Effects of Sucrose Ester on the Kinetics of Polymorphic Transition in Hydrogenated Sunflower Oil

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ABSTRACT: The effect of a commercial emulsifier, sucrose ester, on the crystallization kinetics of hydrogenated sunflowerseed oil was studied by means of an optical method. Induction times were measured for hydrogenated oil with the addition of 0.01, 0.05, and 0.1 wt% sucrose ester. This emulsifier delayed nucleation, thus affecting the formation of critical nuclei and prolonging induction times. Kinetics of the β′→β polymorphic transition was followed by X-ray diffractometry. Addition of the emulsifier delayed the appearance of the signal at 4.6 Å. Moreover, longer times were needed to complete the transition. The kinetic model chosen to describe the transition process was based on the theory of Avrami. Avrami's exponent **n** was approximately 1 in all cases. The **n** value was in agreement with the fact that only one β′ pattern was found. The β form could not be obtained directly from the melt, and it is unlikely that the β′→β transition occurred through a melt-mediated mechanism. Transition was hindered by the rigidity of the sucrose ester structure.
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KEY WORDS: Crystallization, induction time, polymorphism, sucrose ester, sunflowerseed oil, X-ray diffractometry.

Polymorphism of natural fats has been extensively investigated. Properties of cocoa butter have been the subject of extensive research (1–6). The unique sensory characteristics of cocoa butter, which are mainly due to its sharp melting point, make it the preferred fat in confectionery products. Among animal fats, the polymorphic behavior of beef tallow and lard has been widely studied because of their use in shortening (7,8). Among the vegetable oils, palm oil is becoming increasingly important because of its use in cooking oil, margarine, shortening, and confectionery fats. Its polymorphic behavior also has been widely studied (9–11).

Polymorphism describes phase changes and structural modifications of the solid-fat phase. This phenomenon significantly affects the physical and functional properties of end-products. The polymorphic form required for a fat depends on the product. For both all-purpose and emulsified shortenings, it is essential that the solids of the fat crystallize in the β′ form, whereas β crystals are desirable in salad dressings because their physical dimensions prevent the crystals from settling (12).

The kinetics of the β′ to β transition is important from a technical point of view. A major problem in many fat-based food products is the polymorphic transition of fat crystals during storage. Margarine and chocolate are well-known examples in which transitions to the most stable crystal form lead to unacceptable product qualities. Undesirable physical properties of the stable polymorph, which arise at the expense of the unstable form, should be avoided (i.e., excessively high melting points, excessively large crystals, unpleasant texture).

It is clear that retarding polymorphic transformation in solid fats can help, at least for some time, to delay loss in quality. Emulsifiers, such as lecithin and monoglycerides, are used as both viscosity controllers and as antibloom agents (13). Some vegetable fats, such as partially hydrogenated sunflowerseed oil and low-erucic rapeseed oil, have a strong tendency to form β-crystals and cause sandiness in margarine. Several food emulsifiers, such as saturated and unsaturated fatty acid monoglycerides, act as modifiers of crystal structure, thus helping to prevent this unwanted phenomenon. The addition of 0.3% sorbitan tristearate inhibits the β′ to β transition in margarine (14).

Sucrose esters can be used in food as emulsifiers because they are nontoxic, tasteless, odorless, and are digested to sucrose and fatty acids in the stomach. Sucrose esters can also be used in pharmaceuticals, cosmetics, foods, and in other products where a nonionic, nontoxic, biodegradable emulsifier is required (15). The aim of the present work was to determine the effects of sucrose ester on the nucleation and kinetics of the β′ to β polymorphic transition in the crystallization of hydrogenated sunflowerseed oil.

MATERIALS AND METHODS

Sunflowerseed oil. Hydrogenated sunflowerseed oil was supplied by Molinos Río de La Plata S.A. (Buenos Aires, Argentina) and is used in margarines in Argentina. Its composition was determined by high-pressure liquid chromatography

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(HPLC) and gas chromatography (GC), and its iodine value was calculated (Table 1).

Isothermal crystallization. The crystallization process was monitored by using an optical set-up as described previously (16). A helium–neon laser was used as the light source. A photodiode detected the occurrence of optically anisotropic fat crystals. The photosensor output was recorded along with the cell temperature. A typical chart-recorder output of the CdS photodiode, as well as the thermocouple's record for the crystallization of hydrogenated sunflowerseed oil, were used (16). The induction time is the interval between the moment crystallization temperature is reached and the start of crystallization (first deviation from the laser baseline signal). Cooling rates were calculated from the slopes of the cell temperature record. Two different cooling rates were used, 2 and 7°C/min. The sample was crystallized by reducing the temperature to 30 and 33°C. When the laser signal reached a peak, crystals were filtered through a 53 GA Pyrex filter (pore diameter 5 μm); Aldrich Chemical Company, Milwaukee, WI) under vacuum. The solid sample was then analyzed for polymorphic form by X-ray diffractometry (XRD) and differential scanning calorimetry (DSC) and for chemical composition by capillary GC and HPLC.

Emulsifier. A sucrose ester (P-170) was supplied by Mitsubishi-Kasei Food Corporation (Tokyo, Japan). The sucrose ester had a Mettler dropping point of 58°C and was added at concentrations of 0.01, 0.05, and 0.1 wt%.

(XRD). Polymorphic transformation β′ to β was followed by XRD. Short spacings were measured by means of an X-ray diffractometer (Rigaku, Tokyo, Japan) (Cu Kα λ = 0.1542 nm) at room temperature. The polymorphic transformation was induced by tempering the sample at 25°C, which was placed on the glass plate used for XRD. Patterns were obtained immediately after filtering and each day thereafter until the 4.6 Å signal appeared, then every three days until transition was complete.

DSC. A programmed Du Pont 910 calorimeter (Du Pont, Wilmington, DE), fitted to a cooling apparatus and a thermal analyzer (model 99; Du Pont), was used. Samples (ranging from 15 to 20 mg) were placed in hermetically-sealed aluminum pans and subjected to the temperature program of 10 min at −40°C and further heated at 5°C/min to 80°C. The equipment was calibrated with indium as the standard. Diagrams of heat flow (dQ/dt) were plotted as a function of time. Although the sensitivity used varied from 1.038 to 0.414 mJoule/s, based on the quantity and quality of the samples, diagrams could be compared because they were printed on the same scale, and values of dQ/dt were divided by mass. Fusion enthalpies were calculated as reported earlier (17). Samples were run in duplicate, and values given are the means of two thermograms.

(GC). Fatty acids were analyzed with a Hewlett-Packard 5890 A chromatograph (Hewlett-Packard, Palo Alto, CA) with an SP 2330 column (60-m length and 0.25-mm i.d.). Methyl esters were prepared by transesterification with a mixture of methanol/benzene (3:1) and 3% wt/vol sulfuric acid.

(HPLC). Triacylglycerols (TAG) were analyzed by HPLC (16). The HPLC columns (Alltech Associates, Inc., Deerfield, IL) consisted of two 150 mm × 4.6 mm i.d. in series. They were packed with 3-μm C18 bonded-phase particles. The columns were maintained at 40°C by a column oven. Analyses were carried out by mixing acetonitrile and tetrahydrofuran (70:30, vol/vol) at 0.6 mL/min, the usual flow rate. A laser light-scattering detector was used to identify the separated TAG.

RESULTS AND DISCUSSION

Composition of the crystals. No difference in fatty acid composition was found when either cooling rate to 30 or 33°C was used (Table 1). However, fatty acid compositions of both fractions varied from the original sample and exhibited higher contents of 18:0. Comparison of both fractions showed that the 18:1 content was higher for 33°C, whereas the 18:2 content was higher for 30°C. Contents of 18:1 and 18:2 were the only differences in fatty acid compositions of the fractions.

The TAG found in percentages higher than 2% were SSO, SOO, POO, OOO, and LOO (S denotes stearic; O, oleic and elaidic; P, palmitic; L, linoleic). Glyceride compositions obtained were: 2.9% SSO, 38.7% SOO, 26.4% POO, 15.8% OOO, and 9.4% LOO for the original sample; 5.9% SSO, 36.5% SOO, 28.0% POO, 17.0% OOO, and 9.9% LOO for the slow cooling rate to 30°C; and 5.5% SSO, 36.9% SOO, 28.1% POO, 17.1% OOO, and 10.1% LOO for the fast cooling rate. By cooling to 33°C, the crystal compositions were 7.5% SSO, 33.6% SOO, 29.3% POO, 17.0% OOO, and 7.9% LOO for the slow cooling rate and 7.7% SSO, 33.6% SOO, 29.1% POO, 17.0% OOO, and 7.8% LOO for the fast cooling rate. Crystal fractions had slightly higher contents of SSO,

TABLE 1
Fatty Acid Composition (%) and Other Properties of Hydrogenated Sunflowerseed Oil Crystals

Sample	Fatty acid (%)					*Trans* acid content (%)	Calculated iodine value
	16:0	18:0	18:1	18:2	Others		
Original	7.2	10.9	72.1	7.5	2.3	32.5	72.4
Cooled slowly to 30°C	8.5	15.6	60.4	12.4	3.1	35.5	70.2
Cooled quickly to 30°C	8.3	15.4	60.1	12.8	3.4	35.2	70.4
Cooled slowly to 33°C	8.2	15.3	67.7	6.7	2.1	34.4	67.5
Cooled quickly to 33°C	8.1	15.1	68.0	6.9	1.9	34.9	68.3

POO, and OOO than the original sample. Comparison of the fractions showed that the fraction crystallized to 33°C had about 2% more SSO, 3% less SOO, and 2% less LOO than the fraction crystallized to 30°C.

With regard to the use of hydrogenated oil in margarine, POO is present in high percentages. Therefore, we selected a P-sucrose ester that could be expected to affect the transition kinetics, namely a compound that should cocrystallize with the fat and is structurally dissimilar so that it would not allow polymorphic transition. The activities of such inhibitors are also related to the composition of the fat (18).

Thermal behavior of the crystals. Figure 1 shows DSC thermograms of both the original sample and the crystals obtained by slow and fast crystallization to 30 and 33°C. The DSC thermogram of the original sample showed two endotherms at 0 and 23.7°C. At the fast cooling rate to 30 and 33°C, two endotherms were also observed, but their peak temperatures were −5.0 and 36.2°C, and −7.5 and 37.5°C, respectively. The DSC profiles for the fractions crystallized at the fast cooling rate were similar and differed little from the original sample. At the slow cooling rate, fractionation occurred for both crystallization temperatures (Fig. 1). Melting enthalpies were higher in comparison with that of the original sample (54.4 Joule/g). At 33°C, they were 66.8 and 65.9 Joule/g for the slow and fast rate, respectively, while at 30°C, these enthalpies were 62.5 and 63.1 Joule/g, respectively. Differences in composition and thermal behavior of the fractions were small although significant.

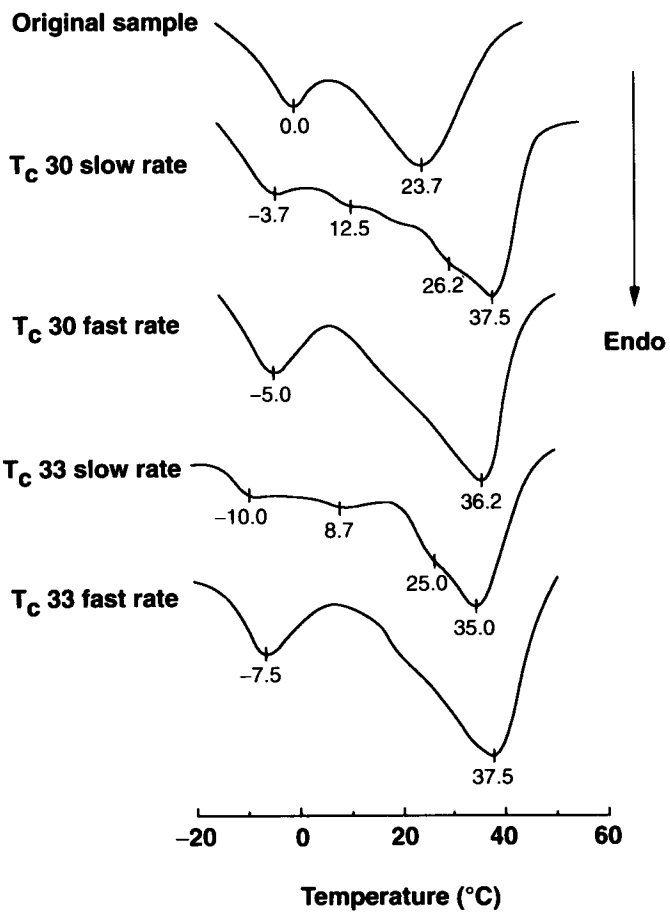

FIG. 1. Calorimetric diagrams of the original sample and crystals obtained when hydrogenated sunflowerseed oil was crystallized to 30°C at slow (T_c30S) and fast (T_c30F) rates and to 33°C at slow (T_c33S) and fast (T_c33F) rates; T_c, crystallization temperature.

Effect of sucrose ester on induction time of crystallization. Induction times of crystallization are reported in Table 2. Hydrogenated sunflowerseed oil was crystallized by cooling to T_c = 30 and 33°C at two cooling rates. At T_c = 30°C, there was only a small difference in induction time at slow and fast rates. Instead, at T_c = 33°C, the effect of cooling rate on induction time was more noticeable. Induction times were shorter at slow crystallization rates.

With the addition of 0.01% sucrose ester, induction times were longer than those of the control at both T_c values and cooling rates. For T_c = 30°C and slow cooling rate, there was a small delay of crystallization. The induction time was 21.1% longer than with no sucrose ester addition. At the fast cooling rate, the effect was larger, 77.2% longer than that of the control. At T_c = 33°C, induction times were 55.5 and 185.6% longer than with no sucrose ester addition for the slow and fast rates, respectively. When 0.01 wt% sucrose ester was added, the induction time for crystallization was influenced more than with other sucrose ester levels at the cooling rate to 30°C.

The addition of 0.05% sucrose ester delayed crystallization longer than with 0.01% sucrose ester. At 30°C, induction times were 336 and 302% longer than those of the control for the slow and fast rates, respectively; and at 33°C, they were 99 and 430% longer. At T_c = 33°C, the induction times were strongly dependent on the cooling rate.

At the 0.1% concentration, induction times were the longest. However, they were not dependent on cooling rate as they were for the 0.01 and 0.5% levels. By adding sucrose

TABLE 2
Induction Times for Crystallization of Hydrogenated Sunflowerseed Oil

Amount of sucrose esters (%)	T_c (°C)	Cooling rate (°C/min)	Induction time (min)[a]
0	30	2	10.4 ± 0.1
		7	13.6 ± 0.3
	33	2	36.6 ± 0.4
		7	50.7 ± 0.8
0.01	30	2	12.6 ± 0.4
		7	24.1 ± 0.4
	33	2	56.9 ± 1.1
		7	144.8 ± 1.7
0.05	30	2	45.3 ± 1.2
		7	54.6 ± 1.2
	33	2	72.8 ± 1.3
		7	268.4 ± 2.6
0.1	30	2	105.8 ± 2.1
		7	115.5 ± 2.0
	33	2	456.7 ± 5.3
		7	453.5 ± 4.2

[a]Mean ± one standard deviation; T_c, crystallization temperature.

ester, induction times were lengthened. Nucleation was delayed, as well.

β′→β Transition. Tables 3 and 4 show the effect of the emulsifier on the β′ to β transition when the sample was crystallized under different cooling rates to 30°C. At all concentrations, the emulsifier delayed the transition 24 h. One-half of the transition was delayed for the 0.05 and 0.1% sucrose ester levels. Addition of sucrose ester led to longer times to complete transition. Addition of 0.05% sucrose ester was needed to delay apparition of the 4.6 Å signal. The same concentration was necessary to delay one-half of the transition. However, the transition was also delayed when 0.01% sucrose ester was added.

At the fast cooling rate, induction times were longer, and polymorphic transformation was slower. These results imply that the inhibitory effect of the solid surfactant on the β′ to β transition is not absolute, but rather varies with cooling rate. It has been reported that the temperature regime controls the mobility of the fat molecules, the number of local crystal imperfections, and the degree of liquefaction. Because these factors are kinetic, they may also affect the rate of polymorphic transition (19).

Table 5 shows the effect of the emulsifier on the β′ to β transition when the sample was crystallized slowly to 33°C. The addition of 0.01% sucrose ester was sufficient to delay the apparition of the 4.6 Å signal. Times for one-half and complete transitions were longer at all sucrose ester concentrations.

By crystallizing slowly to 33°C, a 4.6 Å signal appeared before the signal obtained for the same cooling rate to 30°C, both for the control and for 0.01% sucrose ester. One-half of the transition was faster in all samples cooled to 33°C, but was complete only at longer times for both the control and for the sample with 0.01% sucrose ester. The addition of up to 0.5% sucrose ester similarly affected the transition at both crystallization temperatures.

Table 6 shows the effect on the transition for the fast crystallization rate by cooling to 33°C. At all concentrations, the 4.6 Å signal apparition, one-half of the transition, and the end of the transition were delayed by added sucrose ester.

TABLE 3
Effect of Sucrose Ester of β′→β Polymorphic Transition on Hydrogenated Sunflowerseed Oil, Crystallized Slowly at 30°C (storage temperature 25°C)

Storage time (d)	Sucrose ester content (%) 0	0.01	0.05	0.1
0	β′	β′	β′	β′
1	β′	β′	β′	β′
2	β′<<β	β′	β′	β′
3		β′<<β	β′<<β	β′<<β
18	β′ = β	β′ = β		
31			β′ = β	β′ = β
60	β			
76		β		
98			β	β

TABLE 4
Effect of Sucrose Ester on β′→β Polymorphic Transition of Hydrogenated Sunflowerseed Oil, Crystallized Quickly at 30°C (storage temperature 25°C)

Storage time (d)	Sucrose ester content (%) 0	0.01	0.05	0.1
0	β′	β′	β′	β′
1	β′	β′	β′	β′
2	β′	β′	β′	β′
3	β′<<β	β′<<β	β′	β′
4			β′<<β	β′<<β
18	β′ = β	β′ = β		
35			β′ = β	β′ = β
76	β			
88		β		
106			β	
120				β

TABLE 5
Effect of Sucrose Ester on β′→β Polymorphic Transition of Hydrogenated Sunflowerseed Oil, Crystallized Slowly at 33°C (storage temperature 25°C)

Storage time (d)	Sucrose ester content (%) 0	0.01	0.05	0.1
0	β′	β′	β′	β′
1	β′<<β	β′	β′	β′
2		β′<<β	β′	β′
3			β′<<β	β′<<β
8	β′ = β		β′<<β	β′<<β
10		β′ = β		
15			β′ = β	
23				β′ = β
70	β			
88		β		
100			β	β

TABLE 6
Effect of the Emulsifier on the β′→β Polymorphic Transition of Hydrogenated Sunflowerseed Oil, Crystallized Quickly at 33°C (storage temperature 25°C)

Storage time (d)	Sucrose ester content (%) 0	0.01	0.05	0.1
0	β′	β′	β′	β′
1	β′	β′	β′	β′
2	β′<<β	β′	β′	β′
3		β′<<β	β′	β′
4			β′<<β	β′<<β
9	β′ = β			
17		β′ = β		
20			β′ = β	
34				β′ = β
85	β			
98		β		
110			β	
134				β

TABLE 7
Avrami Exponent *n*, Obtained After Fitting the Transformation Curves

Sample	Sucrose ester content (%)	*n*	r^2
Cooled slowly to 30°C	0	0.9	0.996
	0.01	0.8	0.989
	0.05	1.0	0.992
	0.1	0.9	0.993
Cooled quickly to 30°C	0	1.0	0.996
	0.01	1.0	0.997
	0.05	1.1	0.997
	0.1	1.3	0.999
Cooled slowly to 30°C	0	0.8	0.999
	0.01	0.8	0.999
	0.05	0.9	0.994
	0.1	0.9	0.996
Cooled quickly to 30°C	0	0.9	0.998
	0.01	1.0	0.998
	0.05	1.1	0.998
	0.1	1.1	0.998

By crystallizing at the fast rate to 33°C, the 4.6 A signal appeared earlier than crystallizing at the fast rate to 30°C when the control was stored, whereas the delay was the same for all concentrations of added sucrose ester at both temperatures. For the control and with 0.01 and 0.05% of sucrose ester, one-half of the transition was faster than when crystallizing to 30°C. The transition was complete at longer times, both for the control and 0.01% sucrose ester.

Crystals obtained when crystallizing to 33°C had slightly different composition than those obtained when crystallizing to 30°C. For the control and added sucrose ester, the transition required a longer time to reach completion at 33°C than at 30°C for both cooling rates. The effect was variable at low sucrose ester concentrations, as a result of the different compositions of the crystals.

Kinetic model. The kinetic model chosen to describe the transition process was based on the theory of Avrami (18–20). Avrami's equation ($1-X = e^{-kt^n}$), where X = β fraction, describes the kinetics of the global transformation—nucleation, growth, and coalescence of nuclei. The value n corresponds to the mode of nucleation and growth of β nuclei; the value k to the shape of β nuclei and nucleation and growth rates. Experimental n values were obtained by fitting the kinetic curves obtained by measuring the intensity of the short-spacing line of the β form (19.2° 2θ) vs. time. The height of the signal when the transformation was complete was considered to be 100%; the other heights are expressed as fractions.

Avrami exponent. Table 7 shows the n values obtained for both crystallization temperatures and both rates, for the control and for the addition of 0.01, 0.05, and 0.1% sucrose ester, after fitting of the transformation curves (β fraction vs. time) with Avrami's equation. The n value, on which the shape of the kinetic curves depends, was approximately 1 in all cases. According to Avrami (20–22), this could correspond to the apparition, with a constant probability into space and time, of weakly-growing nuclei. The high values of n observed for some pure TAG were related to the existence of two β′ forms (23). The β'_1 to β'_2 transition, associated with the existence of these two polymorphic forms, could precede the growth of the β nuclei. The n value found for hydrogenated sunflowerseed oil was in agreement with the fact that only one β′ form was found when the polymorphic form was studied by XRD. The fact that the β form could not be obtained directly from the melt suggests that the β′ to β transition is not liquid-mediated, it probably occurs in the solid state. As previously reported (24), any polymorphic transition through the solid phase, associated with slight movement of fat molecules, will be hindered by the rigidity of the emulsifier structure.

Sucrose ester lengthens induction times for crystallization, i.e., it delays nucleation. The effect was very noticeable at low concentrations. Sucrose esters influence critical nuclei formation and polymorphic transition. X-ray patterns, obtained immediately after filtering of the crystals, corresponded to the β′ form for the control and with the addition of up to 0.1% sucrose ester. Four signals at 3.9, 4.1, 4.3, and 4.4 Å could be seen, whereas only one β′ pattern was found. The emulsifier should produce a rigid structure, which stabilizes the β′ form, so that transition is delayed

REFERENCES

1. Riiner, J., Investigation of the Polymorphism of Fats and Oils by Temperature Programmed X-Ray Diffraction, *Lebensm. Wiss. Technol. 3*:101–106 (1970).
2. Duck, W., Measurement of Unstable Fat in Finished Chocolate, *Gordian 67*:28–31 (1967).
3. Wille, R.L., and E.S. Lutton, Polymorphism of Cocoa Butter, *J. Am. Oil Chem. Soc. 43*:491–496 (1966).
4. Witzel, H., and K. Becker, Crystalline Structure of Cocoa Butter, *Fette Seifen Anstrich. 71*:507–516 (1969).
5. Chapman, G.M., A.E. Akehust, and W.B. Wright, Cocoa Butter and Confectionary Fats. Studies Using Programmed Temperature X-Ray Diffraction and Differential Scanning Calorimetry, *J. Am. Oil Chem. Soc. 48*:824–830 (1971).
6. Davis, T.R., and P.S. Dimick, Solidification of Cocoa Butter, *Proc. PMCA Prod. Conf. 40*:104–108 (1986).
7. Timms, R.E., The Physical Properties of Blends of Milk Fat with Beef Tallow and Beef Tallow Fractions, *Aust. J. Dairy Technol. 34*:60–65 (1979).
8. Weiss, T.J., *Food Oils and Their Uses*, AVI Publishing Co. Inc., Westport, 1970, pp. 141–210, 218.
9. Berger, K., Palm Oil Products. Why and How To Use Them, *Food Technol. 9*:72,74–79 (1986).
10. Persmark, U., K.A. Melin, and P.O. Stahl, Palm Oil, Its Polymorphism and Solidification Properties, *Riv. Ital. Sost. Grasse 53*:301–306 (1976).
11. Yap, P.H., J.M. deMan, and L. deMan, Polymorphism of Palm Oil and Palm Oil Products, *J. Am. Oil Chem. Soc. 66*:693–697 (1989).
12. de Man, L., J.M. deMan, and B. Blackman, Polymorphic Behavior of Some Fully Hydrogenated Oils and Their Mixtures with Liquid Oil, *Ibid. 66*:1777–1780 (1989).
13. Garti N., *Crystallization and Polymorphism of Fats and Fatty Acids*, Marcel Dekker, Inc., New York, 1988, p. 280.
14. Madsen, J., and G. Als, Sandiness in Table Margarine, in *Crystallization and Polymorphism of Fats and Fatty Acids*, edited by N. Garti and K. Sato, Marcel Dekker, Inc., New York, 1988, pp. 11–17, results from the 9th International Society for Fat Re-

search Congress, Vlaardingen, The Netherlands, hkeld Sept. 16–21, 1968, pp. 11–17.
15. Gupta, R.K., K. James, and F.J. Smith, Sucrose Esters and Sucrose Ester/Glyceride Blends as Emulsifiers, *J. Am. Oil Chem. Soc. 60*:862–869 (1983).
16. Herrera, M.L., Crystallization Behavior of Hydrogenated Sunflowerseed Oil: Kinetics and Polymorphism, *Ibid. 71*:1255–1260 (1994).
17. Herrera, M.L., and M.C. Añón, Crystalline Fractionation of Hydrogenated Sunflowerseed Oil. II Differential Scanning Calorimetry (DSC), *Ibid. 68*:799–803 (1991).
18. Lee, S., and J.M. de Man, Effect of Surfactants on the Polymorphic Behavior of Hydrogenated Canola Oil, *Fette Seifen Anstrichm. 86*:460–465 (1984).
19. Aronhime, J.S., S. Sarig, and N. Garti, Mechanistic Considerations of Polymorphic Transformations of Tristearin in the Presence of Emulsifiers, *J. Am. Oil Chem. Soc. 64*:529–533 (1987).
20. Avrami, M., Kinetics of Phase Change. I General Theory, *J. Chem. Phys. 7*:1103–1112 (1939).
21. Avrami, M., Kinetics of Phase Change. II Transformation-Time Relations for Random Distribution of Nuclei, *Ibid. 8*:212–224 (1940).
22. Avrami, M., Kinetics of Phase Change. III Granulation, Phase Change, and Microstructure, *Ibid. 9*:177–184 (1941).
23. Desmedt, A., C. Culot, C. Deroanne, F. Durant, and V. Gibon, Influence of *Cis* and *Trans* Double Bonds on the Thermal and Structural Properties of Monoacid Triglycerides, *J. Am. Oil Chem. Soc. 67*:653–660 (1990).
24. Garti, N., J.S. Aronhime, and S. Sarig, Effect of Food Emulsifiers on Polymorphic Transitions of Cocoa Butter, *Ibid. 63*:230–236 (1986).

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