Mechanistic Considerations of Polymorphic Transformations of Tristearin in the Presence of Emulsifiers

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Fat polymorphs influence the quality of some food and cosmetic products. Emulsifiers traditionally have been added in order to retard undesired polymorphic transformations. The present study is an attempt to understand the role of selected emulsifiers on such transformations. Tristearin was heated or aged under controlled conditions using differential scanning calorimetry (DSC) and X-ray techniques, and the extent of transformation was evaluated in view of the possible pathways of α transforming into β. The temperature regime controls the extent of mobility of fat molecules, the local crystal imperfections and the degree of liquefaction. As a result, it dictates the kinetics of the polymorphic transformation.

The surfactant added as an impurity does not have a straightforward effect, as thought previously, but rather varies with the kinetic conditions. During aging some selected solid emulsifiers will retard the α-β transformation while others still enhance it (during heating, all of them will inhibit β form crystallization). Their effect probably is related to different crystalline organizations and the creation of imperfections. Liquid emulsifiers in any case will enhance the α-β transformation, due probably to their weak structure compatibility with tristearin, which causes a higher mobility of triglyceride molecules.

Polymorphism in triglycerides, a general phenomenon in long hydrocarbon chain compounds, has been known for some decades; the possibilities of crystallization into different molecular arrangements with identical chemical composition has drawn the attention of many investigators, owing to its practical implications in fatty products.

The various polymorphic forms differ in their thermodynamic stability and therefore in their physical properties (free energy, volume, density, melting point, x-ray diffraction patterns, etc.). In triglycerides polymorphism is monotropic, i.e. one form is stable throughout the range of its existence. Consequently, the transformation can occur in only one direction.

Rapid crystallization of triglyceride molecules from the melt produces the thermodynamically unstable α form, which "remembers" the molecular configuration of the molten state; it has a hexagonal structure and shows a single peak in its x-ray diffraction pattern, which corresponds to a distance of approximately 4.15 Å between the aliphatic chains. The more thermodynamically stable β form, which can be obtained from the melt only by a very slow cooling, is easily crystallized from solution. Its lower free energy and higher stability derive from a compact arrangement of molecules, due to their stretched configuration. The triclinic structure of the β form has been determined by Larsson (1) by a single crystal analysis; the space group $P\bar{1}$, and the unit cell contains two molecules. The powder x-ray diffraction pattern of the triclinic β form shows three main peaks in the short spacings range ($18° < \theta < 25°$) which result from the reflecting planes 100, 010 and 110. The interplanar distances that correspond to these crystallographic planes, though varying slightly from trilaurin to tristearin, are close to the values (Å):d_{100} = 3.70, d_{010} = 4.60, d_{100} = 3.85 (2). Recently, computer models have been developed for determining various possibilities of arrangement in the same basic configuration of the molecule (3), and transformation energetics have been estimated (4). A comprehensive inspection of the mechanism and process of polymorphic transformations, however, has not been reported though it seems to be a determinant for understanding of the general phenomenon of polymorphism in fats.

The transformation between different forms in fatty acids, the polymorphic and crystallization behavior of

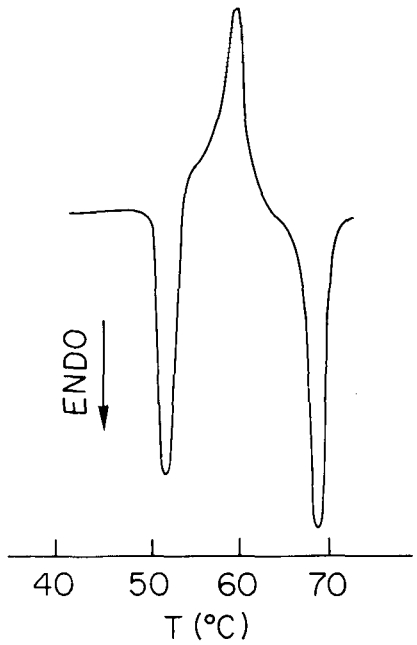

FIG. 1. Thermogram of tristearin. Heating rate, 5 C/min.

TABLE 1
ΔH_α and ΔH_β Values of Tristearin Heated at Different Heating Rates

Rate of heating (C/min)	ΔH_α (J/g)	ΔH_β(J/g)
0.5	42.5	201.7
1	79.6	207
2	99.8	196.9
5	110.31	181.96
10	117.8	45.7

which has been systematically investigated (5), is as a rule solution mediated (6). The thermodynamic stability alternates between forms C and B depending on the temperature range (enantiotropism) and the growth of the more stable crystal occurs at the expense of the dissolving less stable crystal. In triglycerides, however, the monotropic polymorphic transformation may occur either in the solid state at temperatures below the melting point of the unstable α form (aging) or through controlled heating of the sample (screen). Owing to this versatile thermal behavior, triglycerides provide a useful system for investigating the mechanism of polymorphic transformation in crystalline compounds.

The addition of surface active agents at low percentages into the fat is known to affect the rate of polymorphic transitions both in fatty acids (7) and in fats (8-10). The effect on the kinetics of polymorphic transformations due to the presence of surfactants may shed light upon the mechanism of phase transition.

The DSC technique is a useful tool for studying polymorphic transitions; in a previous study on the effect of sorbitan monostearate addition on the polymorphic transformation in tristearin, using the DSC (11) it was shown that the presence of this emulsifier significantly retards the transformation of unstable α form to stable β form. It was assumed (according to previous reports) that an endothermic ΔH value represents the fusion enthalpy of the corresponding polymorph, and an exothermic ΔH value represents the quantity of heat released in the transformation process.

In the present work the DSC has been used for studying possible pathways for polymorphic transformation in tristearin, which are dictated by different temperature regimes and by the presence of solid emulsifiers. A better understanding of the effect of emulsifiers on the kinetics of the transformation may be useful in the industry for delaying quality degradation of fatty products.

EXPERIMENTAL

Materials. Tristearin was purchased from Sigma Chemical Co., St. Louis, Missouri, and was 99% pure. The additives were available commercially from Grinsted Products of Denmark. The additives tested were sorbitan monostearate (Span 60); glycerol-l-stearate (Dimodan); citric acid ester of monoglyceride (Acidan); ethoxylated sorbitan monostearate (Tween 60); triglycerol-l-oleate (3G10), and sorbitan monolaurate (Span 20). The emulsifiers were added at the level of 10 wt%; each sample was then blended in the molten state in order to obtain a homogenous mixture.

Methods. The thermal measurements were performed on the Mettler Differential Scanning Calorimeter TA3000, calibrated for temperature readings and calorimetric accuracy with zinc and indium. The weighed samples were sealed in an aluminum pan; a similar empty pan served as reference.

Procedure of DSC screen and its interpretation. The DSC detects the enthalpy changes involved in the crystallization and melting processes; phase transitions in fats are easily recognized, providing that the heating rate is slow enough. In the thermogram of neat tristearin scanned at 5 C/min (Fig. 1), the first endotherm indicates melting of the unstable α form, the second endotherm indicates melting of the stable β form and the exotherm records the transformation (crystallization) reaction. The identification of each peak in the thermogram was achieved using powder x-ray diffraction analysis of the isolated polymorphs.

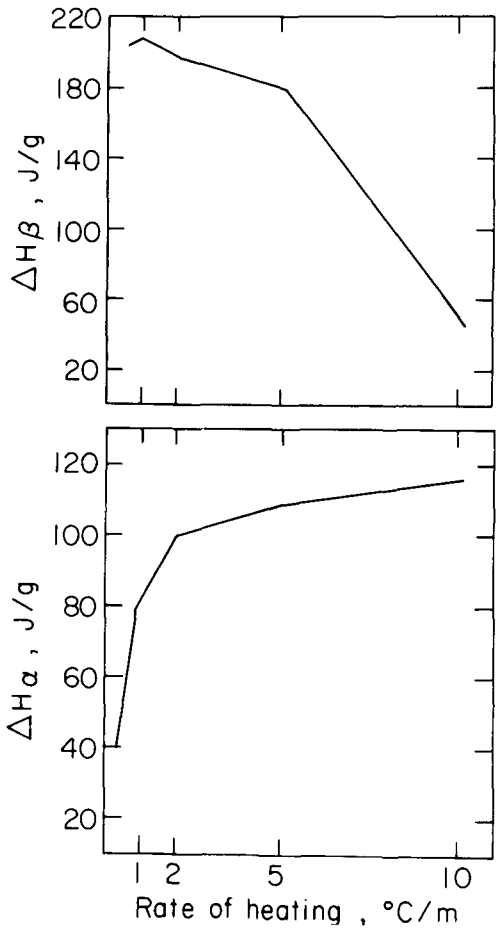

FIG. 2. ΔH_α and ΔH_β values of tristearin at different heating rates.

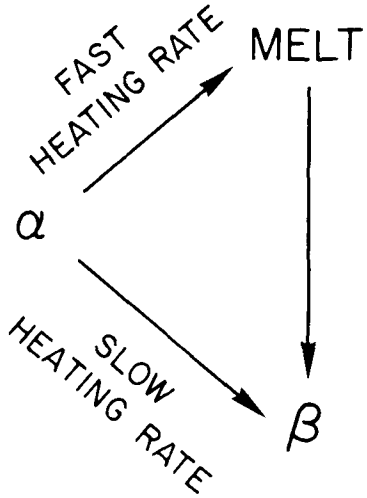

FIG. 3. Paths for α-β transformation during heating.

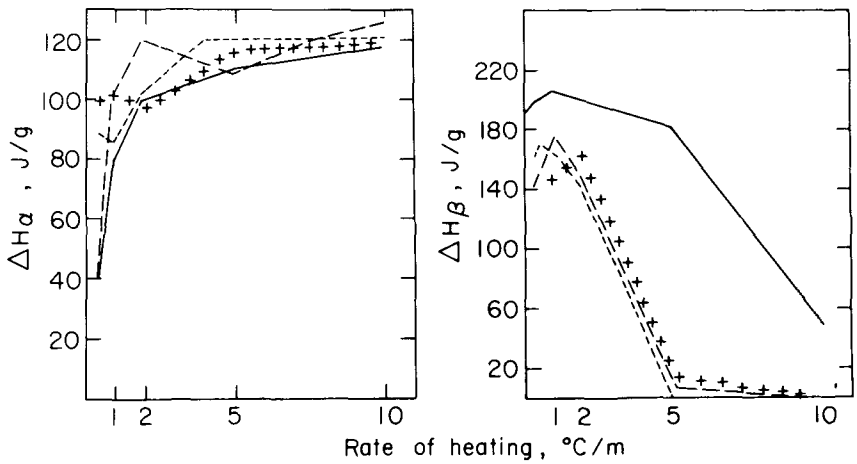

FIG. 4. ΔH_α and ΔH_β values of tristearin (——) in the presence of Span 60 (----), Acidan (+++) and Dimodan (— —).

The areas under these peaks, ΔH_α, ΔH_t and ΔH_β, respectively, are indicators of the quantity of a solid which liquefies or crystallizes; they are not considered to be the actual enthalpies of fusion or crystallization because the areas under the peaks depend on heating rates. In order to determine a thermodynamic function, the heating rate should be slow enough to perform the experiment as close to equilibrium conditions as possible. However, for this study it was necessary to compare endothermic values of different samples, hence determination of the exact enthalpies of fusion was not feasible.

RESULTS AND DISCUSSION

In order to check the α-β transformation in the sample, first a fast cooling from the melt state to 10 C was performed within the DSC to crystallize the α form, and the sample was kept at this temperature for 5 min. Immediately afterward, the α form was heated at a constant rate. This procedure was repeated at different rates of heating, with the purpose of observing the changes in the thermogram patterns induced by the different heating rates.

Table 1 summarizes the ΔH_α and ΔH_β values for tristearin heated at different heating rates. It can be seen that the ΔH_α values decrease as the heating rate decreases, while the ΔH_β values increase. Figure 2 illustrates the change in ΔH_β with heating rate and stresses the differences in the slopes when the sample was heated at 1-5 C/min vs 5-10 C/min. It can be seen that, while at low heating rates the drop in ΔH_β is moderate, at high heating rates the decrease in ΔH_β is sharper.

Considering that the rate of heating is a decisive factor which determines the extent of ΔH_α and ΔH_β, we can conclude that at the heating rate of 10 C the value of ΔH_α is the highest, while at 1 C/min ΔH_α reaches its highest value. It seems that at the latter rate we have the maximal extent of α transformation. The ratio between the portion of α which melts and the portion of β which crystallizes varies when applying the different heating rates. As we have explained in a previous work (12), two processes may take place during heating of the α form. One is the direct transformation to β without an endotherm detection, and the other is melting and recrystallization to the β form (Fig. 3).

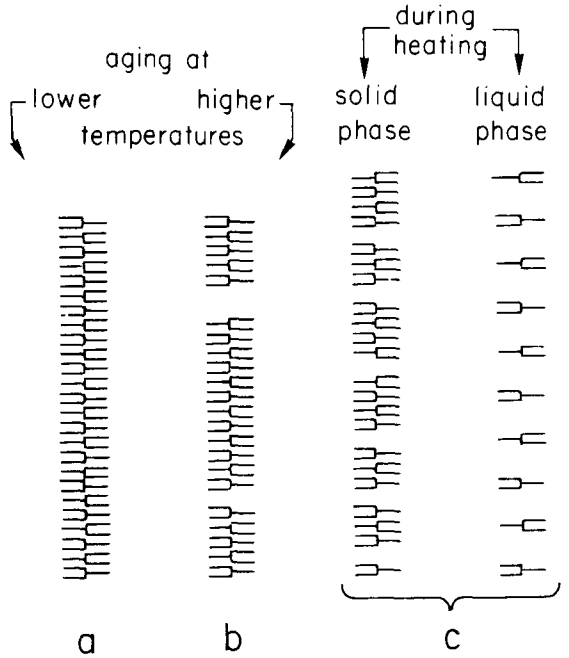

FIG. 5. Scheme of possible crystal imperfections in different temperature regimes.

The factor determining which of the two possibilities is the preferred one, exluding the triglyceride type (12), is the rate of heating. A too high heating rate will prevent the crystallization of β, as was observed at 10 C/min (Fig. 2). The medium heating rate (5 C/min) also causes the fat (α) to melt but allows the β crystallization. The milder heating rate, in addition, will allow a partial direct transformation α-β at the expense of α, which melts. In conclusion, at relatively high heating rates the polymorphic transformation is led predominantly through the melt phase, while at slower heating rates the direct transformation takes place.

The transformation of α-tristearin to the β form was tested in the presence of three solid emulsifiers, at the level of 10 wt%, and the values of ΔH_α and ΔH_β are

shown as functions of heating rate (Fig. 4). At a 5 C/min heating rate, in the presence of Span 60, Dimodan and Acidan the crystallization is entirely inhibited, even if under the same conditions pure tristearin crystallizes almost completely in the β form. When heating was slower the retardation effect of the surfactants was less significant; at 2 C/min only 20% of β crystallization was inhibited in comparison to neat tristearin at the same conditions. In contrast to the effect on β crystallization, the ΔH_α values are not strongly affected by the presence of solid emulsifiers.

These results imply that the inhibitory effect of the solid surfactant on the α-β transformation is not absolute, but rather varies at different heating rates. This fact confirms our supposition that different mechanisms of polymorphic transformation alternate under different kinetic conditions. As mentioned before, the polymorphic transformation may take place in the solid state or through the liquid state; the temperature regime dictates not only the rate of transformation, but also the physical state of the crystal during the polymorphic transition.

Four different situations in which the α form transforms to β can exist in tristearin. The first one is aging of the fat at relatively low temperatures; the fat is completely solid with a high activation energy for transformation. In this range of temperatures (up to 20 C) the configuration adjustment of the molecules to the triclinic β form is restrained by their lack of mobility (Fig. 5a). At higher temperatures, the two-dimensional melting comes about, as treated in previous studies (13-14). The two-dimensional melting implies a gradual increase of dislocations in the crystal lattice of long hydrocarbon chains prior to their complete melting, owing to the particular lamellar structure characteristic to these substances (Fig. 5b). In this case the polymorphic transformation is faster, due to the local dislocations which facilitate the mobility of the molecules and allow their configurational transformation. Above the melting temperature of α, the transition can occur through melting and recrystallization (Fig. 5c) or by direct transition, as mentioned before. The direct transition is therefore a process in which a large number of dislocations forms, creating a state of softening.

In these four conditions the solid emulsifiers act differently. During aging at temperatures both lower and higher than 20 C, Span 60 delays the β formation while the other solid emulsifiers enhance it (Fig. 6). In our previous study on the heat capacity of tristearin (14) we have shown that Span 60 and Span 65 (sorbitan tristearate) do not affect the Cp of α-tristearin, while other solid surfactants do. We can thus suppose that Acidan and Dimodan create imperfections within the crystal owing to their lower structure affinity with tristearin, while Span 60 and Span 65 best fit the crystal lattice. In consequence, the Spans delay the transformation by steric hindrance, while the other surfactants promote it by favoring dislocations.

When heating up the α form (Fig. 5c), the solid emulsifier prevents the recrystallization of the fat into β; on the other hand it does not hinder the transformation through a "softened phase" which takes place at low heating rates. Presumably the formation of an already large number of dislocations in the latter case, which is responsible for the rapid conversion, is indifferently affected by the emulsifier's presence. The prevention of crystallization is confirmed by the fact that it is delayed by the solid emulsifiers also when carried out from the melt phase (Table 2).

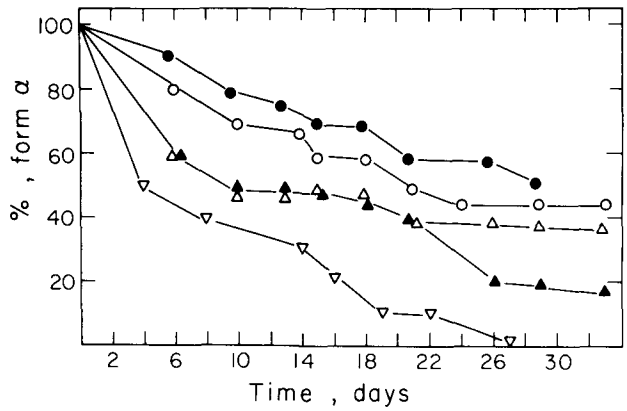

FIG. 6. Aging of tristearin at room temperature in the presence of emulsifiers 5 wt%. ○, neat tristearin; ●, tristearin + Span 60; ▲, tristearin + Dimodan; △, tristearin + Acidan; ▽, tristearin + Span 80.

TABLE 2

Crystallization Temperatures and Enthalpies of Tristearin in the Presence of Solid Surfactants

	T_c(c)	ΔH_c (J/g)
tristearin	62.5	211
tristearin + Span 60	51.5	117.1
tristearin + Dimodan	51.8	122.1
tristearin + Acidan	51.2	110

Summarizing, when the solid-solid transformation occurs, Span 60 delays it, while the other solid surfactants enhance it; by comparison, when transformation takes place through the liquid phase, it is prevented by all the solid surfactants.

Evidently the high melting point of the surfactant is not the only feature necessary for the stabilization of the α form; in addition to that, the high melting point of the surfactant must have a very particular polar moiety. In contrast, for inhibiting solidification of the β form from a melt state, the long saturated hydrocarbon chain of the surfactant seems to be a sufficient requisite. It could imply that a very good structural affinity between the polar sites of triglyceride and emulsifier is required in order to hinder the slow configurational change of the molecules in the solid state; on the other hand, a prevention of β seeds formation apparently requires just the readiness of the emulsifier to crystallize owing to its long hydrocarbon chain and to interfere with the solidification process of the β polymorph.

The demonstration that a minimal structure affinity is needed for delaying or preventing the β crystallization is given in Figure 7, which presents ΔH_α and ΔH_β values of tristearin in the presence of three liquid surfactants. Clearly, all the liquid surfactants enhance the transformation, lowering the ΔH_α values markedly.

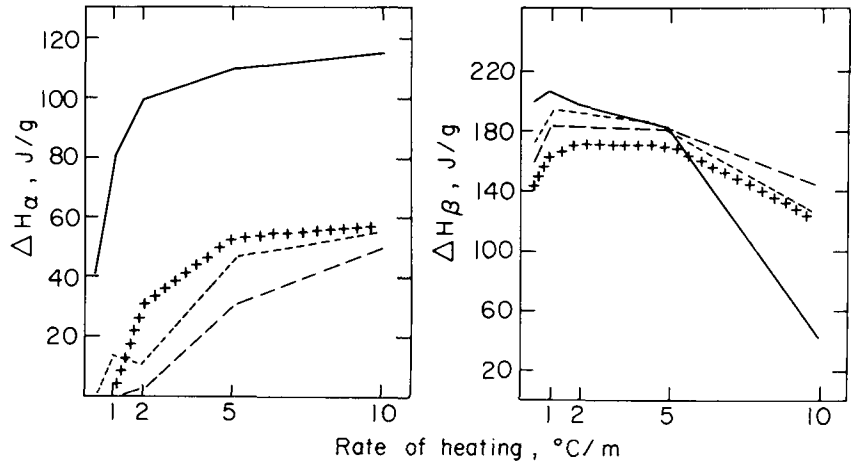

FIG. 7. ΔH_α and ΔH_β values of tristearin (——) in the presence of Tween 60 (----), 3G10 (– –) and Span 20 (+++).

The high ΔH_β with the three additives confirms the facilitation of the α-β transition in comparison with neat tristearin. Obviously, liquid surfactants do not have any structural affinity with tristearin and probably create local imperfections which facilitate the mobility of triglyceride molecules; this effect is also seen during aging of tristearin at room temperature (Fig. 6).

Temperature regime (rate of heating) controls the extent of mobility of the fat molecules, the number of local crystal imperfections and the degree of liquefaction. These factors, being kinetic, can also dictate the rate of polymorphic transformation. The surfactant added as an impurity does not have a straightforward effect as previously thought, but rather varies as the kinetic conditions dictate.

A tentative explanation for the mechanism of polymorphic transformations has been presented, which is strengthened by the different effects of the emulsifier.

REFERENCES

1. Larsson, K., *Ark. Kemi 23*:1 (1964).
2. Precht, D., and E. Frede, *Acta Cryst. 339*:381 (1983).
3. de Jong, S., and T.C. van Doest, *Acta Cryst. B34*:1570 (1978).
4. Hagemann, J.W., and J.A. Rothfus, *J. Am. Oil Chem. Soc. 60*:1123 (1983).
5. Sato, K., K. Suzuki, M. Okada and N. Garti, *J. Cryst. Growth 72*:699 (1985).
6. Wellner, E., N. Garti and S. Sarig, *Cryst. Res. Tech. 16*:1283 (1981).
7. Garti, N., and K. Sato, *J. Am. Oil Chem. Soc. 63*:236 (1986).
8. Schlichter, J., S. Sarig and N. Garti, *Therm. Acta 85*:517 (1985).
9. Lee, S., and J.M. de Man, *Fette, Seifen, Anstrichm. 86*:460 (1984).
10. Hernqvist, L., and K. Anjou, *Ibid. 85*:64 (1983).
11. Garti, N., E. Wellner and S. Sarig, *J. Am. Oil Chem. Soc. 59*:181 (1982).
12. Garti, N., J. Schlichter and S. Sarig, *Fette, Seifen, Anstrichm.* In press.
13. Simpson, T.D., D.P. Hockett and L. Harris, *J. Am. Oil. Chem. Soc. 61*:883 (1984).
14. Schlichter, J., N. Garti and S. Sarig, *Ibid. 63*:788 (1986).

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