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APPLICATION OF THERMAL ANALYSIS (DSC) IN THE STUDY OF POLYMORPHIC TRANSFORMATIONS

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ABSTRACT

The effects of chemical structure and composition on phase transitions in triglycerides are reviewed. The presence of surfactants may help to better discern between the polymorphic behaviour of isomorphous triglycerides. The effect of different surfactants depends on their hydrophilic group and on the thermal properties of the triglyceride. The mechanism of the effects on the polymorphic transitions in triglycerides is interpreted considering the different modes of their transformations either through solid/melt/solid or through solid/solid.

The DSC technique used was effective in estimating the extent and the mechanism of transformations. The thermal history and rate of scanning affect strongly the kinetics of polymorphic transformations.

INTRODUCTION

Phase transformations are very important in solid state science and crystallization processes. Besides being scientifically interesting, they assume an especially important function in technology. Phase transformations are involved in the synthesis of diamond from graphite, in the processes for strengthening of steel, in the properties of ferromagnetism, and also in processes which occupy a major role in the food technology industry: polymorphic transformations of fats. Fats, mostly triglycerides from vegetable origin, constitute the basis for many alimentary products which are familiar to the consumer as margarine, chocolate, ice cream, etc. The polymorphic nature, characteristic of the fats, may affect the physical properties of the product when undesired phase transitions occur. The characterization, by the Differential Scanning Calorimeter (DSC), of the different packings and crystalline forms existent in triglycerides has been extensively treated in the literature (1-14), but less accentuation has been put on the nature of the polymorphic transitions. It is of particular interest to clarify the circumstances and conditions in which the polymorphic tranformations occur, for better control of the undesired phenomena in the industrial products and for a general study on crystallization processes. In this respect thermal analysis is the leading technique for following the polymorphic transformations in fats, which are accompanied by slight enthalpy changes easily detected by the DSC. Moreover, the possibility of programming and controlling temperature regimes enables the evaluation of the consequences of different thermal histories on the polymorphic behavior of fats. The present paper aims to show that the DSC technique is not only an auxiliary tool for identifying the different polymorphs, but also that it is a powerful technique for the study of transition kinetics.

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Phase Transitions

Phase transitions in a solid material imply changes in crystal structure without changes in composition. Phase transitions are affected by both thermodynamic and kinetic factors. The behavior that is observed under equilibrium conditions is determined by the thermodynamics; on the other hand, the rates at which transitions occur, i.e. kinetics, depend on factors such as temperature, impurities and pressure. When the transitions involve crystallization in a different structure, it is controlled mainly by the nucleation step.

In inorganic chemistry the phase transitions are divided into two groups, according to the classification of Buerger (15): reconstructive transitions and displacive transitions. Reconstructive transitions involve a major reorganization of the crystal structure. Since many bonds must break, reconstructive transitions usually have high activation energy. Their occurrence may often be prevented, in which case the untransformed phase is kinetically stable although it is thermodynamically metastable.

Displacive transitions involve the distortion of bonds rather than breaking of bonds and the structural changes are usually slight. This kind of transition has usually a small activation energy and it cannot be prevented.
In polymorphic substances, each polymorph has its own curve of Gibbs free energy as a function of temperature, e.g. G_I and G_{II} (Fig. 1). At a given temperature the polymorph that has the lower free energy is the stable one. For example, according to Fig. 1 the polymorph II is stable below temperature T_t and polymorph I is stable above T_t. T_t is the equilibrium transition temperature at which the free energies of the two polymorphs are equal. At this point:

$$\Delta G = \Delta H - T\Delta S = 0$$

This means that no discontinuity in free energy occurs on passing from one polymorph to the other. But since $\Delta H = T\Delta S \neq 0$, the transition involves discontinuities in volume and entropy, which correspond to the first derivative of the free energy with respect to pressure and temperature:

$$\frac{dG}{dP} = V \qquad \frac{dG}{dT} = -S$$

The change in volume is associated with the change in enthalpy H (according to the relationship $H = U \Delta PV$) which can be detected by thermal analysis.

The transition is easily followed by observing the endothermic and exothermic peaks and is defined as a first-order transition. A second order transition is distinguished by discontinuities in the second derivative of the free energy, mainly in the heat capacity. In this case the transition is less easily detected because the changes involved are usually much smaller. Many order-disorder transitions are second-order transitions.

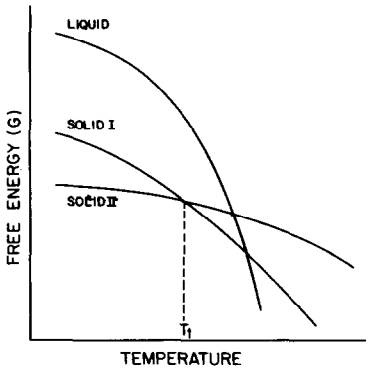

Figure 1 Free energy diagram of an enantiotropic substance.

The entropies of the polymorphs I and II (Fig. 1) are given by the slopes of the curves $-S = dG/dT$. It follows that polymorph II has a higher entropy than polymorph I. It must also have a higher heat content at the transition temperature ($\Delta S = \Delta H/T$). Hence, in order to get a transformation from a low to a high temperature polymorph, the latent heat of transformation (ΔH) must be provided; for this reason, during heating the transformation is endothermic and during cooling it is exothermic.

Phase transitions in triglycerides

The kind of polymorphs represented in Fig. 1 are defined as enantiotropic since their relative stability interchanges according to the temperature. In contrast with an enantiotropic substance polymorphs of triglycerides are monotropic. The characteristic features of such polymorphs are described by the G-T curves in Fig. 2. Through all the temperature range in which the substance remains solid, only one polymorph is thermodynamically stable. This means that the polymorphic transformations occur only in one direction, from the metastable toward the stable forms. The unstable form α is obtained when the melt is quenched to low temperatures; the packing of the long

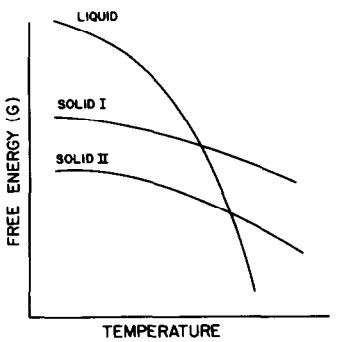

Figure 2 Free energy diagram of a monotropic substance

chain molecules is hexagonal according to the accepted classification in hydrocarbon chain compounds (16). This form, being unstable, transforms spontaneously to a more stable one, with orthorhombic or triclinic packing (respectively β' and β form) according to thermal conditions. This transformation implies a change in the molecular configuration. The decrease in the symmetry of the configuration enables a denser packing of the hydrocarbon chains and causes an increase in the melting point and a change in other physical properties. Transformations to monoacid saturated triglycerides such as trilaurin, tripalmitin or tristearin can be included, in reference to the previous section, in the group of displacive transitions, since the energy of activation is relatively low. Actually most of the physical bonds that hold the crystal lattice are van der Waals bonds. In order to allow the configurational change and recrystallization in another form, these bonds must break; nevertheless these bonds are weak enough to cause a relatively easy transformation. As a disruption of a structure is involved and formation of another structure, the transformations are classified as first order changes.

Enantiotropic and monotropic transformations may show different patterns in behavior. As stated above, an enantiotropic transition is endothermic during heating and exothermic during cooling. The reason must be related to the G-T curve shown in Fig. 1. During heating a lower heat content form transforms to a higher heat content form, and the opposite occurs during cooling.

The monotropic transformation does not always imply an endothermic reaction during heating. This depends on the pattern of the curves I and II, as they are schematically depicted in Fig. 2. In the case of saturated monoacid triglycerides, the transformation during heating involves an exothermic reaction, since the higher stability form has a lower heat content than the transforming form. The exothermic reaction may be accompanied by an endothermic reaction. The endotherm accounts for the energy put into the system for the disruption of the transforming structure (ΔH_t) that is usually interpreted as melting, and the exotherm corresponds to the heat released by the crystallization into the higher form (ΔH_c). If $\Delta H_t + \Delta H_c > 0$ the exothermic value exceeds the endothermic one (according to ICTA convention, the heat released has a positive sign) and the overall reaction is recorded as an exothermic peak.

If the transformation temperature (T_t) is slightly lower than the crystallization temperature (T_c) both an endotherm and an exotherm are recorded.

A typical thermogram of tristearin scanned at the rate of 5°C/min is shown in Fig. 3. The two endothermic peaks correspond to the melting of the α (at 52 C) and β (at 70°C) forms. The exothermic peak corresponds to crystallization from the unstable α into the more stable β polymorph. Clearly, in this case, during the heating the α form melts before transforming into the β form.

The areas under the endothermic peaks can be computed in terms of the enthalpies of fusion of the α and β forms (ΔH_α and ΔH_β) and the area under the exothermic peak can be regarded as the transformation enthalpy. The transformation enthalpy is not an accurate indication of the quantity of heat released from the crystallization to the β form; this is because it probably includes the transition to the metastable β' form, which is not clearly detectable. Similarly, the computed enthalpies of fusion of α and β form cannot be regarded as absolute values since these quantities depend on diverse factors. These factors can be divided into two groups:

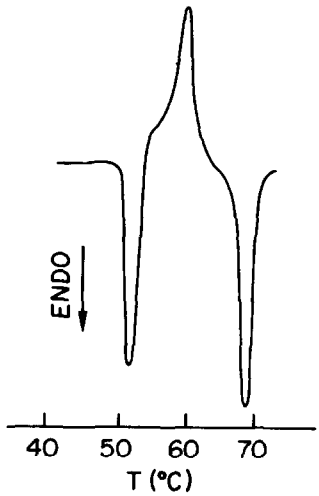

Figure 3 Thermogram of tristearin. Heating rate = 5°C/min.

1) Changes in chemical structure or composition of the triglycerides

2) Changes related to experimental parameters

In this paper the effect of these factors will be shown on the thermograms obtained from saturated triglycerides. The results presented aim to demonstrate the amount of information that can be obtained by thermal analysis about the kinetics of phase transformations in triglycerides.

Effect of chemical structure and composition

The polymorphic and thermal behavior of fats varies according to the chemical structure of the triglyceride, presence of impurities or different components mixed together. A simple comparison can be made among monoacid triglycerides with different chain lengths.

Triglycerides with chain lengths ranging from 12 to 18 carbons are considered isomorphous in the literature (17). In spite of this structural similarity, these triglycerides differ in their polymorphic behavior. Comparison of the thermograms of trilaurin (C_{12}), trimyristin (C_{14}), tripalmitin (C_{16}) and tristearin (C_{18}) shows the difference in the thermal behavior of these triglycerides (Fig. 4).

The thermogram of tristearin shows one single exothermic peak while the lower triglycerides display in their thermograms a split exotherm. This latter behavior indicates clearly the transformation and partial melting of β', immediately followed by the β transformation. It is reported in the literature (1) that in monoacid triglycerides with chain length lower than 18 carbons the orthorhombic packing is relatively stable and can be detected during the temperature scan. The absence of any β' melting detection in tristearin suggests that the β' form in this triglyceride is kinetically very unstable. The reason for this is not yet clear, but is probably related to the effect of end-group interaction on the stability of the crystal form (1).

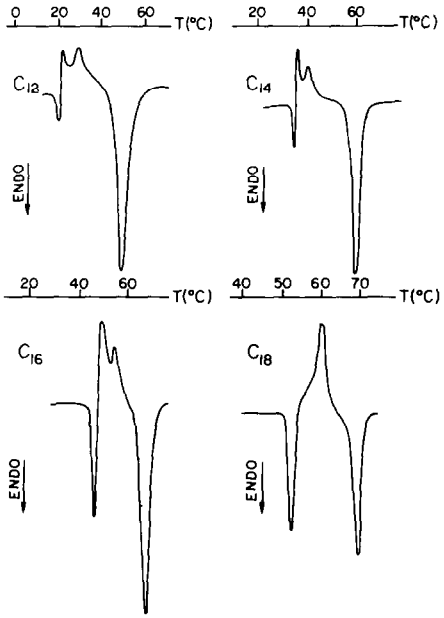

Figure 4 DSC heating curves of saturated triglycerides. C_{12} = triluarin (heating rate: 20°C/min), C_{14} = trimyristin (heating rate: 10°C/min), C_{16} = tripalmitin (heating rate: 10°C/min), C_{18} - tristearin (heating rate = 5°C/min).

If we consider the α-β transition as the overall transformation that occurs during the scan, we can use the computed ΔH_α and ΔH_β values as quantitative estimates of the amount of α and β forms that undergo melting. In the case of β form it is an indication of the extent of transformation, while in the case of α it is associated to the mechanism of transformation. When a small endothermic value of α form, followed by a high β endotherm, is recorded, it implies that the α-β transition occurs when only a small portion of the α form melts. In other words, it can be suggested that a high portion of the fat transforms to the solid state without any detectable endothermic reaction.

This is the main feature that distinguishes the thermal behavior of tristearin from that of trilaurin. It can be seen in Fig. 4 that the thermogram of tristearin displays a high endothermic value of α fusion while in trilaurin the α endotherm is small. This difference in the thermogram patterns reflects the difference in the thermal behavior of these two triglycerides. The α form of tristearin, in these experimental conditions, evidently melts before crystallization to the β form, whereas in trilaurin a high portion of the fat transforms through the solid phase. The difference in transformation mechanism is due to the different equilibrium between hydrophilic and hydrophobic interactions. In the crystallization pattern of tristearin the interactions among the chains are more influential than in trilaurin and the presence of the long aliphatic moiety obstructs the direct transformation. In trilaurin the stability of the α form is low, since the aliphatic interactions are less influential.

The presence of certain additives, namely surfactants, stresses the difference between the polymorphic behavior of these two isomorphous triglycerides. These additives have been shown to affect the ΔH_α and ΔH_β values of the triglycerides, when they were scanned in the same experimental conditions reported above.

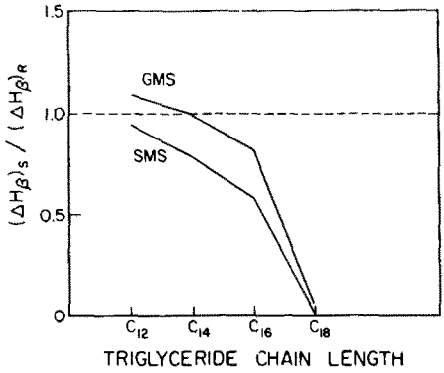

Figure 5 Plot of ratio $\Delta H_{\beta_S} / \Delta H_{\beta_R}$ of trilaurin (LLL), trimyristin (MMM), tripalmitin (PPP) and tristearin (SSS) in the presence of sorbitan monostearate (SMS) and glycerol-1-stearate (GMS).

The change induced by the presence of the surfactants on the thermograms, was expressed in terms of the ratio between the fusion enthalpy of the triglyceride with the additive (ΔH_s) and the fusion enthalpy in the neat triglyceride (ΔH_R). The effect of the surfactants was found to be dependent on their hydrophilic moiety structure as well as on the thermal properties of the triglyceride. In Fig. 5 the effect of two solid surfactants on ΔH_β of the different triglycerides is shown. These surfactants, which were added at the level of 10 wt%, were sorbitan monostearate (SMS) and glycerol-1-stearate (GMS). They both have a long hydrocarbon chain but differ in their hydrophilic moiety.

Their presence affects differently the ΔH_β of tristearin and trilaurin. As can be seen in Fig. 5, both surfactants reduce to zero the ΔH_β of tristearin suggesting that the transformation is completely suppressed by these two additives. On the other hand, the ΔH_β of trilaurin is not affected, indicating that the β crystallization occurs despite the presence of the additives.

The effect of these two additives on ΔH_α values displays a completely different feature (Fig. 6). The fusion enthalpy of tristearin is not affected significantly by the presence of the two surfactants; however, the ΔH_α of trilaurin is drastically affected. In the presence of SMS, ΔH_α is increased twice in its value; and in the presence of GMS ΔH_α is nullified.

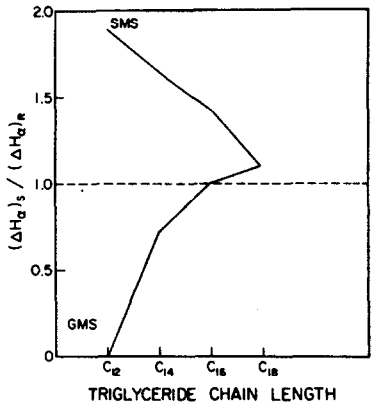

Figure 6 Plot of ratio $\Delta H_{\alpha S} / \Delta H_{\alpha R}$ of trilaurin (LLL), trimyristin (MMM), tripalmitin (PPP) and tristearin (SSS) in the presence of sorbitan monostearate (SMS) and glycerol-1-stearate (GMS).

From these results it can be seen that the surfactants, in addition to controlling the kinetics of transformation according to the nature of the polymorphic behavior, also affect oppositely the fusion enthalpy of the α form in trilaurin in a different way.

These results can be explained by considering the different mechanisms of polymorphic transformations in the two triglycerides. The emulsifier's presence prevents the β crystallization which is determined mainly by hydrophobic interactions. This case is represented by tristearin, in which the surfactant probably interferes with the packing of the hydrocarbon chains regardless of the structure of the hydrophilic moiety. The case of trilaurin is quite different since most of the fat transforms from α to β directly. Here the influence of the surfactant is strictly associated with the hydrophilic moiety: SMS hinders the solid-solid transformation causing the fat to melt before transforming to β, while GMS enhances this transformation.

From the results presented above, it is clear that the presence of the surfactant affects the kinetics of the polymorphic transformation, without influencing the thermodynamic aspect of the transformation, and the specific polymorph obtained. Fig. 7 shows thermograms performed at the rate of 5 C/min of neat tristearin (A), tristearin in the presence of SMS 10 wt% (C) and a mixture of tristearin and tripalmitin at the rate 90:10 (B). Thermogram A shows the melting of the α form and the transformation to the β form. Thermogram C shows the depression of the transformation caused by the presence of the emulsifier. Differently, thermogram B shows the appearance of an additional peak which most probably corresponds to the intermediate β' form. This is in accordance with the statement found in the literature (1) concerning the stabilization of the β' form in mixtures of triglycerides with different chain lengths. Comparison of the three thermograms stresses the difference of the effects caused by the addition of emulsifier and tripalmitin: while the presence of the surfactant does not influence the polymorphism of tristearin, in the presence of tripalmitin the intermediate β' form is apparently stabilized. This is a clear demonstration that the emulsifier interferes with the kinetic process of transformation, but does not dictate the polymorphic behavior.

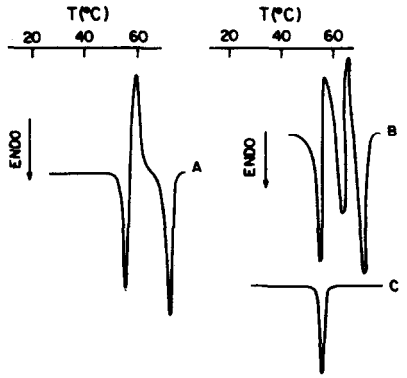

Figure 7 Thermograms at 5°C/min heating rate of A) neat tristearin, B) tristearin with 10 wt% tripalmitin added, C) tristearin with 10 wt% sorbitan tristearate (STS) added.

The effect of triglycerides of different chain lengths on the stabilization of the intermediate β' form is emphasized in mixtures with varying composition (Fig. 8). The two components, which are compatible, were well-mixed in the molten state and quenched before each experiment; hence it is reasonable to assume that one mixed crystal was formed for each mixture. It follows that the extent of formation of the β' form depends on the composition of the mixture. As the ratio of tripalmitin increases the β' endotherm becomes larger while the β endotherm becomes smaller. This is an indication that the difference in the chain length of the component triglycerides improves the kinetic stability of the form. As pointed out previously, in triglycerides with hydrocarbon chains shorter than 18 carbons, the β' form is stable enough to be detected during the scan; in addition, it has also been shown that the transformation endotherms are smaller in lower triglycerides.

This last feature is accentuated by the comparison of the mixtures tristearin - tripalmitin (Fig. 8) and tripalmitin - trimyristin (Fig. 9). In the latter mixture the endothermic values for transformation are relatively low. This confirms the assumption that in lower triglycerides (neat or in mixtures) a higher part of the fat transforms through the solid state.

Up to now it has been established that the triglyceride chemical structure and composition can influence the thermogram obtained. The next section deals with the influence of experimental parameters, such as heating and cooling rate, on the thermograms obtained in the same triglycerides.

Effect of experimental parameters

The heating rate is a decisive parameter which can determine the extent and mechanism of polymorphic transformation.

The values of ΔH_α and ΔH_β of tristearin change when the α form is heated at different heating rates. Fig. 10 shows the plots of ΔH_α and ΔH_β as a function of

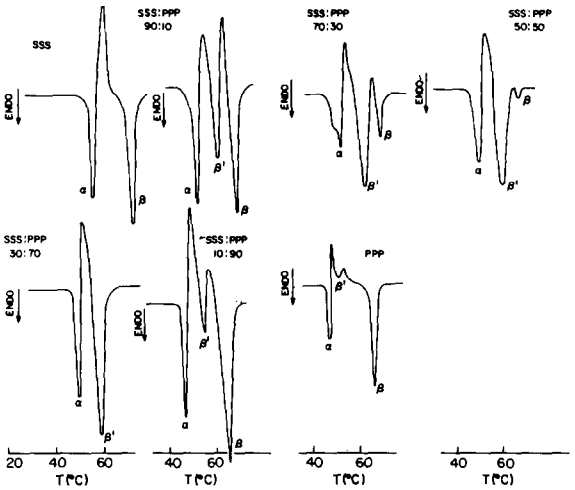

Figure 8 Thermograms at 5°C/min heating rate of mixtures of tristearin (SSS) and tripalmitin (PPP) at different ratios.

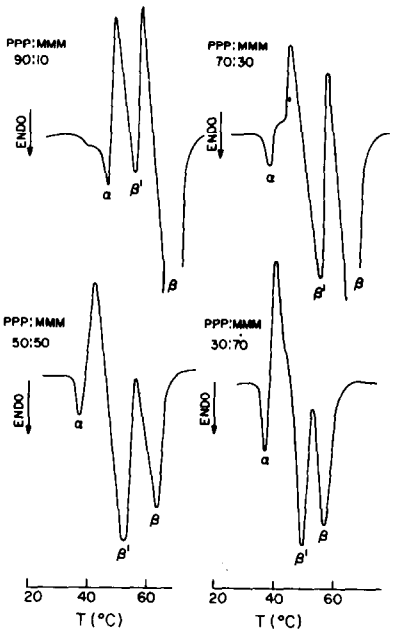

Figure 9 Thermograms at 10°C/min heating rates of mixtures of tripalmitin (PPP) and trimyristin (MMM) at different ratios.

heating rate. It can be seen clearly that the $\Delta H_{\beta'}$ values decrease as the heating rate decreases while the ΔH_{β} values increase. The plot of ΔH_{β} as a function of heating rate 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 at low heating rates the drop in ΔH_{β} is moderate, but at high heating rates the decrease in ΔH_{β} is sharper.

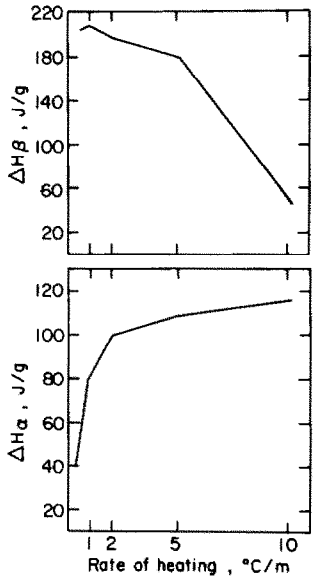

Figure 10 ΔH_α and ΔH_β values of tristearin at different heating rates.

The ratio between the portion of α which melts and the portion of β which crystallizes varies when applying the different heating rates. As already pointed out in the previous section, two processes may take place during the heating of the form: one is the direct transformation without an endotherm detection and the other one is melting and recrystallization to the β form (Fig. 10). The factor determining which of the two possibilities is the preferred one, (excluding the triglyceride type), is the rate of heating. A high heating rate will prevent the crystallization of β, as was observed at 10°C/min. 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 the melting process.

In conclusion, at relatively high heating rates, the polymorphic transformation occurs predominantly in the melt phase, while at lower 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. 11). At a 5°C/min heating rate, in the presence of SMS, GMS and citric acid ester of glycerol monostearate (CGMS) the crystallization is entirely inhibited, even if under the same conditions pure tristearin crystallizes almost completely to the β form. When heating was slower the retardation effect of the surfactant was less significant; at the rate of 2°C/min only 20% of the 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.

The cooling rate is also a parameter which can affect the rate of transformation. The thermal history can determine the crystalline form which solidifies and in the case of mixtures, it affects the co-crystallization of the components. If two components are not compatible, the change in the crystallization rate can affect the homogeneity of the solid mixture obtained.

One indication of different compatibilities between emulsifiers and tristearin is given by testing the inhibition of crystallization after different rates of cooling. The α-β transformation in tristearin was performed at a constant rate of 5°C/min after different rates of cooling for α crystallization prior to the start of the experiment. Fig. 12 presents the ΔH_β values of tristearin with different emulsifiers added, as functions of the prior cooling rate. While in neat tristearin the ΔH_β value does not change as a function of cooling rate, in the presence of most solid surfactants the decrease in ΔH_β value depends on the cooling rate. After slow cooling the β crystallization is less inhibited than after fast cooling. On the contrary, in the presence of SMS the prevention

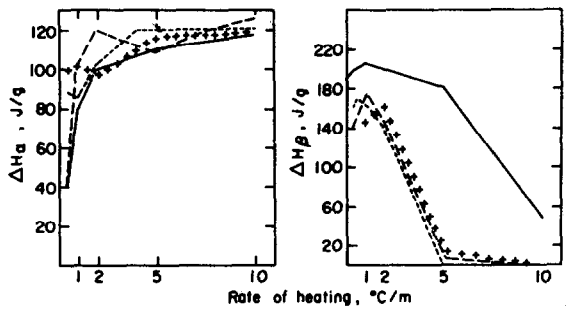

Figure 11 ΔH_α and ΔH_β values of tristearin (——) in the presence of SMS (– – –), CGMS (###) and GMS (— —), 10 wt%.

of β crystallization is, in the same experimental conditions, maximal. This can be interpreted as higher structural affinity of SMS to the triglyceride than the other solid surfactants. Presumably, during slow cooling the less compatible surfactants aggregate into clusters and then decrease their effect. On the other hand, it seems that the performance of SMS is not affected by the previous

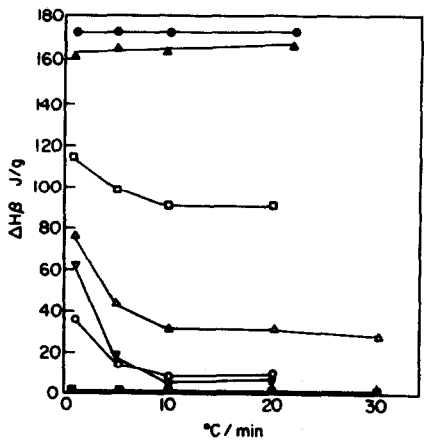

Figure 12 ΔH values of β-form in tristearin transformed from α at the heating rate of 5°C/min, as a function of cooling rate from melt prior to the experiment. ● = neat tristearin, ▲= with SML added, □ = with SMP added, △= with CGMS added, ▽ = with 3G1S added, ○ = with GMS added, ■ = with SMS added.

solidification rate since the molecules most probably do not form clusters even during slow cooling. The particular structural affinity can be further sustained by Cp measurements (18) and phase diagrams (19). In such a way the DSC technique enabled us to create a hypothesis on interaction between the emulsifier and the fat.

CONCLUSIONS

In the present work DSC was employed in order to follow the polymorphic transformations in triglycerides. This technique has demonstrated its effectiveness in estimating the extent of transformation and the mechanism of transition. On the basis of enthalpy measurements, it has been shown that the chemical structure of the triglyceride and the presence of additives influence the kinetics of transformation. Moreover, the thermal history and rate of scanning were also proved to be decisive factors in affecting the process of transition. On the other hand, in a mixture of neat triglycerides the intermediate β' form seems to be stabilized in addition to α and β.

In contrast to the other effects, this is a thermodynamic influence, probably due to the stabilization of the orthorhombic packing when triglycerides with different chain lengths are mixed together. These observations are highly relevant to the use of fats in the alimentary industry and can be considered fundamental concepts for better understanding the thermal behavior of natural fats.

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