Polymorphism of POS. II. Kinetics of Melt Crystallization

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Melt crystallization of four polymorphs of POS, α, δ, pseudo-β′ and β, was examined with pure samples (>99.9%). Induction time, τ, for newly occurring crystals was measured with a polarizing microscope equipped with a temperature-controlled growth cell. Rate of crystallization, 1/τ, was obtained for each polymorph, whose identification was done with x-ray diffraction (XRD) and differential scanning calorimetry (DSC). Two modes of crystallization, melt cooling and melt mediation, were applied. From these experiments, the following conclusions were obtained: (i) The rate of melt-mediated crystallization was always higher than of simple melt cooling; (ii) the pseudo-β′ form was crystallized in a wider range of temperature than the less stable δ form; (iii) the occurrence behavior of the polymorphs differed between simple melt cooling and melt mediation; (iv) the δ form was crystallized only by simple melt cooling in a narrow range of temperature, 25.5°C∼28.3°C. This means that there is a possibility that δ may result from racemic compounds that are crystallized in a specific manner. The experimental results are discussed in comparison to 1,3-dipalmitoyl-2-oleoylglycerol (POP), 1,3-distearoyl-2-oleoylglycerol (SOS) and cocoa butter.

KEY WORDS: Cocoa butter, crystallization, DSC, kinetics, polarizing microscope, polymorphic transformation, polymorphism, POS, x-ray diffraction.

The polymorphism of cocoa butter is an important physical aspect for the confectioner, especially for chocolate manufacturers, because the major fat in chocolate is cocoa butter (1). To solidify chocolate in desired polymorphs, careful temperature treatment is needed because the polymorphism of cocoa butter is quite complicated, and therefore its crystallization phenomena are not easily controlled (2).

Cocoa butter consists mainly of three symmetric triacylglycerols (TAGs), 1,3-dipalmitoyl-2-oleoylglycerol (POP), 1,3-distearoyl-2-oleoylglycerol (SOS), and 2-oleoylpalmitoyl-stearoylglycerol (POS). To fully understand the polymorphism and crystallization behavior of cocoa butter, we have so far dealt with polymorphic transformations and crystallization behavior of POP and SOS (3–5). This paper presents crystallization behavior of the polymorphs of POS. There are two reasons for dealing with POS: cocoa butter contains 34% POS, which is the highest, and the polymorphism of POS is largely different from POP and SOS as described in a companion publication (6).

MATERIALS AND METHODS

The purity of the sample of POS used was 99.9%. The methods for sample preparation and purity determination were fully described (6).

We employed a polarizing microscope equipped with a CdS photo sensor to measure the rate of crystallization. The output of a photosensor is proportional to the amount of newly occurring crystals in the supercooled melt. The sample was crystallized in a glass growth cell, whose temperature was controlled by thermostated water. In parallel to the optical measurement, the crystals were picked off the glass plate in the growth cell so that their polymorphic forms could be identified by X-ray diffraction (XRD) (Rigaku, CuKα, Ni-filter, Tokyo, Japan) and DSC (Seiko Denshi SSC580, Tokyo, Japan).

Two modes of crystallization were examined, melt cooling and melt mediation. Two thermostats were employed to rapidly change the temperature of the crystallizing growth cell. In melt cooling, the sample was completely melted at 80°C for 5 min prior to cooling. Then, the temperature of the growth cell was rapidly changed to the crystallization temperature, T_c. In melt mediation, we examined α melt mediation and pseudo-β′ melt mediation. In the α melt-mediated crystallization, the first crystallized α form was melted by rapidly raising the temperature of the growth cell above the melting point of α. The occurrence of the more stable polymorphs was detected while keeping the temperature constant after the α melted. Pseudo-β′ melt-mediated crystallization was done similarly with α melt mediation.

RESULTS

Figure 1 shows a typical output of the photo sensor in melt cooling of POS. The crystallization rates at two different T_c values are shown. At T_c = 25.4°C, there was no output until after 43.2 min. Then, a rapid increase of the output was detected, indicating the onset of crystallization. In this case, an induction time τ was defined as 43.2 min, and the polymorphic modification was determined as pseudo-β′. At T_c = 26.7°C, δ form was crystallized

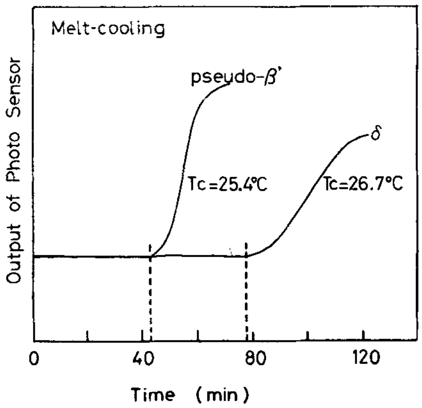

FIG. 1. Output of photo sensor for simple melt cooling of POS at T_c = 25.4 and 26.7°C.

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with a τ value of 77.1 min. The slope of the increase of the output of the photo sensor was lower than that at $T_c = 25.4°C$.

Figure 2 shows a typical result of α melt-mediated crystallization of POS. The melt was rapidly cooled to 15°C to crystallize the α form, as shown by an immediate increase in the output of the photo sensor. Then, the output decreased due to clouding caused by light scattering from the many crystals of α. After awhile, the temperature of the growth cell was rapidly raised to $T_c = 25.5°C$. During this process, the α crystals melted as expressed in a rapid decrease in the output, because the melting point of α is 19.5°C, and new crystals of pseudo-β′ started to appear. In Figure 2, the induction time τ of the α melt mediation was defined as 4.73 min.

Figure 3 shows the temperature dependence of an inverse of τ, 1/τ, which corresponds to the rate of crystallization. 1/τ decreased with increasing crystallization temperature, being smallest for δ and largest for α. The time constant of the growth cell expressed in 1/τ was 0.8. To compare each polymorph numerically, 1/τ was 0.6 for α at $T_c = 16°C$. As to pseudo-β′, 1/τ was 0.15 at 19°C and 0.03 at 25°C. The 1/τ values of δ were as low as 0.01 to 0.02 around 26°C.

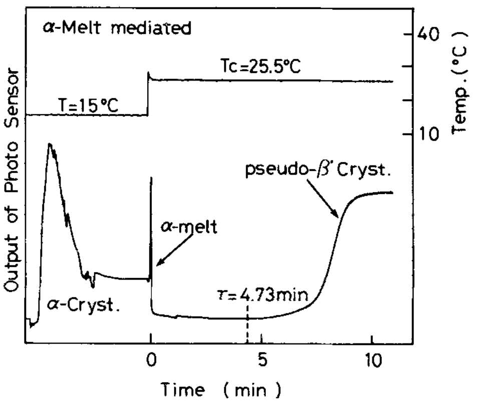

FIG. 2. Output of photo sensor for α melt-mediated crystallization of POS.

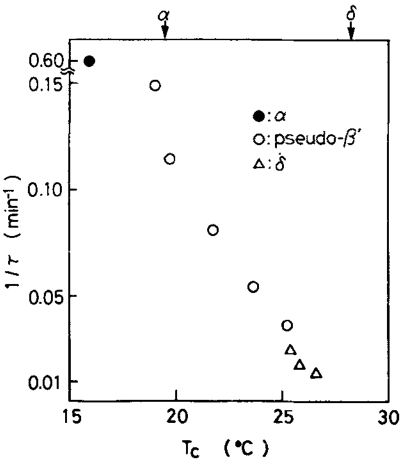

FIG. 3. Rate of crystallization, 1/τ, of melt cooling of POS.

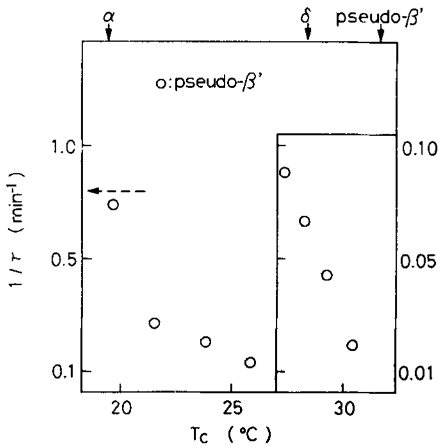

FIG. 4. Rate of crystallization, 1/τ, of α melt-mediated crystallization of POS.

TABLE 1

Occurrence of POS Polymorphs in Melt Crystallization

Tc (°C)	20 25 30 35
Melting point	↑ α ↑ δ ↑ pseudo-β′ ↑ β
Melt cooling	α → ← pseudo-β′ → ← δ →
α Melt-mediated	— ← pseudo-β′ →
Pseudo-β′ melt-mediated	— β ← – – –

Figure 4 shows the rate of α melt-mediated crystallization. The time constant of the growth cell is indicated by an arrow. It is clear that the crystallization rate decreased with increasing crystallization temperature. To compare with melt cooling in Figure 3, the values of 1/τ for the α melt-mediated crystallization was quite larger than that of melt cooling, *e.g.* 5.8 times at 20°C and 3 times at 23°C. Accordingly, the crystallization via α melt mediation was remarkably enhanced in comparison to simple melt cooling.

Table 1 summarizes the occurrence domains of different polymorphs of POS at three different crystallization modes. In melt cooling, no supercooling was observed for α; the crystallization of α was initiated just at its melting point. Pseudo-β′ was obtained in a temperature range between the melting point of α, 19.5°C, and 25.5°C. Delta (δ) was only crystallized between 25.5°C and its melting point, 28.3°C. In the α melt mediation, only pseudo-β′ occurred below the melting point of pseudo-β′. Beta (β) was crystallized through pseudo-β′ melt mediation, but its crystallization rate was extremely low. For example, 1/τ was 0.013 (75 min) at 34.7°C.

DISCUSSION

This study provides proof of existence of the four polymorphic forms, α, δ, pseudo-β′ and β. All of these polymorphs were crystallized from the melt. As described earlier (6), three forms (not including δ) revealed common properties with the corresponding forms observed in POP and SOS. Delta (δ) was observed only in POS.

Common conclusions can be drawn from the three crystallization modes examined here: (i) the crystallization rate was much higher in α melt mediation than in simple cooling, and (ii) the occurrence behavior was dependent on the mode of crystallization. As to the first conclusion, melt-mediated crystallization may be influenced by the presence of crystal nuclei or molecular clusters, which tend to accelerate the crystallization. These nuclei or clusters would be formed during rapid heating of the α polymorph.

Recently, Kellens *et al.* (7) carried out a time-resolved X-ray diffraction experiment on phase transformation from α to β of tripalmitin polymorphs by means of synchrotron radiation. They observed that, after the melting of α at a heating scan rate of 5°C/min, the melt revealed an x-ray diffraction short-spacing peak with the same lattice parameter as α, and that β was rapidly crystallized from the α melt. This phenomenon shows the occurrence of nuclei of β after the melting of α in tripalmitin. In the case of POS, the melting of α was followed by the crystallization of pseudo-β', not β. Similarly, the γ form, which is more stable than α but less stable than pseudo-β', was crystallized via α melt mediation in POP and SOS (4). In all cases, the most stable forms, β in POS and β_1 in POP and SOS, did not occur after the melting of α.

As to the second conclusion, β only occurred through the pseudo-β' melt mediation. Cooling of the melt phase did not crystallize β at any temperature. The α melt mediation crystallized only pseudo-β' as stated above. Such an extremely slow crystallization of β in POS may be attributed to its most close-packed crystal structure. Therefore a step-wise crystallization via melt mediation, such as $\alpha \rightarrow$pseudo-β' and pseudo-$\beta' \rightarrow \beta$, may solve this packing constraint. It is supposed that the nuclei formed after the melting of α are too unstable to form β, thus pseudo-β' is crystallized. The melting of pseudo-β' may provide the nuclei for β crystallization due to its thermodynamic stability.

These results are consistent with the melt cooling and melt-mediated crystallization of POP and SOS (4).

To compare the present results with those of POP and SOS, the following three major differences are notable as to (i) supercooling for α, (ii) predominant crystallization of pseudo-β', (iii) occurrence of β from melt via the pseudo-β' melt mediation. We discuss them in more detail.

Supercooling for α. Supercooling is related to an activation free energy for crystallization due to interfacial energy of crystal nuclei: the smaller the supercooling, the smaller is the activation free energy (8). Therefore, a comparison of the degree of supercooling of the specific modifications of POP, POS and SOS may characterize the crystallization kinetics. In the case of POP, no supercooling was observed for α, but SOS has supercooling of 1.5°C.

We consider this difference due to the lamellar structures of the α forms of the two substances. Alpha (α) is of double chain length structure in which oleoyl chains and palmitoyl chains in POP and stearoyl chains in SOS are packed in the same lamellae. The same structure was attained in α of POS (6), namely, palmitoyl, stearoyl and oleoyl chains are packed together. The length of oleoyl and palmitoyl chains are similar but the stearoyl chains are longer than the oleoyl chain, because the *cis* double bond in the oleoyl chain may be shorter than the total chain-length. In fact, the long-chain axes of the C modification of stearic acid (9), the γ form (low melting form) of oleic acid (10), and the LM (low melting) form of petroselinic acid (*cis*-12-octadecanoic acid) (11) are 50.1, 40.6, and 44.0Å, respectively. Therefore, the lamellar plane of SOS of the double chain length α form may be destabilized in comparison to POP. As to POS, there was no supercooling. This means that the interlamellar stability of POS is more similar to POP than to SOS. This stability would result from intermixing of palmitoyl, stearoyl and oleoyl chains.

Predominant crystallization of pseudo-β'. The fact that pseudo-β' was predominantly crystallized by melt cooling and α melt mediation is very specific, as we compare POS with POP and SOS. In POP and SOS, γ occurred most predominantly in a range of temperature closer to the melting point of α.

However, POS does not possess the γ form, so pseudo-β' form crystallized predominantly above the melting point of α. The δ form of POS has the intermediate thermal stability between α and pseudo-β', but it only occurred by simple melt cooling at higher temperatures than the crystallizing temperatures of pseudo-β'. We think that the δ modification is a quite specific polymorph as described earlier (6). So, the phenomena observed for δ cannot be compared with POP and SOS in a same way.

Occurrence of β from melt. The structural properties of the β form of POS are quite identical to those of β_1 of POP and SOS. In case of POP and SOS, β_1 did not occur from the melt, but β_2 was crystallized only through γ melt mediation in both TAGs. Beta subscript 1 (β_1) of POP and SOS is obtained through the solid-state transformation form β_2 and from solvent crystallization. Hence, the crystallization of β of POS was achieved through pseudo-β' melt mediation, like β_2 of POP and SOS, at a low rate of crystallization.

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