybean lecithin (Metarin P; Lucas Meyer, Hamburg, Germany). The first four nonionic emulsifiers and the lecithin were of food grade, ethoxylated castor oils were for feed applications, and ethoxylated alkyl ether was aimed for research purposes. The emulsifiers were characterized in previous reports (19–21,23). Emulsifiers were added to the oil phase in all systems studied.

Other chemicals. Acetone for recrystallization of solid fat (palm stearin) was of analytical grade and supplied by Merck (Darmstadt, Germany).

Sedimentation experiments. Simple sedimentation experiments, often cited in the literature (21,36), provide a powerful method for qualitative comparison of particle adhesion in dispersions. As adhesion between particles increases, they stick to each other and form large flocks and bulky sediments. Increased repulsion has the opposite effect, the particles do not stick to each other, they pass each other more easily when settling, and they form dense compact sediments. For studies of weak adhesion, sedimentation experiments are more suitable than rheology because the force involved in the sedimentation process (gravity) is much weaker than shear forces in conventional rheometers.

In each sedimentation sample, fat crystals were weighed together with the oil, or oil solution of sintering fat and/or emulsifier. In each series of experiments, the type and concentration of sintering fat were varied with other parameters kept constant. A post-crystallization process was created by lowering the sample temperature from 20 to 10°C in a water bath, controlled by a computer program (crystallization rate was controlled by varying the time gradients 20→10°C from 5 min to 60 h). The samples then were allowed to settle at 10°C for a period of weeks until the sediment volumes were constant with time. Calibrated (with steps of 0.1 mL) test tubes with tight locks were used. The accuracy of sediment volume determination was about ±0.05 mL, which was less than 1% of the total sample volume (~6 mL). The reproducibility within the same sample series was ±5%, although reproducibility between different sample series was poorer. Therefore, to compare trends between different sample series, relative sediment volume units were used ($V/V_{\text{reference}}$, where V is sediment volume of a sample in the series and $V_{\text{reference}}$ is the sediment volume of a sample without additive in the same series). For relative volumes close to unity, there are no changes in adhesion between fat crystals in the network during the post-crystallization process. If relative volumes are significantly larger than 1, there is an increase in crystal adhesion that can be interpreted as sintering.

Rheology. A Bohlin CS rheometer from Bohlin Rheology (Lund, Sweden) was used in rheological studies. Samples were located in a gap between a plate and cone, or between two plates. In our studies, Bingham yield stress, the stress necessary to achieve uniform flow through the whole sample, was determined. This corresponds to breaking of all (weak and strong) bonds in the sample. Thus, Bingham yield stress is expected to be most sensitive for formation of solid bridges (sintering) because these bridges are expected to be strong.

Other techniques. HPLC, DSC, and X-ray diffraction at Karlshamns AB were used to determine the composition of fatty acids and triglycerides of fats and oils and to determine the melting ranges of palm stearin and palm kernel fats, as well as the stability of their polymorphic forms. Melting properties of the sintering fats were estimated by DTA (Mettler Instruments AG, Grefensee, Zurich, Switzerland). BET adsorption analysis with nitrogen gas was performed at Chalmers University (Gothenburg, Sweden) to determine the specific surface area of dry palm stearin and tristearin crystals.

Sample preparation. Palm stearin and tristearin fats were recrystallized in acetone prior to use to get well-defined crystals. The crystals were characterized with respect to melting points, polymorphic forms morphology, and specific area by the methods mentioned previously. Four batches of palm stearin were crystallized, and their specific areas were as follows: (i) 7.44; (ii) 9.7; (iii) 10.5; and (iv) 9.6 m^2/g. One batch of tristearin was recrystallized (specific area 3.6 m^2/g). To prepare samples, the oil was first warmed to 40°C together with sintering fats and/or emulsifiers to obtain a uniform solution. The oil solution was then cooled to room temperature (no precipitation of additives was observed). A desired amount of high-melting crystals (3% tristearin or 5% palm stearin for sedimentation experiments, and 10% palm stearin for rheological experiments) were mixed into the oil. After dispersing on a Vibro-Mixer (Winn B.V., Leeh, The Netherlands), air and traces of water were removed in a vacuum dryer.

RESULTS AND DISCUSSION

Sintering of β′ networks by β′ stable palm kernel fat. Sedimentation of palm stearin β′ in soybean oil, containing small amounts (≤1%) of palm kernel fat, has been studied. The sedimentation temperature was 10°C, and the time for gradient 20→10°C was 24 h (slow cooling rate). Palm kernel fat caused an extensive increase in the network strength of palm stearin, observed as a 20–30% increase in the sediment volume at an addition level of 0.25–0.5% (sediment volume of 5% palm stearin rose from 3.7 to 4.8 mL).

Sintering of β′ networks by β stable Lobra 34 fat. Sedimentation of palm stearin β′ in soybean oil, containing small amounts (≤1%) of Lobra 34 fat, was studied. The sedimentation temperature was 10°C, and the time for gradient 20→10°C was 24 h (slow rate of cooling). No significant increase in the sediment volume of 5% palm stearin (3.7 mL) resulted upon addition of 0.25 and 0.5% Lobra 34.

The influence of cooling rate Relative sediment volumes of palm stearin β′ in soybean oil, containing 0.5% of palm kernel fat and Lobra 34, are presented in Figure 2 as a function of cooling rate, expressed as the time for gradient 20→10°C. Palm kernel caused an increase in sediment volume of palm stearin. This increase was more than 40% of the initial volume for a gradient time of 8 min (quick cooling) and was 10–20% for gradient times longer than 1 h (slow cooling). Lobra 34 caused less pronounced changes in sediment volume of palm stearin β′: 15% for a gradient time of 8 min, and no significant increase for a gradient time longer than 1 h.

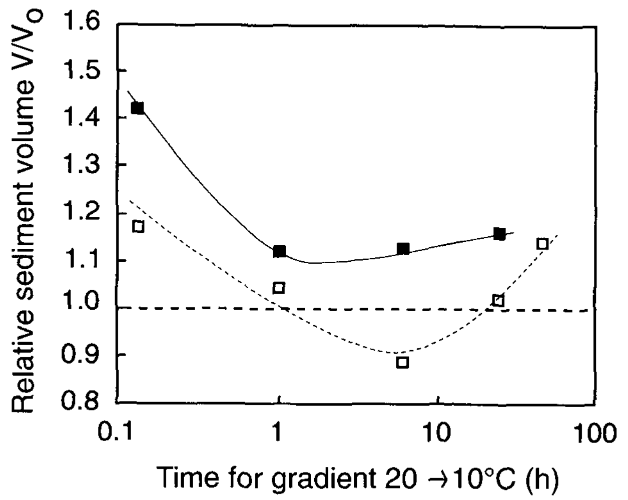

FIG. 2. Relative sediment volume ($V/V_{\text{reference}}$) of 5% palm stearin β′ crystals in soybean oil with 0.5% palm kernel fat (■) and Lobra 34 (□), presented as a function of cooling rate (expressed as time for gradient 20 → 10°C). The water bath temperature was lowered from 20 to 10°C during controlled gradient times as specified. See Figure 1 for company source.

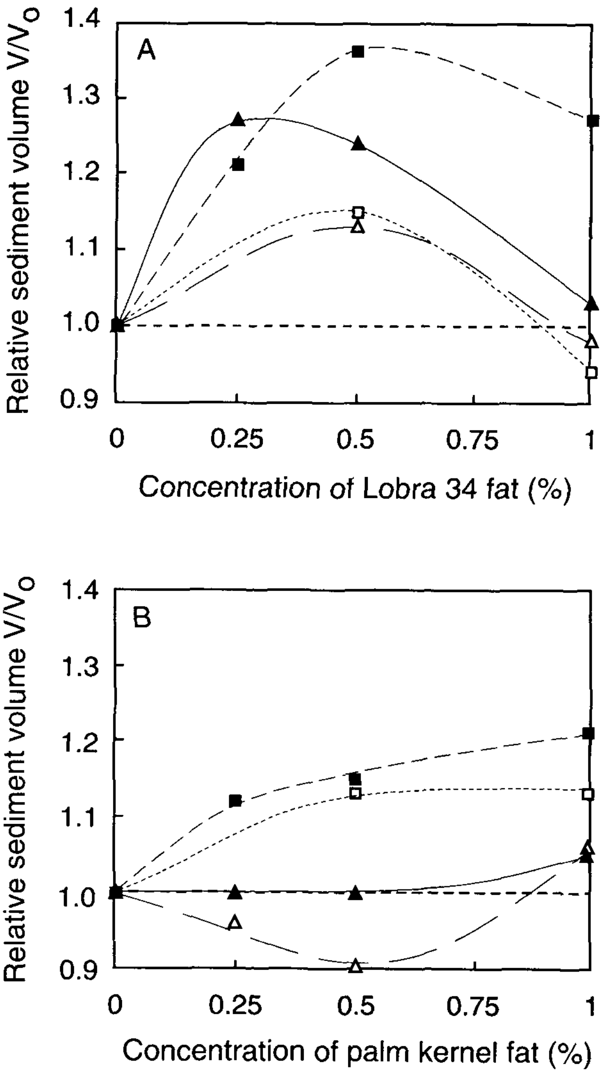

FIG. 3. Relative sediment volume ($V/V_{\text{reference}}$) of palm stearin β′ crystals is presented as a function of additive concentration in the oil. The additives were palm kernel fat (A) and Lobra 34 (B). Sample temperature was lowered at different cooling rates, expressed as time for gradient 20 → 10°C: 8 min (■), 1 h (□), 6 h (△), and 24 h (▲). See Figure 1 for company source.

The influence of sintering fat concentration. Relative sediment volume of palm stearin β′ crystals is presented in Figure 3A as a function of palm kernel fat concentration in soybean oil, and in Figure 3B as a function of Lobra 34 concentration in the oil. The curves represent various cooling rates, expressed as time for gradient 20→10°C. Palm kernel fat caused an increase in sediment volume of palm stearin β′ crystals. The increase was most pronounced (25–35%) for gradient times of 8 min and 1 h (relatively rapid cooling) and showed a maximum at palm kernel concentrations of 0.25–0.5%. For 1% concentration, the increase nearly disappeared. In the presence of Lobra 34, sediment volume increased by 10–20% for gradient times of 8 min and 1 h, and no volume maximum was observed. No significant increase was observed for the slow cooling rate (times for gradient 20→10°C above 1 h).

Rheology. The results from the sedimentation experiments were confirmed by rheological measurements. Bingham yield stress was determined for 10% palm stearin β′ in soybean oil without additives and with addition of palm kernel and Lobra 34 fats at concentrations 0.5 and 1%. The results are presented in Table 3 in Pa units and as change relative to a reference sample. The time for gradient 20→10°C was 8 min (rapid cooling). Samples were stored at 10°C for 24 h prior to measurement.

Palm kernel fat (0.5%) in oil caused a 40% increase in Bingham yield stress of a palm stearin β′ dispersion. No increase appeared for 1% palm kernel fat. Thus, the increase and the maximum in network strength with palm kernel fat, observed by sedimentation, was confirmed by rheology. The addition of 0.5 and 1% of Lobra 34 fat caused an increase in yield stress of a palm stearin β′ dispersion by 50 and 70%, respectively, which is also in qualitative agreement with the sedimentation experiments. The magnitude of changes is larger in rheological experiments than in sedimentation.

Sintering of β networks by β′ stable palm kernel fat and β stable Lobra 34. Relative sediment volume of 3% tristearin β crystals in soybean oil without additives (a reference sample) and with 1% palm kernel fat and Lobra 34 is presented in Figure 4. Two slow gradients of 20→10°C were examined: 24 and 52 h. Palm kernel fat caused no increase in sediment volume of tristearin β crystals when the 24-h gradient was examined, and an increase of 10–15% with a gradient of 52 h. Lobra 34 caused an increase of 10–15% for the shorter gradient time, and 20% for the longer gradient time.

The triglyceride composition of fats and their solubility. Solubility of fats in soybean oil has been calculated as a function of temperature (37):

$$X_M = e^{-\frac{\Delta H_M}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_m}\right)} \qquad [1]$$

where X_M is the dissolved mole fraction , ΔH_M the enthalpy of fusion in [J/mol], R the gas constant (8.3143 J/mol • K), T_m the melting point of the pure fat (K), and T the temperature (K). Equation 1 is valid for ideal solutions. Tristearin solubility calculated from Equation 1 is ~0.002% at room temperature (~22°C) and less than 10^{-4}% at 10°C. Solubility of complex fats has been calculated from their triglyceride composition (Table 1), and solubility of each triglyceride at 10, 22, and 35°C (Table 2) has been calculated according to Equation 1. We assumed that different triglyceride components crystallize independently without forming mixed crystals. The results were transformed to solid-fat content and plotted in Figure 5 as a dotted line for palm stearin and as a continuous line for palm kernel fat.

TABLE 3
Bingham Yield Stress (Pa) for 10% Palm Stearin β′ Crystals in Soybean Oil Without any Additives (reference sample), with Addition of Sintering Fats, and a Combination of Monoolein and Sintering Fat[a]

	Added amount of sintering fat (w/w%)			
Additive	0% (reference)	0.5%	0.5% + 1% Monoolein	1%
Storage time at 10°C: 24 h				
Palm kernel	118	165	335	99
	(1.00)	(1.40)	(2.84)	(0.84)
Lobra 34[b]	118	185		202
	(1.00)	(1.57)		(1.71)
Storage time at 10°C min				
Palm kernel	35			
Lobra 34	(0.3)			

[a] Sintering was performed by a rapid lowering of the temperature from 20 to 10°C (8 min). Most of samples were stored 24 h at 10°C prior to measurements, and one reference sample was stored for only 10 min. The numbers in brackets show change in Bingham yield stress relative to the reference sample.

[b] From Karlshamns AB (Karlshamn, Sweden).

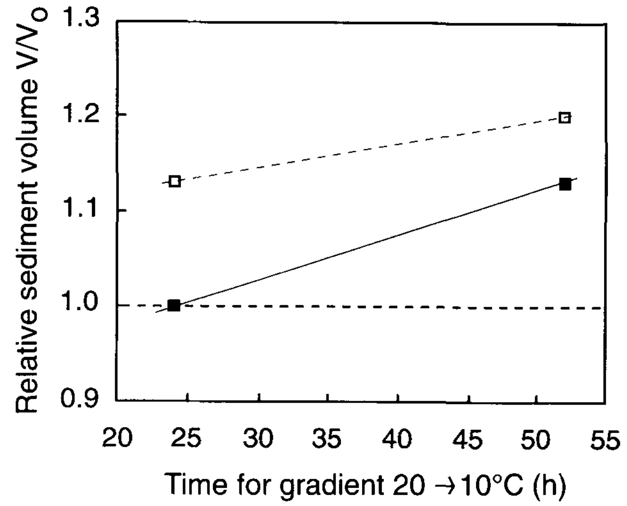

FIG. 4. Relative sediment volume ($V/V_{\text{reference}}$) of 3% tristearin crystals in soybean oil without additives (reference), and with 1% palm kernel fat (■) and Lobra 34 (□), as a function of cooling rate expressed as time for gradient 20 → 10°C. See Figure 1 for company source.

The solubility at 10°C was also determined experimentally by pulse nuclear magnetic resonance (NMR) for solid-fat content. The results (Fig. 5) indicate that Lobra 34 has about twice the solubility in soybean oil as palm kernel fat, 3–4% compared to 1–2%. There is no significant effect of tristearin or palm stearin in samples on the crystallization of Lobra 34 or palm kernel fat because the response in Figure 5A (only one type of fat crystal in the oil) is similar to the response in Figure 5B (samples contain the sintering fat and the high-melting fat, the response of high-melting fat is withdrawn). Comparison of experimental and theoretical results shows a good agreement for palm stearin. For palm kernel fat, the theoretical solid-fat content is lower than the experimental, probably due to the fact that only 94% of the fat composition is known and/or due to formation of mixed crystals.

During visual precipitation experiments, the solutions with increasing concentrations of Lobra 34 and palm kernel fat (0.25–4%) were prepared at 40°C and put into the water bath at 10°C. After one-day equilibration, the precipitation degree was recorded as determined visually. Results showed that no

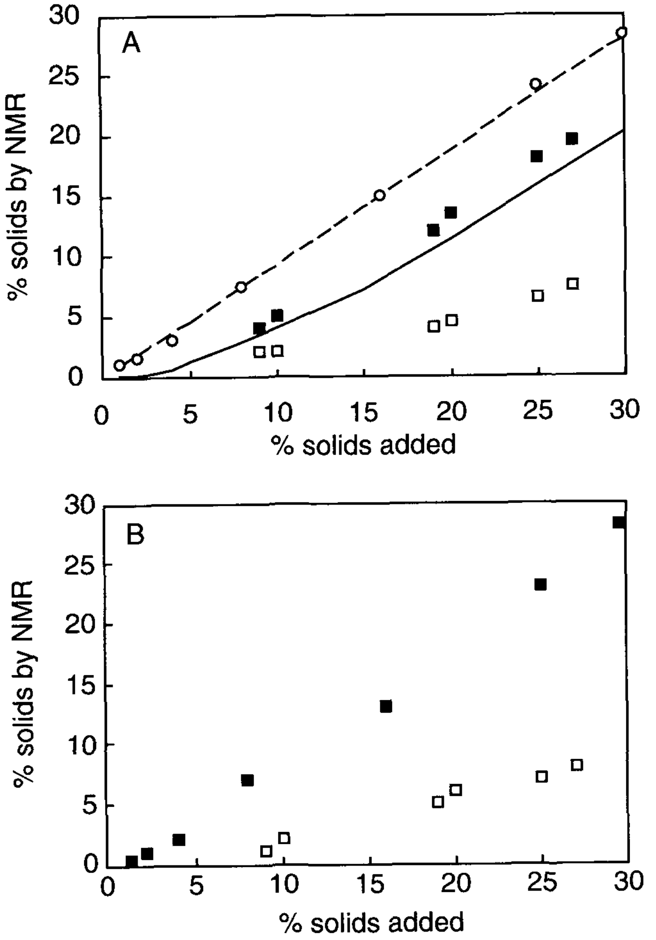

FIG. 5. Solid-fat content in samples of different composition at 10°C, calculated from data in Tables 1 and 2 (assuming that different triglyceride components crystallize independently) for palm stearin (dotted line) and for palm kernel fat (continuous line). Solid-fat content also has been determined by pulse nuclear magnetic resonance (NMR) (Bruker Minispec P20i apparatus; measurements performed at van den Bergh Foods, Lindingö, Sweden). The NMR results for samples that contain only one fat in oil are presented in A, and the results for samples containing a combination of an intermediate fat (Lobra 34 or palm kernel) and a high-melting fat (palm stearin or tristearin) are presented in B. In the latter case, the response for high-melting fats was omitted. ○, Palm stearin and tristearin; ■, palm kernel fat; and □, Lobra 34 fat. See Figure 1 for other company source.

precipitation could be observed up to 1% fats. Concentrations at 2% or more gave clear precipitation. Thus, the solubility of palm kernel and Lobra 34 fat is about <2%, which is in agreement with the theoretically estimated values.

According to Tables 1 and 2, roughly 1% triglycerides from palm stearin should crystallize in all sedimentation samples (5% palm stearin), including the reference, during temperature gradient 20→10°C. The corresponding amount is ~2% for rheological samples with 10% palm stearin. No crystallization of oil components should be observed unless the addition of high and medium fractions may cause a co-crystallization of monounsaturated–disaturated oil components with similar fat components. Rheological measurements presented in Table 3 showed that prolonged storage (~24 h) of 10% palm stearin in soybean oil at 10°C produced stronger crystal networks than short storage time (~10 min), most likely due to a slow recrystallization and sintering of triglycerides in palm stearin, as mentioned, previously.

Palm kernel and Lobra 34 fats at concentrations below 1% should be almost totally dissolved in oil at 10 and 20°C. However, co-crystallization of triglycerides from sintering fats, soybean oil, and palm stearin may occur and cause a lowering of fat solubility compared to values from Tables 1 and 2 and Figure 5. This co-crystallization is most likely necessary for the additional sintering to occur, as observed in sedimentation and rheology (Figs. 2–4, Table 3).

Crystal growth, nucleation, and sintering. During crystallization of triglyceride components from soybean oil, palm stearin, and palm kernel or Lobra 34, the following three processes may occur (Fig. 6): nucleation of new crystals, crystal growth, and formation of bridges between crystals (sintering). Bridges formed also may be different: true solid bridges or bridges of small flocculated crystal nuclei. All these processes may occur simultaneously.

Any additional nucleation or precipitation of new crystals is not expected in our samples because no such effect was observed in the two-component system of soybean oil + sinter-

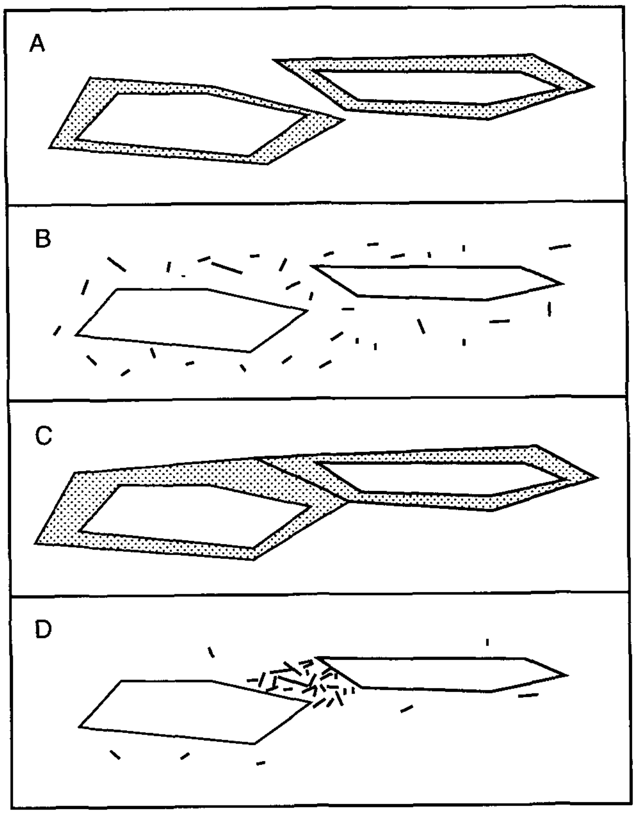

FIG. 6. A schematic representation of different phenomena taking place during post-crystallization: (A) nucleation of new crystals, (B) crystal growth, (C) solid bridge formation; and (D) formation of bridge by flocculation of small nuclei between two fat crystals.

ing fat. Crystallizing triglycerides may precipitate on existing palm stearin β′ crystals, leading to crystal growth. Crystal growth is not expected to lead to any significant changes in the crystal network due to the small amount of material precipitated. Thus, the reason for the observed increase in network strength must be the formation of additional bridges between crystals (sintering). Because network strength depends greatly on the strongest bonds in the structure, formation of few such bonds may produce extensive effects.

Closer consideration of Figures 2 and 3 indicates that β′ crystals of palm stearin were easily sintered by β′ bridges of palm kernel fat. That was facilitated by rapid cooling (short gradient time) by promoting the crystallization of the less stable β′ form of fat. β′ Crystals could not be sintered by β stable Lobra 34 unless an undercooled β′ bridge of this fat was formed during rapid post-crystallization. This conclusion created an expectation that β crystals should be sintered by β bridges, facilitated by slow cooling (promotes fat crystallization in the β form). This expectation was verified by the results presented in Figure 4—β crystals of tristearin were easily sintered by β bridges of Lobra 34, facilitated by slow cooling. Further, β crystals of tristearin could be sintered by β′ stable palm kernel fat only for extremely slow cooling, when a β bridge likely may be formed by palm kernel fat. The necessity of the same polymorphic form of the high-melting crystal and the bridge, summarized in Table 4, indicates formation of true solid bridges rather than bridges of small flocculated nuclei (Fig. 6).

In conclusion, it can be speculated that rapid cooling and large temperature gradients may limit sintering because they promote formation of the undercooled α form, which cannot bridge β′ or β crystals.

Crystallization kinetics for sintering fats. Crystallization kinetics of palm kernel fat and Lobra 34 was qualitatively characterized by microscopic observation. A small amount of dry crystals of palm stearin was spread on a microscope slide, and a droplet of an oil solution of Lobra 34 or palm kernel fat was spread over the crystals. Microscopic observations indicated that palm kernel fat crystallized directly in the form of small crystals, located preferentially close to the palm stearin crystals, whereas Lobra 34 crystallized slowly by forming larger crystals, with no preferential location in the existing network.

TABLE 4
Conditions for Controlled Sintering

	β′ Stable sintering fat	β Stable sintering fat
β′ Network	Sintering facilitated by rapid cooling	Sintering only if undercooled β′ bridge is formed (extremely rapid cooling)
β Network	Sintering only if a β bridge is formed (extremely slow cooling)	Sintering facilitated by slow cooling

A maximum in sintering power, observed in Figure 3A, indicates a competition between sintering and other processes. This competition is won by sintering at low concentration (≤0.5%) of palm kernel fat. At higher concentrations of palm kernel fat (>0.5%), the competition is won by nucleation. Thus, the concentration of sintering fat with rapid crystallization kinetics is an important parameter in controlling the balance between sintering and fat crystal nucleation. No maximum was observed with Lobra 34 (Fig. 3B), which has a slow nucleation rate compared to palm kernel fat.

The effect of emulsifiers. The effect of eight emulsifiers was studied. However, only the addition of technical lecithin and monoolein produced systematic changes in sediment volume and Bingham yield stress. Thus, sediment volume of 5% palm stearin β′ crystals in soybean oil without any additives (a references sample), with 0.5% palm kernel fat, with 0.5% lecithin Metarin P (one gradient), and with 0.5% palm kernel fat and 0.5% lecithin are presented in Figure 7. Times for the temperature gradient 20 → 10°C were 1 and 24 h. Addition of palm kernel fat alone increased sediment volumes of palm stearin by more than 10%. Addition of lecithin alone lowered the sediment volume by ~25%. This effect of lecithin also has been previously observed at room temperature (21). Addition of palm kernel fat and lecithin produced opposite effects—a decrease in sediment volumes by 20–25% in relation to the reference sample and by ~40–50% in relation to the sample containing palm kernel fat. Thus, lecithin appears to obstruct sintering.

The sediment volumes of 5% palm stearin β′ in soybean oil without additives (reference sample), with 0.5% palm kernel fat, with 1% monoolein (one gradient), and with 0.5% palm kernel fat and 1% monoolein are presented in Figure 8.

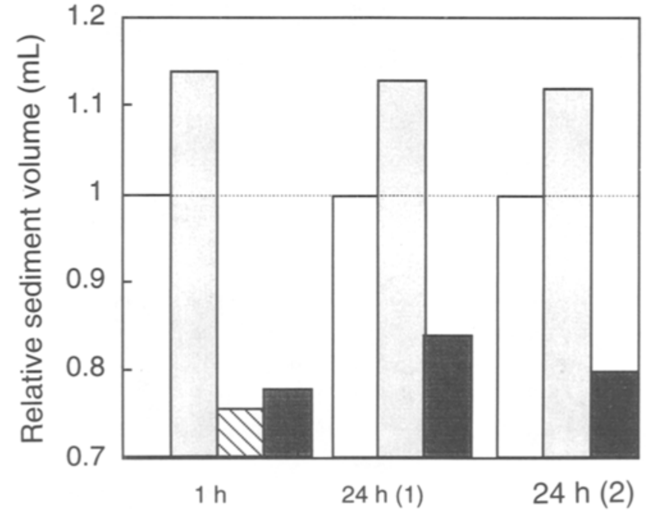

FIG. 7. Relative sediment volume of 5% palm stearin β′ crystals in soybean oil without additives: reference (☐), with 0.5% palm kernel fat (lightly shaded bar), with 0.5% lecithin Metarin P (Lucas Meyer, Hamburg, Germany) (gradient time 1 h, stripped bar) and with 0.5% palm kernel fat + 0.5% lecithin Metarin P (■). The water bath temperature was lowered from 20 to 10°C during 1 and 24 h.

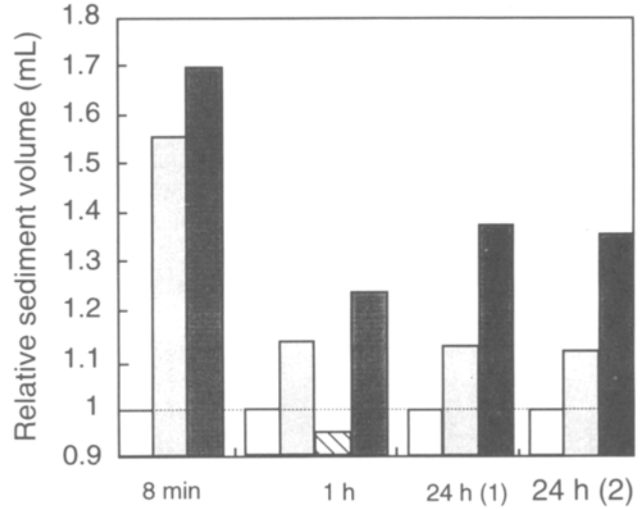

FIG. 8. Relative sediment volume of 5% palm stearin β′ crystals in soybean oil without any additive: reference (◇), with 0.5% palm kernel fat (lightly shaded bar), with 1% monoolein (gradient time 1 h, stripped bar) and with 0.5% palm kernel fat + 1% monoolein (■). The water bath temperature was lowered from 20 to 10°C during 1 min, 1 and 24 h.

Times for the temperature gradient 20 → 10°C were 8 min, 1 h, and 24 h. Addition of palm kernel fat increased sediment volumes by 55% for a gradient time of 8 min, and by 10–15% for longer gradients. Addition of monoolein alone lowered the sediment volume of fat crystals by ~5%. A similar effect for monoolein previously has been observed at room temperature (21). Addition of a combination of palm kernel fat and monoolein produced further increases in sediment volume to 60% (gradient 8 min) and 30–40% (longer gradients). Thus, monoolein seems to enhance the sintering process by palm kernel fat. The synergistic effect is even more pronounced in rheological measurements (Table 3). Bingham yield stress of 10% palm stearin β′ in oil increased by 40% on addition of 0.5% palm kernel fat (short time for gradient 20 → 10°C), and the increase rose to almost 300% on simultaneous addition of 0.5% palm kernel fat and 1% monoolein.

Emulsifiers adsorb to fat crystals in oils (20,21) and may enhance or prevent adsorption of sintering triglycerides. For example, lecithin adsorbs strongly to the crystals and forms double layers. These layers appear to prevent the adsorption of sintering triglycerides and to diminish the sintering process (Fig. 7). Lecithin layers usually repel solid-fat crystals in oils (19), counteracting sintering.

Monoolein adsorbs weakly and forms a loosely-packed layer on fat crystals in oil (21) causing a small decrease in crystal adhesion (19). The adsorbed layer is compatible with sintering triglycerides and may enhance their adsorption to fat crystals. Bridging consequently may be enhanced, and monoolein may participate in bridge formation. The effect of monoolein is greater for slow cooling rates, when the degree of sintering tends to be smaller otherwise (Fig. 8).

ACKNOWLEDGMENTS

We thank Karlshamns AB for providing us with materials. Special thanks are addressed to Jari Alander from Karlshamns AB, who contributed with great knowledge and expertise of fats and their crystallization, and for analyses at Karlshamns AB. We also are grateful to Eva Lundgren for splendid laboratory work. This work would not be possible without financial support from Nutek (The Swedish National Board for Industrial and Technical Development), and from the following Nordic companies and organizations: Akzo Berol Nobel AB, Karlshamns AB, Köttforsknings-institutet (Swedish Meat Research Institute), Raisio Oy, SMR (Swedish Dairies Association), and Van den Bergh Foods.

REFERENCES

1. Mulder, H., and P. Walstra, *The Milk Fat Globule. Emulsion Science as Applied to Milk Products and Comparable Foods*, Commonwealth Agricultural Bureaux, England, and Centre for Agricultural Publishing and Documentation, The Netherlands, 1974.
2. Walstra, P., in *Food Structure and Behaviour*, edited by J.M.V. Blanchard, and P. Lillford, Academic Press, London, 1987, p. 67.
3. Garti, N., and K. Sato (eds.) *Crystallization and Polymorphism of Fats and Fatty Acids*, Marcel Dekker, Inc., New York, 1988, p. 305.
4. Minifie, B.W., *Chocolate, Cocoa and Confectionery; Science and Technology*, AVI Publishing Company, Inc., Westport, 1992.
5. Wesdorp, L.H., H.J. Human and S. Bruinn, *Adv. Food Eng. 32*:409 (1992).
6. Buchheim, W., and A.M. Abou El-Nour, *Fat Sci. Technol. 94*:369 (1992).
7. Precht, D., in *Crystallization and Polymorphism of Fats and Fatty Acids*, edited by N. Garti, and K. Sato, Marcel Dekker, Inc., New York, 1988, p. 305.
8. Deffense, E., *J. Am. Oil Chem. Soc. 70*:1193 (1993).
9. Schlichter-Aronhime, J., and N. Garti, in *Crystallization and Polymorphism of Fats and Fatty Acids*, edited by N. Garti and K. Sato, Marcel Dekker, Inc., New York, 1988, p. 363.
10. Jeffery, M.S., in *The European Food and Drink Review*, Food Ingredients Europe ′93, Paris, France, 1993, p. 65.
11. Guth, O.J., J. Aronhime and N. Garti, *J. Am. Oil Chem. Soc. 66*:1606 (1989).
12. deMan, L., J.M. deMan and B. Blackman, *Ibid. 66*:1777 (1989).
13. Watanabe, A., I. Tashima, N. Matsuzuki, J. Kurashige and K. Sato, *Ibid.* 69:1077 (1992).
14. Koyano, T., I. Hachiya and K. Sato, *Food Structure 9*:231 (1990).
15. Heertje, I., *Ibid. 12*:77 (1993).
16. M. van den, Tempel, *J. Colloid Sci. 16*:284 (1961).
17. Shama, F., and P. Sherman, *J. Texture Stud. 1*:196 (1970).
18. deMan, J.M., and A.M. Beers, *Ibid. 18*:303 (1987).
19. Johansson, D., and B. Bergenståhl, *J. Am. Oil Chem. Soc. 69*:718 (1992).
20. Johansson, D., The Influence of Food Emulsifiers on Fat and Sugar Dispersions in Oils, Technology Licentiate Thesis, Institute for Surface Chemistry and Department of Physical Chemistry, Royal Institute of Technology, Stockholm, Sweden, 1993.
21. Johansson, D., and B. Bergenståhl, *J. Am. Oil Chem. Soc. 69*:705 (1992).
22. Arts, T.J.C., J. Laven., F. van Voorst Vader and Th. Kwaaitaal, *Colloids Surf. A: Physicochem. Eng. Aspects 85*:149 (1994).
23. Johansson, D., and B. Bergenståhl, *J. Am. Oil Chem. Soc. 69*:728 (1992).
24. Kamphius, H., and R.J.J. Jongschaap, *Colloid Pol. Sci. 263*:1008 (1985).
25. Vreeker, R., L.L. Hoekstra, D.C. den Boer and W.G.M. Agterof, *Colloids Surf. 65*:185 (1992).
26. Hicklin, J.D., G.G. Jewell and J.F. Heathcock, *Food Microstructure 4*: 241 (1985).

27. Heertje, I., M. Leunis, W.J.M. van Zeyl and E. Berends, *Ibid. 6*:1 (1987).
28. Heertje, I., P. van der Vlist, J.C.G. Blonk, H.A.C.M. Hendrickx and G.J. Brakenhoff, *Ibid. 6*:115 (1987).
29. Juriaanse, A.C., and I. Heertje, *Ibid. 7*:181 (1988).
30. Heertje, I., J. van Eendenburg, J.M. Cornelissen and A.C. Juriaanse, *Ibid. 7*:189 (1988).
31. Heertje, I., J. Nederlof, H.A.C.M. Hendrickx and E.H. Lucassen–Reynders, *Food Structure 9*:305 (1990).
32. Brooker, B.E., *Ibid. 12*:115 (1993).
33. Johansson, D., Colloids in Fats. The fat crystal as a functional particle, Ph.D. Thesis, Lund University, Lund, 1994.
34. Weast, R.C. (ed.), *Handbook of Chemistry and Physics*, 56th edn., CRS Press, 1975–1976.
35. Hernqvist, L., Polymorphism of Fats, Ph.D. Thesis, Lund University, Lund, 1984.
36. Tiller, F.M., and Z. Khatib, *J. Colloid Interface Sci. 100*:55 (1984).
37. Atkins, P.W., *Physical Chemistry*, Oxford University Press, Oxford, 1982.

[Received September 14, 1994; accepted March 5, 1995]