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## Phase transitions of saturated triglycerides

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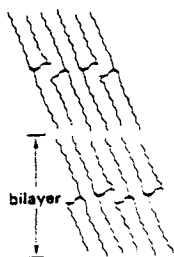
### ABSTRACT

The  $\alpha \rightarrow \beta$  phase transition of Tristearin (SSS) has been investigated both by Differential Scanning Calorimetry and Small Angle X-Ray Diffraction as a function of temperature at the same heating rate ( 2 deg/min ) in order to elucidate either this transition occurs in the solid state or is melt mediated.

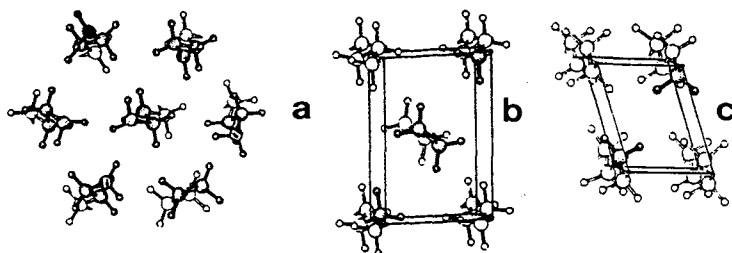
### INTRODUCTION

Triglycerides display a complex monotropic polymorphism. They frequently exhibit from 3 to 6 crystalline varieties, the occurrence of which depends on the nature of the fatty acid chains esterified on the glycerol molecule, crystallization procedure (melt cooling or solvent mediation), and samples purity. These crystals are made by the stacking of triglyceride layers, the thickness of which depends on the length and insaturation of the fatty acid chains, and their angle of tilt with respect to the basal planes formed by the methyl end groups (figure 1). These thicknesses, also called "long spacings", can be measured by Small Angle X-Ray Diffraction at  $0 < q < 0.9 \text{ \AA}^{-1}$ . The lateral packing of the aliphatic chains (crystalline subcell) (figure 2) is characterized by "short spacings" at  $0.9 < q < 1.8 \text{ \AA}^{-1}$ .

Transitions between these polymorphic varieties are irreversible and only possible when leading to the formation of more stable species (monotropism). The very fast kinetics observed for transitions between short chain compounds didn't allow to decide whether true melting takes place or whether the transitions occur in the solid state [1]. However, monotropism implies that these transitions occur via the melting of the most stable species. In order to investigate these mechanisms, slower transitions between polymorphic species of a long chain triglyceride (tristearin:SSS) have been studied. One of them will be presented here.



**Figure 1** - Examples of bilayer triglyceride packings (long spacings).



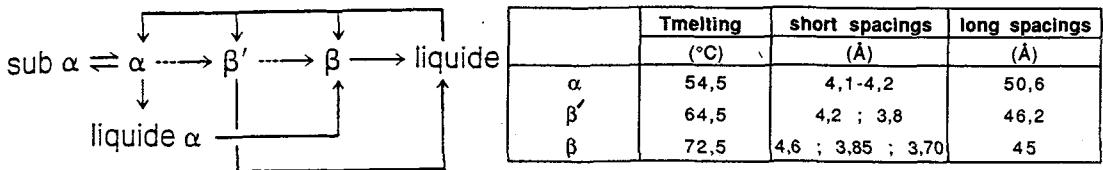
**Figure 2** - Schematic representation of possible chain packings of long chains compounds: (a) Hexagonal packing, (b) Orthorhombic packing ( $O_2$ ), (c) Triclinic packing ( $T_1$ ). (short spacings).

## MATERIAL AND METHODS

Tristearin has been synthesized and purified at the laboratory (purity 99.9 %) [2].

The  $\alpha \rightarrow \beta$  transition is recorded by DSC (DSC-4 Perkin-Elmer calorimeter) at a heating rate of  $+2^\circ\text{C}/\text{min}$ . 10 mg of melted tristearin is placed in a sealed aluminium pan and rapidly quenched from  $90$  to  $20^\circ\text{C}$  to get  $\alpha$  form.

For X-Ray Diffraction,  $\alpha$  form has been prepared by rapid quenching of the melt from  $90^\circ\text{C}$  to  $5^\circ\text{C}$ . 20 frames of 45 seconds are recorded as a function of temperature in the  $q=0.005 \text{ \AA}^{-1}$  ( $\Theta=0.04^\circ$ ) to  $q=1.855 \text{ \AA}^{-1}$  ( $\Theta=13.73^\circ$ ) range using D24 high flux of L.U.R.E as X-Ray source ( $1.608 \text{ \AA}$ ), while heating at  $2 \text{ deg}/\text{min}$  the sample contained in a thin capillary tube  $1.4\text{mm}$ ,  $0.01\text{mm}$  walls. Heating is monitored by Eurotherm 902P temperature controller using  $2 \times 0.2 \text{ mm}$  type E thermocouple as a sensor. In order to minimize the temperature deviations from linear increase versus time during heating, thermocouple was located between the sample and the heating device rather than very close to the sample. The thermal gradient created by this set-up resulted in a temperature lag between recorded and sample temperature which has been evaluated to be about  $+1^\circ\text{C}$ . A 1024 channels gas-filled one-dimensional position sensitive detector is used for data collection.



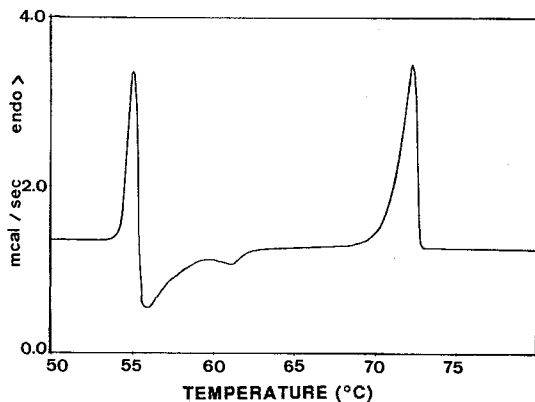
**Figure 3** - Transitions between polymorphic varieties of SSS.

**Table 1** - Thermal and structural features of SSS polymorphs [3].

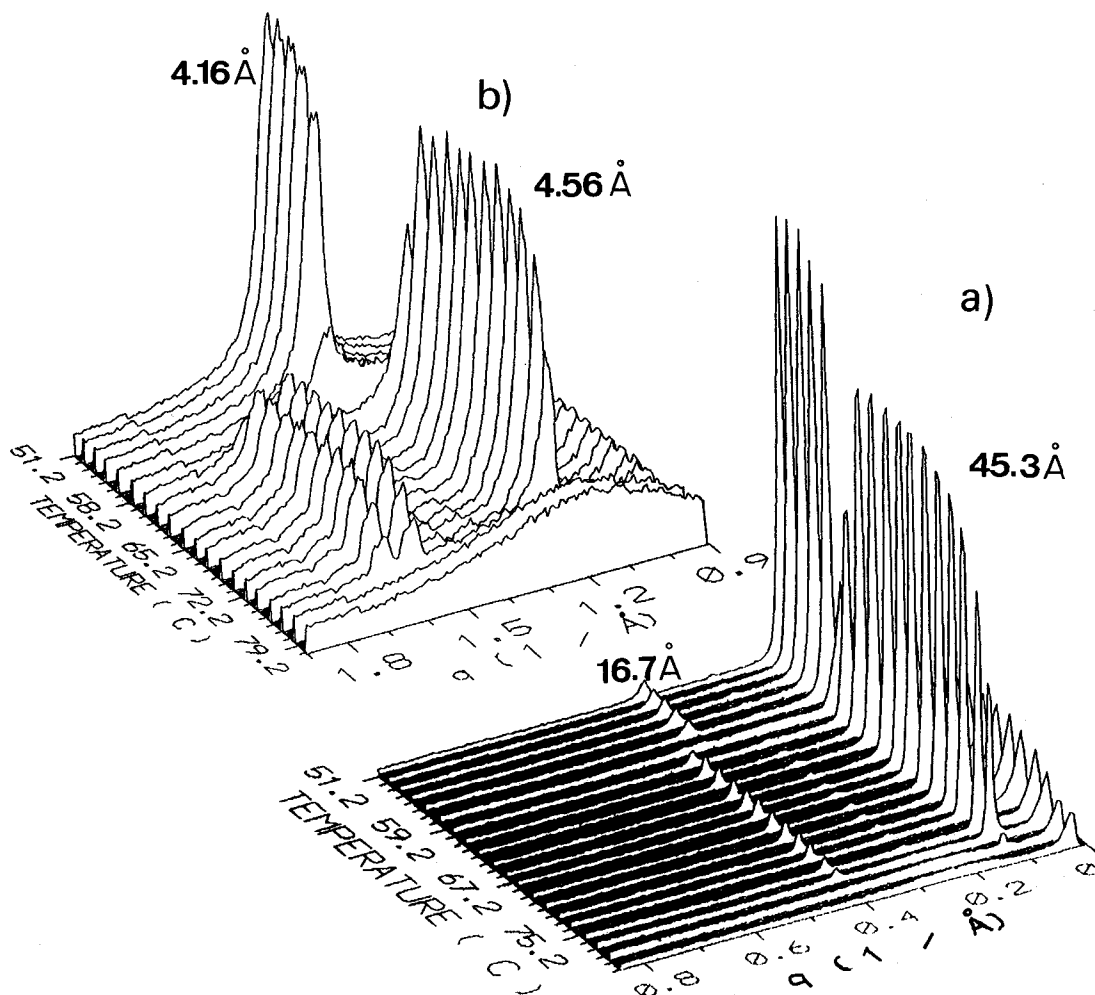
## RESULTS AND DISCUSSION

Trisaturated triglycerides generally crystallize under 3 main polymorphs called  $\alpha$ ,  $\beta'$ , and  $\beta$ . Alpha, which is the less stable form, is obtained by rapid quenching of the melt. Chains are vertical and hexagonally packed with almost statistical orientation. The slow melting of this unstable species leads to the formation of the most stable variety  $\beta$ , the subcell of which is triclinic parallel ( $T_{//}$ ), while annealing of the supercooled liquid down to close to the melting point of  $\alpha$  yields  $\beta'$  species. This last exhibits a melting point intermediate between  $\alpha$  and  $\beta$  and orthorhombic perpendicular ( $O_{\perp}$ ) subcell. Both  $\beta'$  and  $\beta$  present tilted chains. The main features of these SSS polymorphs are summarized in Table 1 [3]. Possible transitions between SSS polymorphs are summarized in figure 3. The process of  $\alpha \rightarrow \beta$  transition of SSS has been investigated by both X-Ray Diffraction and Differential Scanning Calorimetry as a function of temperature at the same heating rate.

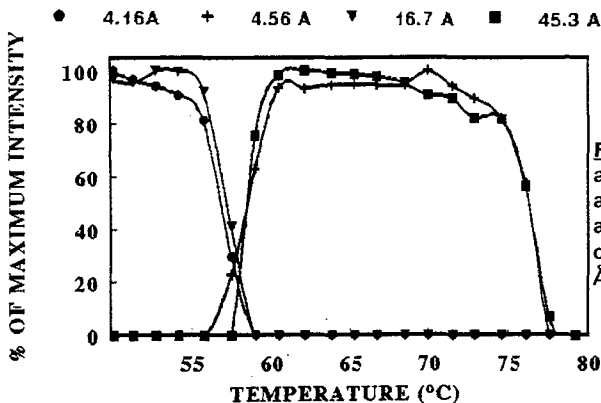
Figure 4 represents the  $\alpha \rightarrow \beta$  transition of SSS recorded at  $2 \text{ deg}/\text{min}$  by DSC. The melting of  $\alpha$ , which starts at  $53.4^\circ\text{C}$  (max:  $54.9^\circ\text{C}$ ), is immediately followed by a broad exotherm spreading until about  $64^\circ\text{C}$ . The overlapping of  $\alpha$  melting and subsequent  $\beta$  recrystallization results in a complex recording in which both events partially neutralize each other. The small exothermic bump observed at about  $61^\circ\text{C}$  corresponds to the melting of some  $\beta'$  variety transiently formed between  $55$  and  $61^\circ\text{C}$  and its subsequent and immediate recrystallization into  $\beta$ . The melting of this last polymorph finally occurs at about  $71^\circ\text{C}$  (max:  $72.1^\circ\text{C}$ ).



**Figure 4** - DSC recording of  $\alpha \rightarrow \beta$  transition of SSS. Heating rate = 2 deg/min.



**Figure 5** - Evolution of long (a) and short (b) spacings during the  $\alpha \rightarrow \beta \rightarrow$  liquid transitions of SSS. Heating rate = 2 deg/min. Short and long spacings are presented as 3D plots versus temperature.



**Figure 6** - Distribution of the different polymorphs as a function of temperature as obtained by the analysis of peak intensities corresponding to long and short spacings of figure 5. 4.16 and 16.7 Å correspond to  $\alpha$  polymorph while 4.56 and 45.3 Å are characteristic distances of  $\beta$  polymorph.

Figures 5a and 5b show the dynamic diffraction patterns corresponding to the  $\alpha \rightarrow \beta$  transition of SSS heated in the same conditions than for DSC measurements. Below 55°C, short spacings indicate a single sharp peak at 4.16 Å characteristic of  $\alpha$  subcell, while long spacings pattern show a main diffraction line at 50.1 Å with its second and third orders (25.7 and 16.7 Å respectively). From 53.8 to 58.5°C, intensities of the 16.7 and 50.1 Å peaks simultaneously vanish as shown by figure 6, while a new set of long (45.3 Å ( $n=1$ )) and short (4.6, 3.9, and 3.8 Å) spacings appears and is close to previously observed values for  $\beta$  SSS (table 1). This temperature range of  $\alpha$  melting correlates nicely with the DSC recording (taking account of the thermal lag, see Material and Methods). As shown by figure 6, intensities of these new peaks increase from 60°C and reach their maxima around 62°C, which is in good agreement with the temperature range of the recrystallization exotherm of figure 4. This overall  $\alpha \rightarrow \beta$  transition is similar to those recently reported for PPP by KELLENS et al. [4].

Final melting of  $\beta$  form starts at around 70°C for short and long spacings, and at 78°C broad diffusion peaks of the melt can be seen in both figures, corresponding to an incomplete disorganization of the liquid state. One can notice in figure 5a that the same diffusion pattern appeared between the melting of  $\alpha$  form and recrystallization of  $\beta$  form, which supports the hypothesis of solid-liquid-solid polymorphic transitions of triglycerides. Moreover, the recording by DSC of an endothermic peak before the exotherm corresponding to the formation of  $\beta$  clearly indicates that  $\beta$  recrystallizes from  $\alpha$ -melt rather than directly from  $\alpha$  itself.

## CONCLUSION

Small Angle X-Ray Diffraction using synchrotron high intensity beam allowed us to observe dynamically phase transitions of SSS. Differential Scanning Calorimetry recordings nicely correlate observed phase changes. Moreover, it seems that saturated long chain triglycerides exhibit solid-liquid-solid transitions instead of the apparent solid-solid phase changes of short chains compounds. Similar study on unsaturated long chain triglycerides should be very useful in trying to understand their much more complex polymorphism.

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