Polymorphism of POP and SOS. II. Kinetics of Melt Crystallization[1]

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Melt crystallization of the polymorphs of SOS, α, γ, pseudo-β', β_2 and β_1, and of POP, α, γ, pseudo-β'_2, pseudo-β'_1, β_2 and β_1, was examined using pure samples (99.9%). Induction time τ for newly occurring crystals in the melt phase was measured with a polarizing microscope equipped with a temperature-controlled growth cell. Rate of crystallization, $1/\tau$, was obtained for each polymorph of POP and SOS whose identification was done with X-ray diffraction and differential scanning calorimetry (DSC). Two modes of crystallization, melt-cooling and melt-mediation, yielded approximately the same results for POP and SOS: (a) The rates of crystallization were always higher in less stable than in more stable forms, β_2 only crystallized via a γ-melt mediation, but β_1 did not occur by the melt crystallization; (b) the rate of melt-mediated crystallization was always higher than the simple melt-cooling as examined at the same crystallization temperature; (c) the occurrence behavior of the polymorphs differed between the simple-cooling and melt-mediation. The results were related to the solidification behavior of the polymorphs of cocoa butter.

The polymorphic behavior of cocoa butter is an important problem for chocolate manufacturers, because cocoa butter is a major solid fat in chocolate (1,2). Quality of a final product like gross, snap, texture and shelf life is decided by the polymorphic structure of cocoa butter (3). The physical problems in the solidification process involve polymorphic control, which means the crystallization and transformation of cocoa butter into desired polymorphs. Therefore, the polymorphism of cocoa butter in relation to the crystallization behavior has been studied extensively (4–9). Some problems, however, are still open to question, such as molecular structures of independent polymorphs which were categorized Form I through Form VI (5), kinetics of crystallization and transformation, etc. To fully understand the polymorphism of cocoa butter, we first need precise knowledge of symmetric mixed saturated/unsaturated acid triglycerides (TG), most particularly POP, POS and SOS and their mixture systems, because the three TGs are the major components of cocoa butter. We have observed new findings on the polymorphic modifications of POP and SOS (10), among which β_2 and β_1 exhibited thermal and structural behavior almost identical to those of Form V and Form VI of cocoa butter, respectively. This paper presents crystallization behavior of the polymorphs of POP and SOS (10), particularly in relation to the kinetic aspects.

MATERIALS AND METHODS

The purity of the samples of POP and SOS used was 99.9%. The methods for the sample preparation and purity measurements were described in (10).

The rate of crystallization was measured by using polarizing optical microscopy equipped with CdS photo sensor (Fig. 1). The sample was put on a glass-made growth cell whose temperature was controlled by thermostated water at a crystallization temperature, T_c. Time constant of the growth cell was about one min. T_c was regulated within ± 0.2°C, using two thermostats. The polarized light passed through the sample and was measured by an analyzer set at the crossed-Nicols position. Therefore, the occurrence of the optically anisotropic crystal-like triglycerides in the melt phase was detectable by the CdS photo sensor. The objective lens was dismounted, so that the light passing through the whole area of the sample was collected and monitored by the photo sensor whose output was measured by a mV unit. After all the sample crystallized, a part of sample was picked off, so that the polymorphic form was identified with X-ray diffractometer (XRD; Rigaku, CuK_α, Ni-filtered) and DSC (Seiko Denshi SSC 580). The measurements were carried out simultaneously as explained in (10).

RESULTS

Two methods of melt crystallization were examined, melt-cooling and melt-mediation. In the melt-cooling, the sample was first melted at 80°C, then temperature of the growth cell was cooled to T_c. In the melt-mediated crystallization, the initial polymorph was melted by rapidly raising the temperature of the growth cell above the melting point of the initial form. Then the crystallization of the more stable forms was induced. α and γ were used as the initial polymorphs.

Figure 2 shows a typical output of the photo sensor in melt-cooling of POP. The crystallization rates at two

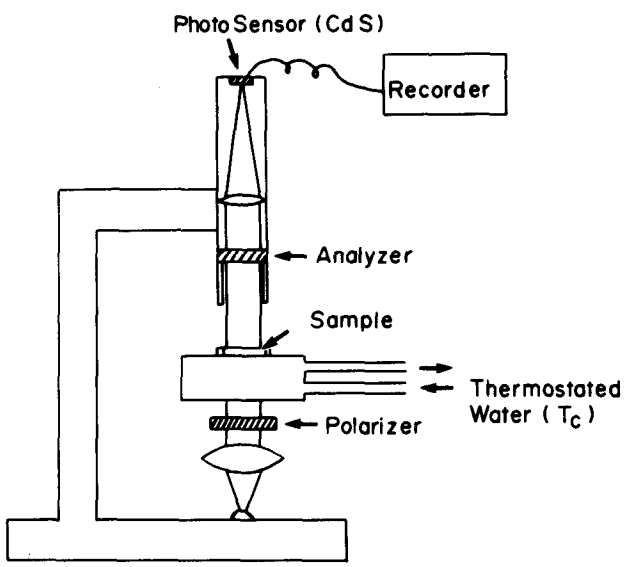

FIG. 1. Optical system for induction time measurement of melt crystallization.

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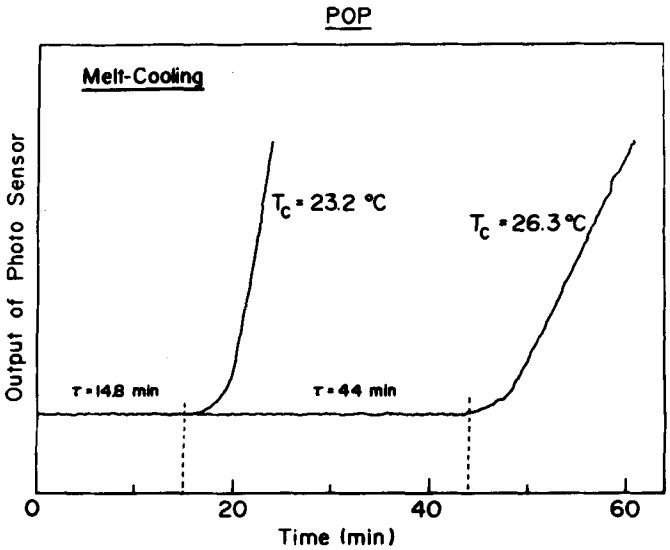

FIG. 2. Output of photo sensor in case of simple melt cooling of POP at T_c = 23.2 and 26.3°C.

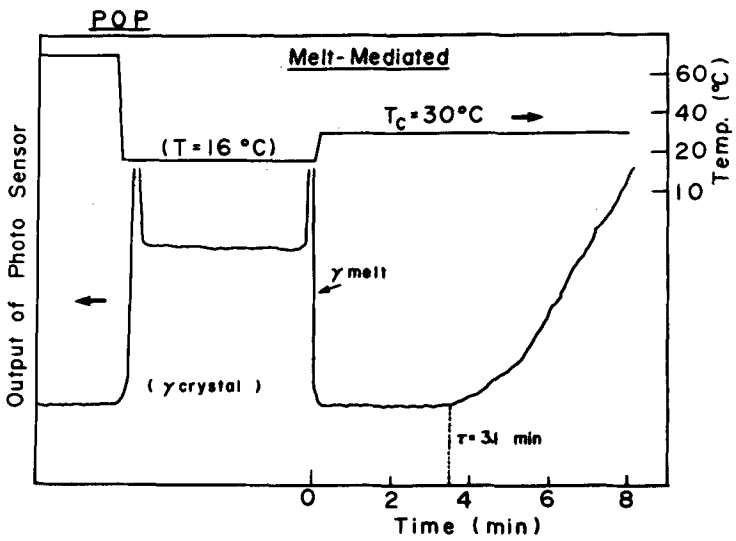

FIG. 3. Output of photo sensor in case of γ-melt mediated crystallization of POP.

different T_c values are shown. At T_c = 23.2°C, there was no output until after 14.8 min. Then, a rapid increase of the output was shown, indicating the onset of crystallization. In this case, an induction period, τ was defined as 14.8 min as shown in the figure.

Figure 3 shows typical data of γ-melt mediated crystallization of POP. The experimental procedure was as follows: in the first, the melt at 60°C was cooled rapidly to 16°C where γ was crystallized as shown by a rapid increase of the output. After a while, the output decreased due to clouding caused by light scattering from many crystals of γ. Five min after the whole sample crystallized in γ, the temperature of the growth cell was raised rapidly to T_c = 30°C. During this process, the crystals melted as expressed in a rapid decrease of the output, because the melting point of γ is 27°C. Then, the occurrence of pseudo-β'_2 and pseudo-β'_1 was detected. In this way, τ of the γ-melt mediated crystallization, was defined as 3.1 min. The experimental results of POP and SOS are described separately.

POP. The results of the occurrence of different polymorphs of POP at three different crystallization modes are summarized in Table 1.

In the melt cooling, no supercooling was observed for α; α was crystallized just below its melting point. Gamma was crystallized in a range of T_c from 15.5°C, melting point of α, to 24°C. Pseudo-β'_2 was crystallized from 23 to 27°C, and pseudo-β'_1 occurred predominantly above 27°C, both forms appearing concurrently around 26 and 27°C. This result proved that POP crystallizes in two different pseudo-β′ forms, which were also observed in the transformation experiments in (10).

In α-melt mediation, γ appeared between the melting point of α and 24°C. Pseudo-β'_2 appeared from 22°C and, with increasing T_c, pseudo-β'_1 started to crystallize and eventually predominated above 28°C. In γ-melt

TABLE 1

Occurrence of POP Polymorphs in Melt Crystallization

T_c (°C)	15	20	25	30	35
Melting point	α		γ	pseudo-β'_2	pseudo-β'_1 β_2
Melt cooling	α →	← γ →		← pseudo-β'_1	
				← pseudo-β'_2 →	
α-Melt mediated		← γ →		← pseudo-β'_1	
				← pseudo-β'_2 →	
γ-Melt mediated				← pseudo-β'_2 →	
				← β_2 →	
				← pseudo-β'_1	

mediation, both pseudo-β'_2 and pseudo-β'_1 were crystallized above the melting point of γ up to 31°C. Above that temperature, only β_2 crystallized, but no β_1 was obtained.

Figure 4 shows the temperature dependence of an inverse of τ, $1/\tau$, which is proportional to the rate of crystallization in melt-cooling. The data below T_c = 21°C, where α and γ crystallized, were not shown here because the τ values are smaller than the time constant of the growth cell. $1/\tau$ was smallest for pseudo-β_1' and largest for α. Thus, we conclude that the crystallization rates were highest for α and lowest for pseudo-β'_1.

Figure 5 shows the rate of α-melt mediated crystallization. Time constant of the growth cell was indicated by an arrow in the figure. $1/\tau$ for γ is not shown because τ was too short to be detectable exactly. $1/\tau$ of pseudo-β'_2 is always higher than pseudo-β'_1. It is clear that the values of $1/\tau$ for the α-melt-mediation are 10 times larger than those of the melt-cooling. Accordingly, the crystallization via α-melt mediation was remarkably enhanced in comparison to the simple melt cooling.

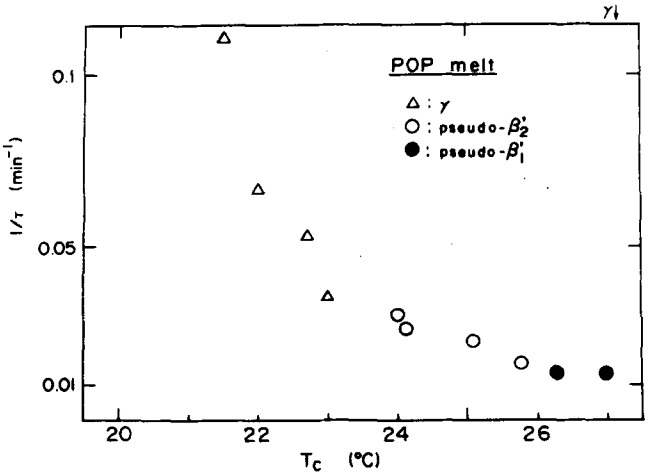

FIG. 4. Rate of crystallization, $1/\tau$, of melt cooling of POP.

Figure 6 shows the results of the γ-melt mediated crystallization. Three points may be noted as differences from the α-melt mediation. In the first, the $1/\tau$ values are larger in the α-melt mediation by a factor of about 10, when compared at the same T_c. Second, pseudo-β'_2 and pseudo-β'_1 were formed concurrently from the γ-melt between 28 and 30°C, where two pseudo-β' forms occurred in a separate manner from the α-melt (Table 1). Lastly, β_2 was formed from the γ-melt.

SOS. The results of occurrence are summarized in Table 2. In the melt cooling, there was supercooling for α by 2.5°C, because α appeared at 21.0°C. The γ form crystallized in a wider range of temperature from 21 to 33°C in comparison to other forms. The α-melt mediated crystallization induced the occurrence of γ in a range of temperature between the melting point of α (23.5°C) and 26°C. Contrary to POP, the pseudo-β' form became predominant in an extended range of T_c. The α-melt mediation produced pseudo-β' above 26°C. β_2 was formed above the melting point of pseudo-β'. $1/\tau$ for melt cooling of SOS is shown in Figure 7. Time constant of the growth cell was indicated by an arrow. Below 22°C, α crystallized very rapidly, τ being shorter than the time constant. γ appeared from below the melting point of α to 32°C.

Figure 8 shows the α-melt mediated crystallization. Only one datum was available for the occurrence of the γ form from the α-melt. Besides, pseudo-β' crystallized in a wider range of T_c. The experimental data were seriously scattered. In γ-melt crystallization of SOS, pseudo-β' appeared only between the melting points of γ and pseudo-β'. β_2 appeared with a long induction period, over 80 min.

DISCUSSION

The present study gave rise to a proof of existence of the five polymorphic forms, α, γ, pseudo-β'_2, pseudo-β'_1, and β_2 of POP, and four forms, α, γ, pseudo-β' and β_2 of SOS. Complicated intermediate forms of POP, pseudo-β'_2 or

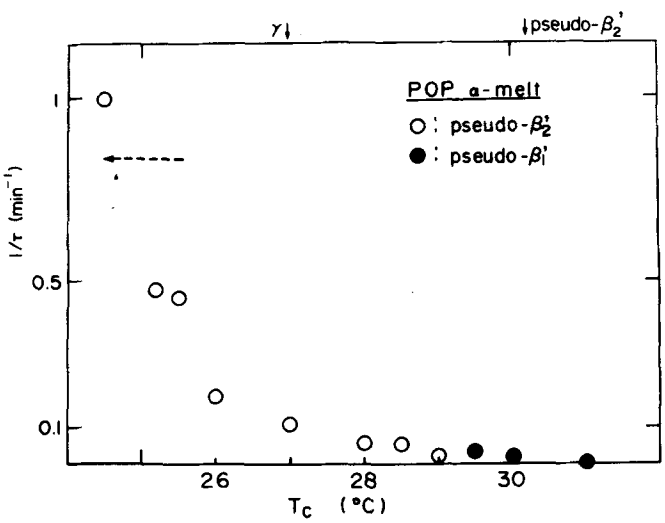

FIG. 5. Rate of crystallization, $1/\tau$, of α-melt mediated crystallization of POP.

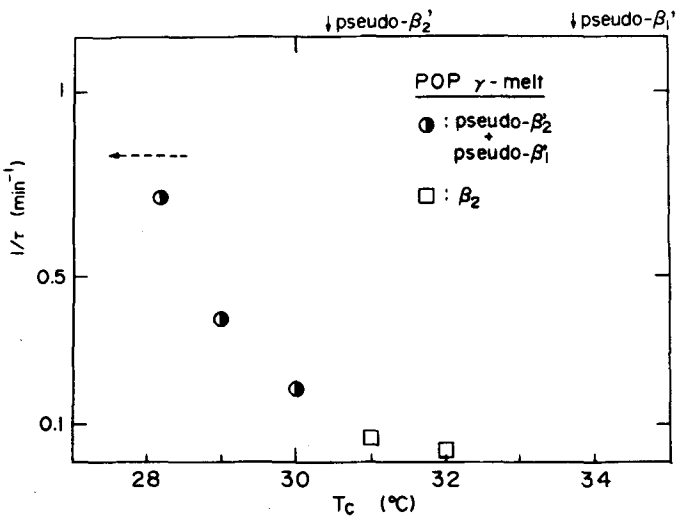

FIG. 6. Rate of crystallization, $1/\tau$, of γ-melt mediated crystallization of POP.

TABLE 2

Occurrence of SOS Polymorphs in Melt Crystallization

T_c (°C)	20	25	30	35	40
Melting point		↑ α		↑ γ ↑ pseudo-β′	↑ β_2
Melt cooling		-- α --→	←------ γ ------→	pseudo-β′ ←--→	
α-Melt mediated		- - -	←-- γ →←---	pseudo-β′ ---→	
γ-Melt mediated			- - - -	pseudo-μ′ ←--→	←β_2 --→

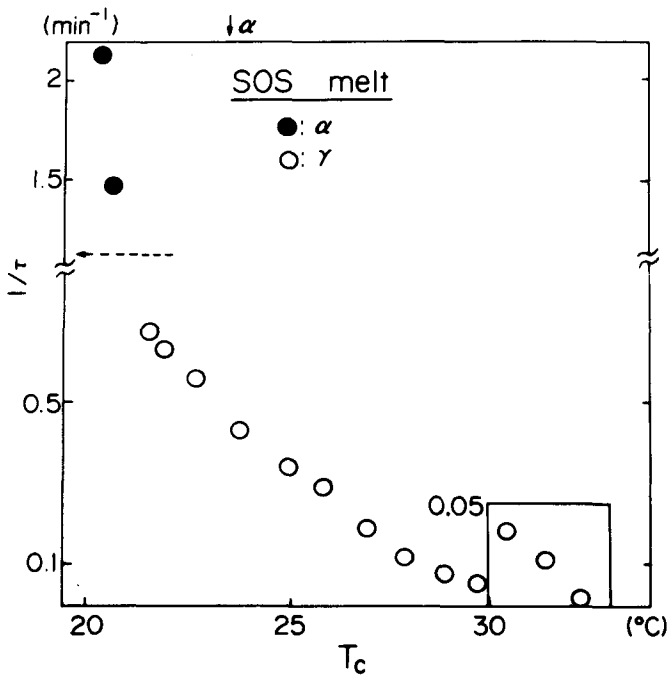

FIG. 7. Rate of crystallization, 1/τ, of melt cooling of SOS.

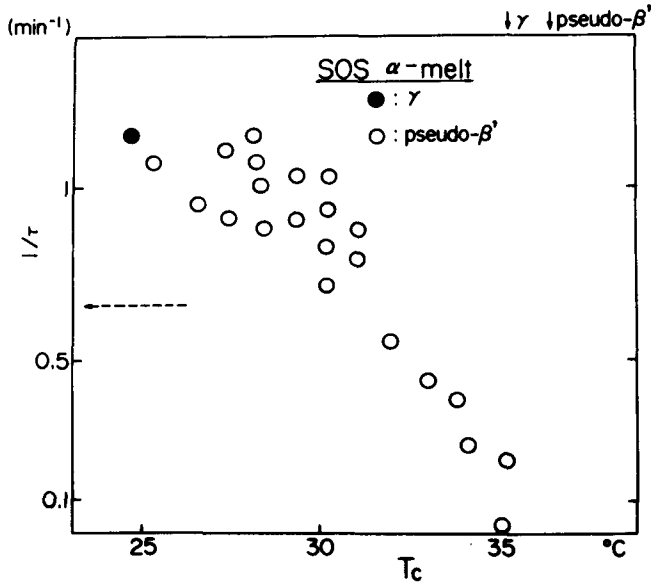

FIG. 8. Rate of crystallization, 1/τ, of α-melt mediated crystallization of SOS.

pseudo-β'_1, were formed as a single polymorph via three crystallization modes. β_1 was not obtained from the melt crystallization, but it was crystallized singly from the solution phase together with β_2 (T. Arishima and K. Sato, unpublished data). It is likely that β_1 may take a very long induction time for crystallization from the melt phase.

Most characteristic was the fact that the α form of POP revealed no supercooling, whereas γ was obtained slightly below the melting point of α in SOS (Tables 1 and 2). The α form has the double layered crystalline structure, so it appears that POP is easier to crystallize in the double-layered structure than SOS. The reason for this may be ascribed to the length of acyl chains composing the triglycerides. The lengths of palmitoyl and oleoyl chains in POP are very similar, for the length of the oleoyl chains is approximately the same as that of the palmitoyl chain due to a bent conformation at a *cis* double bond. Meanwhile, in the case of single lamella composed of stearoyl and oleoyl chains, chain penetration occurs at the lamella interface, because of longer chain length of the stearoyl chain. The larger value of enthalpy of crystallization of POP (α) in comparison to SOS (α) may be due to the same origin (10).

The crystallization rates were always higher in a less stable form than in a more stable form at the three crystallization modes examined. τ involves induction times for both nucleation and crystal growth. As for the rate of nucleation, it is higher for a larger degree of supercooling, but conversely, the nuclei have a lower interfacial energy. The same mechanism affects the rate of crystal growth (11). It is clear from the present experiments that the rates of crystallization were always higher in less

stable forms despite their low degrees of supercooling. This suggests that the interfacial energy of more stable polymorphic forms may be larger than those of less stable forms. A similar argument was discussed in the melt crystallization of β' and β forms of tripalmitin (12).

To compare the three crystallization modes examined, two tendencies are noted: (a) the crystallization rate was much higher in the α- and γ-melt mediation than the simple melt cooling, and (b) the occurrence behavior of the polymorphs differed, particularly between the γ-melt mediation and other two. For the first tendency, the melt crystallization of β' and β of tripalmitin also showed the same results (12). It is plausible that the 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 initial polymorph of α or γ, and persist in the α-melt or γ-melt. Hence, the initial stages for nucleation of molecular clusters, or even the nucleation process itself, might occur during the melt mediation process. In this regard, it was also found that the crystallization rate of the γ-melt mediation was higher than the α-melt mediation. The reason for this may be that the nuclei or molecular clusters formed after the α-melting are rather fragile because the α form is in the disordered structure (13). Hence, the crystallization rate of the α-melt mediation at higher T_c will resemble more the conditions of simple melt cooling. Similar consideration may account for the tendency of (b). The crystal nuclei or clusters produced by the γ-melt mediation would serve for the seeds of more stable polymorphs than those produced by the α-melt mediation. Consequently, the occurrence of β_2 was possible only via γ-melt mediation.

Finally we relate the present study to cocoa butter crystallization. In the solidification process of chocolate, the melt-mediated crystallization must also occur very quickly, because the molten chocolate is first cooled rapidly. Further tempering induces both the melting of unstable polymorphs and the crystallization of the more stable ones. Cocoa butter in the final chocolate products is normally solidified as Form V, which corresponds to the β_2 form of POP and SOS (14). Hence the optimal conditions for crystallization of β_2, like via the γ-melt mediation in the present case of pure POP and SOS systems, may be beneficial in the case of cocoa butter. To make further correlations to cocoa butter crystallization, additional studies on POS and POP/SOS/POS mixture systems will be needed.

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