The Role of Chain Length and an Emulsifier on the Polymorphism of Mixtures of Triglycerides

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The appearance of the β' form in the α-β transformation in tristearin is hardly detectable. On the other hand, in mixtures of tristearin and tripalmitin at different ratios, β' formation has been observed to be favored. This observation confirms the statement in the literature that in mixtures of different chain lengths orthorhombic packing is stabilized. When an emulsifier was added to the mixtures, both the β' and β formation were inhibited. The effect caused by the addition of the emulsifier as an impurity to tristearin is compared to that caused by the addition of tripalmitin: their effects, although both kinetic, were very different. In spite of this difference, they both have implications in the confectionery and fats industries.

It is well known that polymorphism of fats may affect some important physical properties of fat-based food products. Since fats are blends of different triglycerides with variable degrees of unsaturation, their polymorphic behavior is quite complex. Since their polymorphic behavior is relatively simple, monoacid saturated triglycerides have been the model for studying the basic phase transitions and molecular packings (1–13). In our previous studies it was shown that the kinetics of polymorphic transformation may vary according to the chain length, while the crystal packings of the different polymorphs are basically the same in all the triglycerides with chain lengths between C_{12}-C_{18} (14). During the transformation α-β'-β in tristearin, a difficulty has been encountered in isolating the intermediate β' form, in spite of evidence in the literature concerning the identification of the orthorhombic β' form in monoacid saturated triglycerides (15). A complete characterization of the β' packing has not yet been achieved, but its IR spectrum is known and indicates that the hydrocarbon chains are packed with the zig-zag planes perpendicular to each other (16).

In a theoretical study, Hagemann pointed out (17) that the packing density of the hydrocarbon chains is higher in the orthorhombic structure than in the triclinic one. In spite of this, the triclinic structure, usually denominated by the β form, is the most thermodynamically stable, probably owing to the better packing between the methyl end group planes (18), which reduces the lattice energy. The efficiency of the interplanar packing, which is high in triglycerides with uniform fatty acid chain lengths, is reduced when different chain length triglycerides are mixed. It is pointed out in the literature that in a mixture of different chain length triglycerides, the orthorhombic structure is stabilized (19–21), probably because the β'-β transformation is sterically hindered. This is one of the most likely reasons why several β' forms occur before the transformation to the β form in fats. As was shown in our previous work, specific surfactants also have the capability to hinder the polymorphic transformation during constant heating, however, no occurrence of the β' form was recorded as the result of the additive's presence (22).

In the present work, the DSC technique has been employed in order to study the role of triglycerides mixtures on the stabilization of the β' form. For this purpose two monosaturated triglycerides were blended at different ratios and the β-β' transformations were observed. The effects of different triglycerides and of the surfactant may be relevant to the problem of the undesirable polymorphic transformations in confectionery fats. It also may reveal the proper proportion of surfactants necessary to improve the quality of confectionery products.

MATERIALS AND METHODS

Tripalmitin and tristearin were commercially available from Sigma and were 99% pure. The surfactant sorbitan monostearate was purchased from Grindsted, Denmark. The mixtures of tristearin/tripalmitin were prepared by mixing the two components in the molten state and then quenching the mixture. The same procedure was followed for the mixture with the emulsifier. The thermal curves were obtained on a Mettler DSC (TA 3000) calibrated for temperature readings and enthalpy accuracy. The weight of the samples ranged between 3 and 4 mg. An empty crucible served as a reference. The α form was obtained by cooling the sample from 80°C to 10°C at the rate of 50°C/min. Then the sample was immediately scanned, each time at a different heating rate (1,2,5,10°C/min).

RESULTS AND DISCUSSION

In Figure 1 the thermograms of the mixture tristearin-tripalmitin 90:10 (solid line) and the same mixture in the presence of SMS (sorbitan monostearate, dashed line) are shown. In the thermogram scanned at 5°C/min in the neat mixture (Fig. 1B, solid line) three endothermic peaks clearly are visible. The first peak, occurring at 53.7°C, corresponds to the melting of the α form. The last peak, at 70.5°C, corresponds to the melting of the β form. The intermediate peak, occurring at 62.9°C, indicates the melting of the β' form, whereas the exothermic peak indicates the transformation to the β polymorph. Because the kinetic stability of β' is low, melting and transformation processes take place concurrently and the endothermic peak is actually combined with an exotherm. At faster heating rates a high α-endotherm and a smaller β'-endotherm are observed, but practically no transformation to β occurs (Fig. 1A, solid line); moreover, no exothermic reaction is recorded. As the heating rate becomes slower, more exothermic reactions may be detected. The effect of the heating rate on the mechanism of transformation has already been emphasized in our previous work

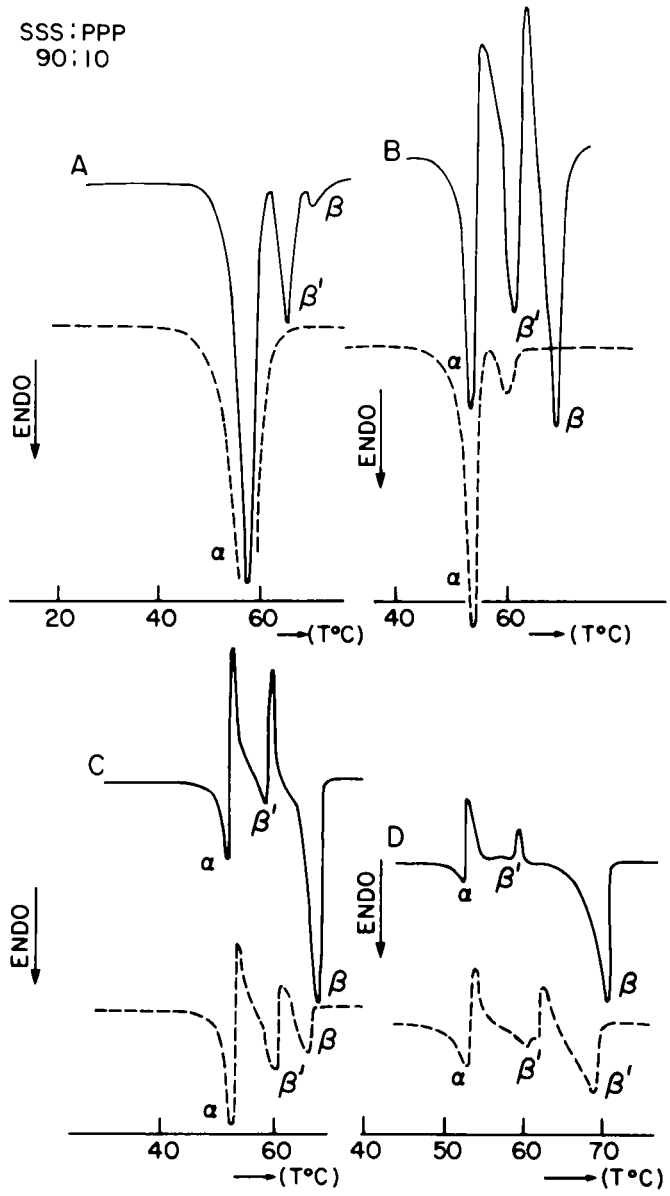

FIG. 1. Thermograms of mixtures tristearin/tripalmitin 90:10 neat (solid line) and in the presence of sorbitan monostearate 10 wt% (dashed line). Heating rates: A) 10°C/min; B) 5°C/min; C) 2°C/min; D) 1°C/min.

on tristearin (22). It was pointed out in that work that low heating rates in tristearin allows a solid state transformation (with a low α-endotherm), but at the same time reduces the extent of transformation (with a low β-endotherm). It seems that the same conclusion is also valid when an intermediate peak is present. The heating rate in this case also affects both the mechanism and extent of transformation. This observation suggests that the triglyceride mixture is homogeneous and the three peaks correspond to three different polymorphs of the same compound. The possibility that the intermediate peak indicates the melting of one single component of the mixture also was considered. In order to clarify this point and show that the mixture behaves as a homogenous solid solution, both tristearin and tripalmitin were crystallized separately in

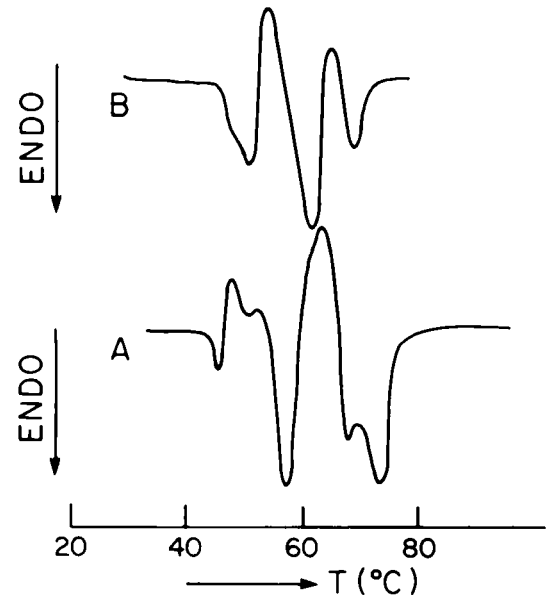

FIG. 2. Thermograms of mixture tristearin/tripalmitin 90:10 at heating rate of 5°C/min. A) of mechanical mixture of the two components; B) of the same sample melted and quenched.

the α form, then mixed at the same ratio (90:10) and scanned at a heating rate of 5°C/min. The resulting thermogram (Fig. 2A) clearly shows that the two components, which were mechanically mixed, transform from α to β separately and their thermograms are simply superposed. After being completely melted the same sample was then solidified in the α form in the DSC, thus turning from mechanical mixture to solid solution. The subsequent scan at the same heating rate (Fig. 2B) shows the same pattern as in Figure 1B.

In Figure 1 the effect of emulsifier's presence can be seen (dashed curves). It is evident that when sorbitan monostearate is added to the mixture, both α-β' and β'-β transformations are inhibited. Moreover, at slow heating rates, the transitions show a higher endothermic reaction than the neat mixture (Fig. 1C and 1D), indicating that the additive hinders solid transformations and induces transitions through the melt. This point has been previously emphasized (23-24) when the effect of a solid emulsifier was tested on α-β transition in trilaurin. Owing to the low stability of the α form in trilaurin, a considerable fraction of the fat transforms to β through the solid state (24). In the presence of sorbitan monostearate, the α-endotherm is increased drastically, indicating a change in the mechanism of the transformation induced by the additive. The inhibiting effect of the emulsifier depends on the heating rate, as it is stronger during faster heating and weaker at slow heating rates. This observation is also in agreement with our previous results (22).

As the ratio tristearin-tripalmitin decreases, the appearance of the intermediate β' form becomes more evident. At the ratio SSS:PPP (90:10) the intermediate peak, attributed to the β' form, is apparent at heating rates of 10 and 5°C/min. At lower heating rates the β' endotherm vanishes, suggesting that a liquid mediated transformation toward the β form takes place. At

ratios SSS:PPP (30:70) the strongest stabilization of β' occurs, as is evident from the lower heating rates thermograms (Figs. 3-6). With the increase of the PPP ratio, the peak of β melting gradually diminishes, indicating a lower extent of the β transformation. In the mixture tristearin-tripalmitin 10:90 the β endotherm appears again, this time concurrently with the β' peak (Fig. 6A). In this mixture, with tripalmitin being the major component, the β'-β transformation is easier because of the shorter chain length of palmitin. In this case the effect of the chain length is predominant, hence the β crystallization is not suppressed. All of the figures indicate that during slow heating rates sorbitan monostearate inhibits the β'-β transition and not the α-β' transition which is mainly affected during faster heating rates.

From these results it follows that in a mixture of triglycerides with different chain lengths, the β' form is stabilized but it is still too unstable to be isolated and detected in the x-ray diffractometer at room temperature. The α form of the mixture tristearin/tripalmitin 50:50 was aged at room temperature and tested regularly every few days in the diffractometer; it was disappointing to recognize only an α-β transition without the detection of the peak characteristic to the β' form.

Because the β' form could not be identified at room temperature, the sample tristearin/tripalmitin 50:50 was heated in a DPT apparatus in order to detect the β' form during heating. As the resolution of the instrument was not high in the region of the short spacings, it is possible that there is a fine structure within the three main peaks as reported in the literature for the β phase (14). In conclusion, only a few, weak indications of the presence of β' in the whole polymorphic transformation were supplied. The effect caused by the addition of tripalmitin on the polymorphism of tristearin has been compared to that caused by the addition of emulsifier. Figure 7 shows the thermograms of neat tristearin (A), tristearin/tripalmitin 90:10 (B), and tristearin with sorbitan monostearate 10 wt% (C). The heating rate was 5°C/min for all the samples. It is possible to see the α-β transition in neat tristearin. In the presence of sorbitan the transformation to β is suppressed. On the other hand, an additional polymorph is stabilized in the mixture with tripalmitin. Both tripalmitin and emulsifier have a kinetic effect on the polymorphism of tristearin. Neither the former nor the latter affect the thermodynamic stability of the polymorphs; in all cases the β form is the most stable one regardless of the presence of any additive. From this comparison it is clear that tripalmitin and sorbitan monostearate have different kinetic effects on the polymorphism of tristearin. The presence of tripalmitin evidently induces structural modification while the emulsifier, on the other hand, does not have any influence on the structure, but only a steric effect on the transition step. During the α-β transformation

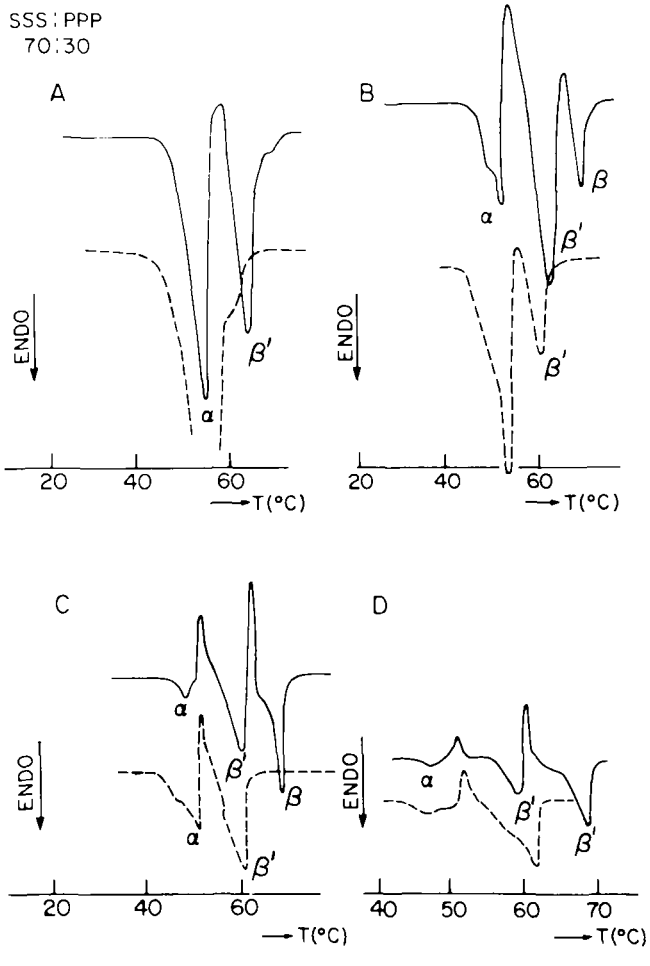

FIG. 3. Thermograms of mixtures tristearin/tripalmitin 70:30.

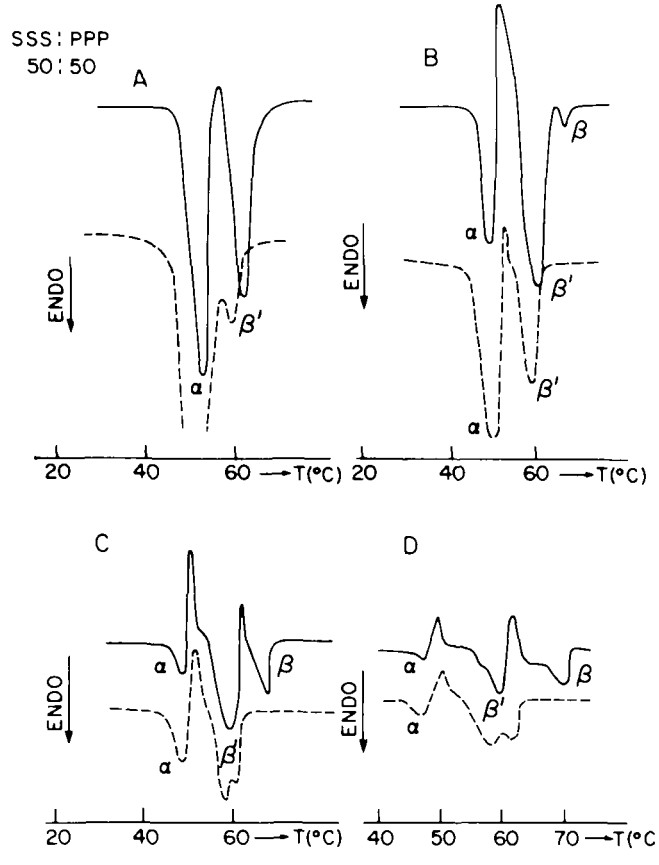

FIG. 4. Thermograms of mixtures tristearin/triplamitin 50:50.

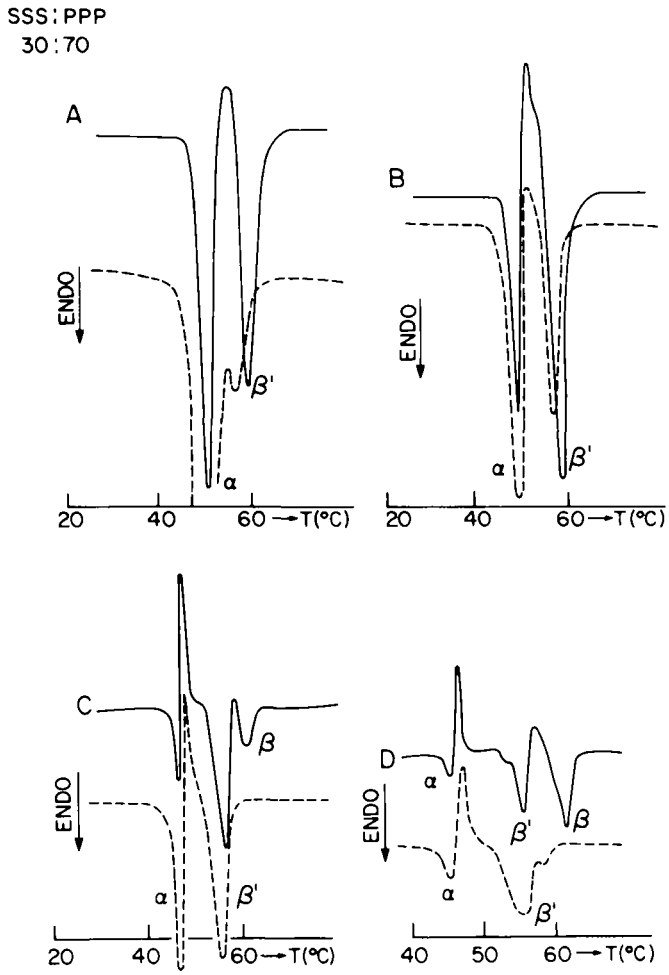

FIG. 5. Thermograms of mixtures tristearin/tripalmitin 30:70.

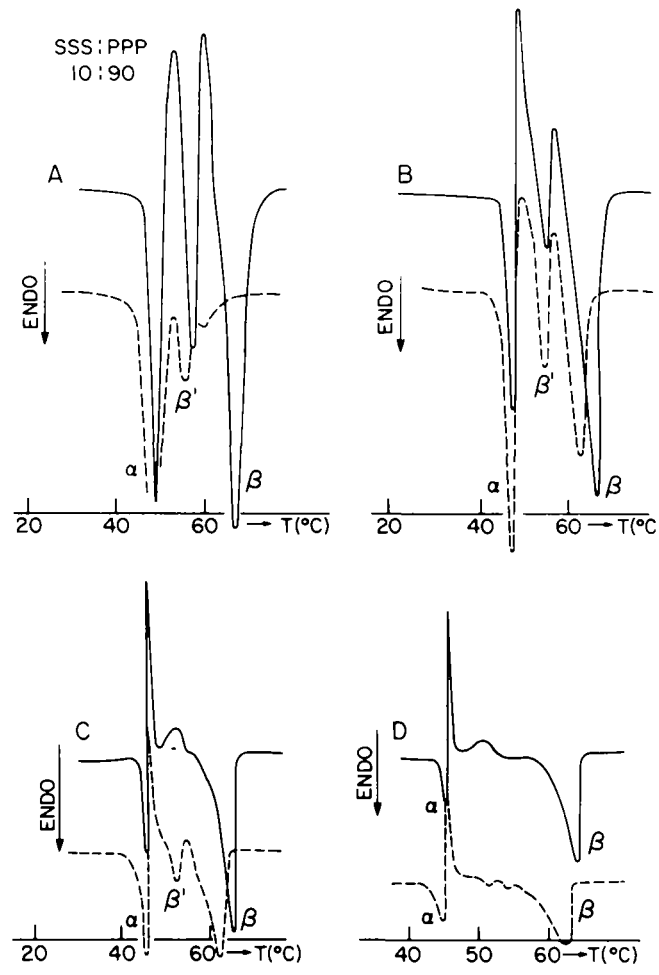

FIG. 6. Thermograms of mixtures tristearin/tripalmitin 10:90.

in neat tristearin the intermediate β' is probably formed, but is not stable enough to be detected during heating. In the mixture with tripalmitin this intermediate form is stabilized kinetically. The inhibition of the β transformation also occurs, but is less significant. This inhibition was observed when a high percentage of tripalmitin was mixed with tristearin (Figs. 3-5). The opposite effect results when the emulsifier is present in tristearin. This additive does not stabilize any intermediate form which does not appear during the transformation in the neat fat, but its inhibitory effect is still very strong.

The influence of tripalmitin and emulsifier is decreased when the transformation occurs at slow heating rates, which is an indication that in both cases the effect is merely kinetic. In the case of tripalmitin, the structural effect is connected with the formation of a mixture of triglycerides with different chain lengths. As confirmed in the literature (19), the difference in chain lengths causes a discontinuous methyl end groups plane, which favors (energetically) the orthorhombic packing. Tripalmitin, forming a solid solution with tristearin, influences the occurrence of a certain crystal structure and stabilizes it. However, the presence of the solid emulsifier does not favor a given crystal structure, but acts on the kinetics of the transformation. Its effect, defined as "the button syndrome", (24) probably derives from a physical bond (hydrogen bond) between the emulsifier and the fat molecules, which hinders the configurational change during the polymorphic transformation. Although in this case the unstable polymorph is stabilized, the effect occurs throughout the transformation stage regardless of the specific transforming polymorph.

The stabilization of the β' form or the delay of its transformation have a practical meaning in both the confectionery and other food industries.

Although more than one β' form exists in complex fats, it seems that the critical transformation (which is deleterious to the product's quality) is that to β. The use of additives, mainly surfactants, can delay the undesirable transformation even when used at low percentages. It is also possible that the use of a specific triglyceride can stabilize the unstable form. The addition of POS or SOS to chocolate in amounts over 10% has been reported to inhibit fat bloom formation (25). The combined addition of a suitable surfactant —one which has been widely shown to be a powerful aid against the transformation to β formation and a specific triglyceride may reveal a good capability to

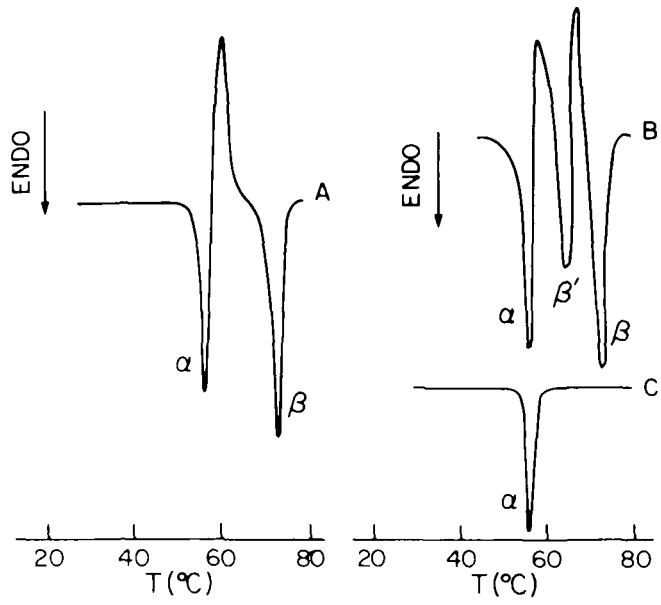

FIG. 7. Thermograms of: A) neat tristearin B) mixture tristearin/tripalmitin 90:10 C) tristearin in the presence of sorbitan monostearate 10 wt%.

delay the formation in those edible fats in which the β'-β transition is relatively fast and harmful to the product quality.

REFERENCES

1. Callaghan, P.T. and Jolley, K.W., *J. Chem. Phys. 67*:4773 (1977).
2. Hernqvist, L. and Larsson, K., *Fette Seifen Anstrichm. 84*:349 (1982).
3. Lovegren, N.V. and Gray, M.S., *J. Am. Oil Chem. Soc. 55*:310 (1978).
4. Hernqvist, L., *Fette Seifen Anstrichm. 86*:297 (1984).
5. Lutton, E.S. and Fehl, A.J., *Lipids 5*:90 (1970).
6. Bociek, S.M., Ablett, S. and Norton, I.T., *J. Am. Oil Chem. Soc. 62*:1261 (1985).
7. Kodali, D.R., Atkinson, D., Redgrave, T.G. and Small, D.M., *Ibid. 61*:1078 (1984).
8. Simpson, T.D. and Hagemann, J.W., *Ibid. 59*:1169 (1982).
9. Whittam, J.H. and Rosano, H.L. *Ibid 52*:128 (1975).
10. Hagemann, J.W., Tallent, W.H. Barve, J.A., Ismail, I.A. and Gunstone, F.D., *Ibid 52*:204 (1975).
11. Hoerr, C.W. and Paulicka, F.R., *Ibid 45*:793 (1968).
12. Dafler, J.R., *Ibid 54*:249 (1977).
13. Hagemann, J.W. and Tallent, W.H. *Ibid 49*:118 (1972).
14. Small, D.M., "The Physical Chemistry of Lipids. From Alkanes to Phospholipids", Handbook of Lipid Research, Vol. 4, Plenum Press, NY and London, 1986.
15. Bailey, A.E., "Melting and Solidification of Fats", *Int. Publ. Inc.* New York, NY, 1950.
16. Chapman, D., "Introduction to Lipids", London, NY, McGraw Hill, 1969.
17. Hagemann, J.W. and Rothfus, J.A., *J. Am. Oil Chem. Soc. 56*:1008 (1979).
18. Kitaigorodsky, I., "Molecular Crystals and Molecules", Academic Press, NY and London, 1973.
19. Hagemann, J.W. and Rothfus, J.A., *J. Am. Oil Chem. Soc. 60*:1123 (1983).
20. Hernqvist, L., Herslof, B., Larsson, K. and Podlaha, O., *J. Sci. Food Agric. 32*:1197 (1981).
21. Larsson, K., *Chemica Scripta 1*:21 (1971).
22. Schlichter, J., Garti, N. and Sarig, S., *J. Am. Oil. Chem. Soc. 64*:529 (1987).
23. Schlichter, J., Sarig, S. and Garti, N., *Thermoch. Acta 85*:29 (1985).
24. Schlichter Aronhime, J., Sarig, S. and Garti, N., *J. Am. Oil Chem. Soc. 65*:1144 (1988).
25. Padley, F.B., Paulussen, C.M., Soeters, C.J. and Tresser, D., *Rev. Int. Choc. (RIC) 27*:9 (1972).

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