Kinetics of Melt Crystallization and Transformation of Tripalmitin Polymorphs

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The rates of melt crystallization and phase transformation of three polymorphs of tripalmitin were examined by optical microscopy, X-ray diffractometry and DSC with and without surfactant additives (sorbitan mono- and tristearates). The following results were obtained: (a) Crystallization rate increased in order of α, β' and β; (b) transformation rate was slower than crystallization rate for each polymorph at the same temperature examined; (c) when the most stable β form was recrystallized from the melt just after the melting of α, its recrystallization rate was much higher than that by simple melt-cooling; (d) surfactant additives retarded both the crystallization and transformation of all the polymorphs, yet β' was influenced the most. A mechanistic interpretation based on the molecular structures both of the melt and of each polymorph is presented.

The utilization of solid triglycerides has encountered complicated problems originating from the existence of a variety of specific crystalline forms: polymorphism. Polymorphism has considerable influence on the fluidity, texture and appearance of the products (1), coming from a multiplicity of molecular conformations and packings of long-chain glycerides in crystals (2).

Recent systematic studies have established the existence of α, β'_1, β'_2 and β forms of triglycerides composed of monosaturated fatty acid moieties (3-5). It appears that thermodynamic stability and monotropic transformation circuits among the above polymorphs have been clarified. The crystal structures of the most stable β form also were reported (6,7). Although the information on the polymorphs of the mixed-acids triglycerides, and on the detailed structures of the metastable α and β' forms, is still open to discussion, the thermodynamic properties of mono-acids triglycerides are better understood (8,9).

However, the kinetic aspects of the crystallization and transformation of the triglyceride polymorphs have been lacking, despite the fact that the kinetic processes have a great effect on the production processes. Malkin speculated (10) that the activation energy for the melt-crystallization increases in the order of α, β' and β, resulting in the highest crystallization rate of α. Precise measurements on the growth rate from the melt (11) and from the solution (12) were carried out, but only on the most stable β form. Dafler reported on fully hydrogenated soybean oil (13) that the transformation rates of $\beta' \rightarrow \beta$ are highly dependent on the mode of the melt crystallization. The effect of cooling rate on the appearance of α, β' and β from melts was examined by Hernqvist (14). Very recently, the crystallization of tripalmitin and tristearin with a mixture of triolein revealed complicated solidification features (15). Despite these studies, quantitative measurements may be lacking for the kinetics of the crystallization and transformation of every polymorph. It is noteworthy to stress that phase transformations and crystallization occur in a conflicting way.

We report here the precise measurements of the crystallization rate of three polymorphs of α, β' and β of tripalmitin from the melt, while determining the rates of the phase transformations with similar heat treatments of the crystallizations. The effects of surfactant additives on the above two kinetics also were examined. Despite many studies on the surfactant effects on the polymorphic transformation of fats (16-18), no quantitative measurements on crystallization rates have been available.

TABLE 1

The Rates of Melt Crystallization (τ) of α,β' and β, Solid State Transformations of $\alpha \rightarrow \beta$ and $\beta' \rightarrow \beta$, and Recrystallization of β from α-melt (melt mediated transformation) of Tripalmitin

	Temperature					
	42	44	46	48	50	52
melt→polymorph (τ)	13 sec[a] (α)	16 sec[a] (α)	70 sec (β')	2 min (β')	4 min (β')	6 min (β)
$\alpha \rightarrow \beta$						
solid state	90 min	60 min	—	—	—	—
melt-mediated	—	—	20 sec[a]	22 sec[a]	25 sec[a]	30 sec[a]
$\beta' \rightarrow \beta$						
solid state	—	2 hr	50 min	30 min	15 min	10 min

[a]A time constant of the growth cell was about 50 seconds.

MATERIALS AND METHODS

Tripalmitin (99%) was purchased from Sigma Chemical Co., St. Louis, Missouri. No further purification was done. We added 5 wt% sorbitan monostearate (span 60) and sorbitan tristearate (span 65). The melting points of the three polymorphs were measured by DSC (Rigaku: DSC-8230) at a heating rate of 5 C/min; α = 45 C, β' = 57 C and β = 66 C, which exhibit good agreement with previous data. We here refer to β', although it was named β_1' by Hagemann et al. (3).

The rate of crystallization of each polymorph was measured as follows: The sample was placed on a growth cell, which was covered with a glass (5 mm wide and 2 mm thick), in contact with thermostated water (±0.1 C). To rapidly change the temperature of the growth cell, we used two thermostats, one for melting and another for crystallizing with a switching circuit. The temperature of the sample was monitored with a thermocouple which was buried in an adhesive (alaldite) very close to the sample. After melting the samples at 90 C for several minutes, the temperature was cooled down to the crystallization temperature. The time constant of the growth cell was at most 50 seconds. The appearance of the crystals in the undercooled melt was detected by a cross-Nicols optical microscope (× 40). We measured a duration (τ) until the appearance of the crystal was detected in the supercooled melt after the crystallization temperature was reached. In parallel with the crystallization experiments, the polymorphic modifications of the first crystals to appear were determined by using a glass plate employed for X-ray diffractometry (Rigaku, Cu-K_α, Ni-filtered). Just after the crystallization with the same heat treatments quoted above, the sample was cooled and subjected to X-ray measurement below 15 C so that the solid-state transformation was actually blocked.

Then, the transformation rates in the solid-state for $\alpha \rightarrow \beta$ and $\beta' \rightarrow \beta$ were examined at different temperatures. The transformation was followed by measuring the relative intensity of the specific X-ray diffraction spectra for the short spacing; α(d = 4.15 A), β'(d = 4.23 A) and β(d = 4.60 A). For $\alpha \rightarrow \beta$, α was obtained by rapidly cooling the melt to 0 C; then the temperature was raised rapidly to 42 and 44 C to induce the transformation into β. As for $\beta' \rightarrow \beta$, β' was solidified from the melt at 47 C, then kept at 44 ~52 C. In addition to the solid state transformation, we measured the rate of occurrence of the most stable β form from the melt which was formed by rapid heating (20 C/min) of the α form up to 46~52 C. This kind of transformation may be called "melt-mediated transformation." Then we measured the duration for the appearance of β.

Finally, the effects of surfactants both on the crystallization and transformation kinetics were examined under thermal conditions similar to those of the pure materials.

RESULTS

Crystallization. The typical τ values of the crystallization and the rate of transformation at different temperatures are summarized in Table 1. Because the crystallization of α was so rapid, τ values became shorter than the time constant of the growth cell even at the highest temperature examined. As a measure of the crystallization rate $1/\tau$ for each polymorph is plotted in Figure 1. From this, the following conclusions were drawn:

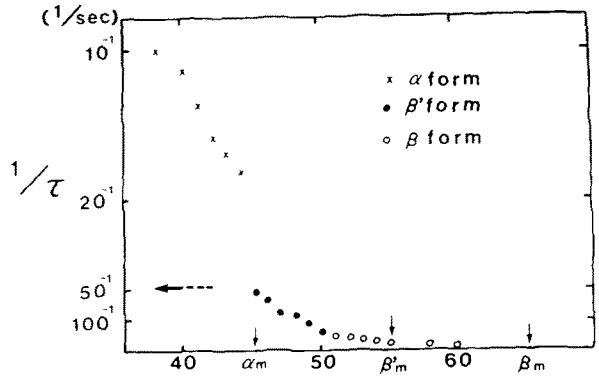

FIG. 1. An inverse of induction time (τ) for melt crystallization of α, β' and β polymorphs of tripalmitin. Melting points of the three polymorphs are denoted by arrows. A time constant of the growth cell is indicated by a broken arrow.

(a) $1/\tau$ increases in the order of β, β' and α. It must be noticed that the slope of $1/\tau$ vs temperature curve is also dependent on the polymorph. Because τ for α obtained in the present study was always shorter than the time constant of the growth cell, it is reasonable to infer that the actual values for $1/\tau$, especially at lower temperatures, may be larger than those displayed in Figure 1.

(b) α starts to crystallize just below its melting point (α_m) with no appreciable supercooling.

(c) In a range of temperatures between α_m and β'_m, β' occurs in a lower temperature range, whereas β prevails at higher temperatures.

(d) β grows exclusively above 57 C.

Transformation. The rates of the solid state and melt mediated transformations also are shown in Table 1. The rates of the solid state $\alpha \rightarrow \beta$ and $\beta' \rightarrow \beta$ transformations increase with increasing temperature, being lower for $\beta' \rightarrow \beta$ than for $\alpha \rightarrow \beta$ at 44 C. A comparison between τ and the solid state transformation rate proves that the rate of the crystallization of every polymorph is always higher than that of the transformation into the more stable forms at the same temperature. In constrast, two peculiar features are noticeable for the melt mediated transformation. First, β appears after α-melting, despite the fact that β' was solidified at 46~50 C when the pure melt was cooled from high temperatures. Second, it is undoubtedly clear that its rates are surprisingly higher than both the solid state transformation and pure-melt crystallization, although the melt mediated transformation occurred in shorter times than the constant of the growth cell. Furthermore, the rate of melt-mediated $\alpha \rightarrow \beta$ transformation decreased as the temperature approached β_m.

Surfactant effect. The addition of span 60 and span 65 at 5 wt% had a remarkable influence on the crystallization, as shown in Figure 2, in which the data for β' and β are displayed. The melt crystallization of all three polymorphs was retarded, yet β' was affected more than the other two forms. This results in a decrease in the

range of temperature at which only β' was solidified in comparison to the pure sample, as illustrated in Figure 2.

DISCUSSION

The present data demonstrate that the rate of crystallization is highest for α, intermediate for β' and lowest for the most stable β form. The τ values may involve two induction times; one is for formation of crystal nuclei in the supercooled melt, and another is for growth of the nuclei until the optically detectable crystal size is achieved (19). We have no clear way to discriminate between these two parameters. However, it may not be unreasonable to infer that the controlling step in the present crystallization process may be nucleation. The nucleation function (19) involves two dominant factors of supercooling (ΔT) and an activation free energy for formation of the nuclei ($\Delta G\#$). These two parameters interact in a conflicting way; the larger ΔT and the smaller $\Delta G\#$, the higher the nucleation rate. The results obtained here are quite contradictory to the influence of ΔT, which is largest for β but smallest for α at all crystallization temperatures. This means that $\Delta G\#$ increases on the order of α, β' and β, and therefore the difficulty of nucleation becomes greater for β (10).

The physical meaning of the $\Delta G\#$ difference may be discussed by taking into account the melt as well as the crystal structures. It has been pointed out (20-22) that the triglyceride molecules are associated together in the melt phase. The hydrocarbon moieties are likely to be randomized, but a partial ordering of the glycerol groups, due to their stronger interactions, may form a disc-like lamellar structure.

Next we consider the molecular conformations and packings in the crystal of each polymorph. The α form has been reported to reveal a freedom of molecular motion with the most loosely packed hexagonal subcell structure (2, 20-22). Instead of such a rotational freedom of the whole carbon chains as in n-paraffin crystals just below the melting points (21), a torsional oscillation of carbon atoms close to the chain-end groups has been proposed (20, 22, 23). Even a smectic liquid crystalline structure is suggested (24). This feature of α has been evidenced by Raman spectra (25) and by spin-lattice relaxation time of high-resolution NMR (15). As an indirect proof, non-alternative melting feature of α between even and odd chain lengths seems to support this model (3). On the contrary, β' and β are of an extended chain conformation with orthorhombic and triclinic subcell structures, respectively. Although the detailed structure of β' is not established, the molecular conformations of β' may be roughly similar to those of β with all-*trans* conformation (6,7). No drastic change from β' to β in the molecular conformation was detectable (5). Thus, it is reasonable to consider how α crystallizes most readily. Due to its higher molecular flexibility and loose packing, thermal activation processes involved in the rearrangement of the molecules from the melt to the crystal may be minimized for α.

Above α_m (45 C), the crystals appearing first from the undercooled pure melt were β' between α_m and 51 C,

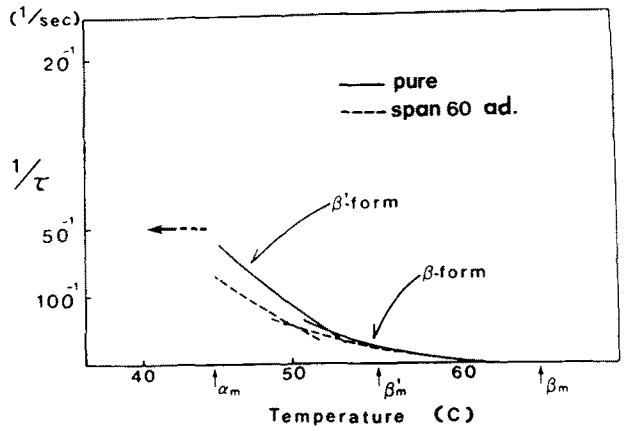

FIG. 2. An inverse of induction time (τ) for melt crystallization of β' and β polymorphs of tripalmitin with an additive of 5 wt% sorbitan monostearate (span 60). Pure material data of Fig. 1 also are displayed.

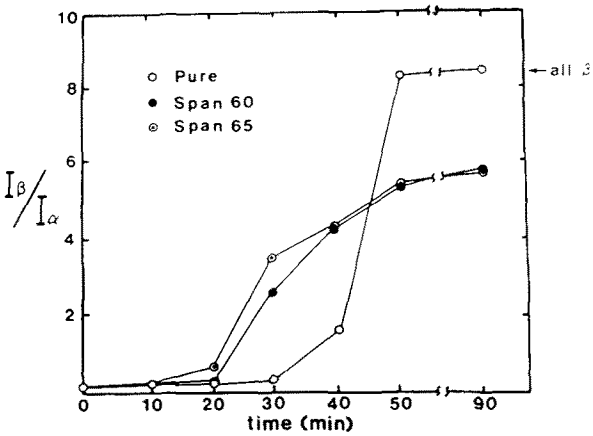

FIG. 3. A solid state transformation from α to β of tripalmitin at 43 C. Intensity ratios of the specific X-ray diffraction spectra: α; d = 4.15 A, β; d = 4.60 A, are shown for the samples with and without the surfactants.

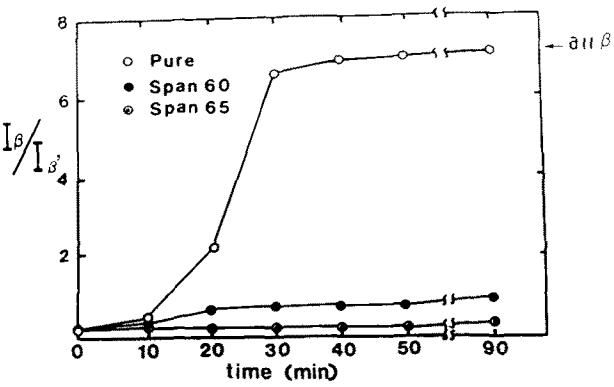

FIG. 4. A solid state transformation from β' to β of tripalmitin at 46 C. The specific X-ray diffraction spectra for β' (d = 4.23 A) was used as a reference as displayed in Fig. 3.

whereas they became β between 51 and β'_m (57 C). This conversion also may be interpreted by the conflicting effect between ΔT and $\Delta G\#$. ΔT always prevails in β. So, β' does not first crystallize approaching its melting temperature due to a decrease of ΔT, then β became predominant. When the crystallization temperature decreased, β' started to appear due to the kinetic effect of its lower $\Delta G\#$ value. The larger slope of τ against temperature for β' in Figure 1 supports this consideration. The factors of ΔT and $\Delta G\#$ for β' and β might be balanced at 51 C. This feature is quite equivalent to the relative occurrence of the B and C polymorphs of stearic acid in the B-stable region from the solution (25). The metastable C form occurred predominantly at higher supersaturation, whereas B prevailed at lower supersaturation.

A peculiarity was revealed in the quite high melt mediated transformation from α to β. There may be two reasons for it. One is the melt structure itself. The liquid formed by a rapid melting of α is in a more ordered state than the pure melt cooled from high temperatures, a lamellar arrangement like a crystalline state being persisting (20). Then nucleation of β may easily be accelerated. The second is more specific: the small β crystals would be formed during heating process of α via the solid state transformation. These small crystals might serve as the crystal seeds in the α-molten liquid. At present, it is uncertain whether one of these mechanisms may act exclusively or both of them may take place concurrently. Callaghan and Jolley compared the pulsed ^{13}C NMR spectrum of the α-melt with those of the undercooled melt of tristearin at the same temperatures (26). They observed that the undercooled melt is more stable than the α-melt, and also that glyceryl spin relaxation times are faster in the α-melt. They considered that the latter might follow from a slower gross molecular rotational diffusion due to the local ordering characterized by the formation of β nuclei. Accordingly, the faster melt-mediated transformation is more likely to be influenced by the second reason.

Finally, the surfactants retarded the crystallization of β' more than the other two polymorphs. In the case of the solid state transformation, Garti et al. reported (17) the depression of the $\alpha \rightarrow \beta$ transformation of the melt-grown tristearin with the addition of span 60 and span 65. Hernqvist et al. examined the similar effect on the $\beta' \rightarrow \beta$ transformation of hydrogenated rapeseed oil with the addition of rac-1,2-dipalmitoyl glycerol (16,18). There is, however, no comparison between the $\alpha \rightarrow \beta$ and $\beta' \rightarrow \beta$ transformations. Therefore, we examined the effects of the sorbitan esters on these two transformation modes: $\alpha \rightarrow \beta$ at 43 C and $\beta' \rightarrow \beta$ at 46 C with an additive of 5 wt%. The results are displayed in Figures 3 and 4, in which the intensity ratios of the specific X-ray diffraction spectra are plotted as a function of time. The detailed analyses on the evolution of transformation both in the pure and impure samples may be of considerable interest, but it is beyond our present scope (it will be interpreted elsewhere). What should be stressed here is that $\beta' \rightarrow \beta$ was more retarded than $\alpha \rightarrow \beta$ at a later stage of the transformation, exhibiting a good correlation with the crystallization rate. This may be due to the fact that the molecules in β' have stronger interactions with the surfactant molecules during either the condensation process or the transformation process. Its mechanistic interpretation will be accomplished by knowing the exact molecular structures of the metastable β' form.

ACKNOWLEDGMENT

Prof. M. Okada encouraged us throughout this work.

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[Received June 16, 1986]