Polymorphism of POS. I. Occurrence and Polymorphic Transformation[1]

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Polymorphic behavior of 1,3-*rac*-palmitoyl-stearoyl-2-oleoylglycerol, 99.9% purity (POS) was examined by X-ray diffraction (XRD), differential scanning calorimetry (DSC), solubility measurements and optical microscopy in comparison with 1,3-dipalmitoyl-2-oleoylglycerol (POP) and 1,3-distearoyl-2-oleoylglycerol (SOS). Melt crystallization and solvent crystallization were examined for the occurrence of metastable and stable polymorphs. The number of independent polymorphs was four; α, δ, pseudo-β' and β. The lowest melting form, α, was identical to that commonly observed in POP and SOS lowest melting forms. As to the highest melting form, β, the XRD short-spacing pattern was identical to β_1 of POP and SOS. This is consistent with crystal habit: β single crystals of POS showed the same shape as those of β_1 of POP and SOS. However, the melting point of β (POS), 35.9°C, was lower than those of β_1 of POP, 36.7°C, and of SOS, 43.0°C. Correspondingly, solubility of β of POS was lower than that of β_1 of POP below about 13°C, but higher above 13°C. POS did not possess β_2, which is the second stable form in POP and SOS. Two forms of δ and pseudo-β' occurred, the latter being more stable. The structural properties of δ showed that δ is not identical to γ previously observed in POP and SOS. Transformation behavior from the metastable to stable polymorphs of POS showed some differences from those of POP and SOS.

KEY WORDS: Cocoa butter, DSC, melt crystallization, phase transition, polymorphic behavior, POP, POS, single crystal, SOS, triacylglycerol, x-ray diffraction.

Triacylglycerols (TAGs) are major components of naturally occurring fats and oils. TAGs are utilized in edible fats, such as margarine, chocolate, and in cosmetics and pharmaceuticals (1). They are usually employed in mixed systems. The polymorphism of mixtures is quite complex and their physical behavior affects the quality of final products. It is required to characterize the polymorphism of individual TAG components and their mixtures in a parallel way.

Recently, the authors have systematically studied symmetric mixed saturated-unsaturated acyl TAGs having an oleoyl chain at the *sn* 2-position and different saturated chains at the *sn* 1,3-positions of the glycerol (Sat-O-Sat TAG): 1,3-dipalmitoyl-2-oleoylglycerol (POP), 1,3-distearoyl-2-oleoylglycerol (SOS), 1,3-diarachidoyl-2-oleoylglycerol (AOA) and 1,3-dibehenoyl-2-oleoylglycerol (BOB) (2-5). We identified five independent polymorphs of α, γ, pseudo-β', β_2 and β_1, which commonly occurred in the four TAGs. As to the nomenclature given above, we have basically obeyed Larsson's principle (6). The polymorphism of these Sat-O-Sat TAGs was more complicated than that of saturated mono-acid TAGs (7). Particularly, the four Sat-O-Sat TAGs have two beta forms, β_2 and β_1, which correspond to Form V and Form VI in cocoa butter (8). We also confirmed the occurrence of β_2 and β_1 in the mixture of POP/1,3-*rac*-palmitoyl-stearoyl-2-oleoylglycerol (POS)/SOS with the same composition as cocoa butter (9). Hence, it was suggested that Form V and Form VI of cocoa butter were independent polymorphs, and thus polymorphic transformation of Form V to VI would be related to chocolate blooming. Based on this knowledge, a method of crystal seeding of β_2 of BOB was developed in dark chocolate to improve fat bloom stability (10-13).

In this report, we describe the occurrence and transformation behavior of the polymorphs in POS from a sample with a purity of 99.9%. From a viewpoint of physical analysis of confectionery fats, it is worthy to characterize the polymorphism of POS, which is the major component of cocoa butter. Solvent crystallization and solubility measurements of the most stable form were conducted, and the polymorphism of POS is discussed in comparison to POP and SOS.

MATERIALS AND METHODS

We employed two kinds of POS samples with purity of 99.9%, which were prepared from different starting materials by the following processes. The first material was prepared by solvent crystallization of cocoa butter from n-hexane. Another one was synthesized through lipase-catalyzed enzymatic interesterification among triolein, ethyl palmitate and ethyl stearate. A 99% sample was first obtained for both starting materials by preparative high performance liquid chromatography (HPLC) (Killoprep 250, Millipore Co. Ltd., Milford, MA). The 99.9% samples were then produced with the same HPLC technique from the initial materials of 99% purity. The purity of 99.9% was determined by HPLC (Japan Spectroscopic Co., Tokyo, Japan), which showed no detectable impurity peaks. No analysis of separation of optical isomers was applied. The physical properties described below were examined for each material independently, but there were no detectable differences.

The occurrence of polymorphic modifications was examined by three modes of crystallization. The first one was simple cooling of a melt from 80°C to varying crystallization temperatures (T_C). The second crystallization was melt-mediated transformation (14), in which more stable forms were crystallized after the melting of less stable forms by rapidly raising the temperature above their melting points. This method provides additional data to those obtained by simple melt cooling. Lastly, solvent crystallization was adopted to obtain the most stable form.

The polymorphic transformation in a solid state was induced by incubating the sample that was crystallized in

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each crystallization mode. The phase transition was examined by X-ray diffraction (XRD) (Rigaku, Cu-K_α, Tokyo, Japan) and differential scanning calorimetry (DSC) (Rigaku, DSC-8230). The two measurements were always taken for the same sample simultaneously by the following procedure: the sample for DSC (1.5∿1.7mg) was separated from the powder sample utilized for XRD (100 mg), and measured at the same time as the XRD scan. The polymorphic transformation was examined at least three times in every case. The room temperature, where the XRD and DSC studies were carried out, was kept at 12°C. Hence, the transformation during the XRD scan was actually hindered at this temperature.

Isolation of an independent polymorph was justified only when the sample exhibited reproducible unique data of the single melting peak in DSC and the long- and short-spacing pattern in XRD. The heating rates of DSC were 1, 2 and 5°C/min, while the cooling rate was 2°C/min. The melting point was defined by computerized data-processing as a crossing point between the base line and the tangential line of a maximal slope for the initial endothermic peak, *e.g.*, an onset temperature. The temperature of the peak-top position was higher than the onset melting point by 1.5∿2°C. With increasing rate of heating from 1°C/min to 5°C/min, the peak temperature of melting was increased by about 2°C. The above defined melting point, however, did not largely depend on the heating rate. A single melting peak was present for each modification even at the heating rate of 1°C/min except for α, whose melting was always accompanied by rapid crystallization to pseudo-β′. Solubility of the β form was determined by measuring the temperature at which the β crystal reached equilibrium with tetradecane solution whose concentration was precisely measured. The β crystal for the solubility measurement was prepared by solid-state transformation from the pseudo-β′ form.

In the solvent crystallization, acetonitrile was chosen, because the solubility was low enough for better crystallization. The solution was put in a thermostated glass cell (30 cc), and cooled to the crystallization temperature. The rapid cooling of the solution of high solute concentration often crystallized metastable polymorphs like pseudo-β′, but not the stable form β. The β crystal was obtained via solution-mediated transformation from pseudo-β′. New β crystals started to grow at the expense of pseudo-β′ crystals in the solution at a constant temperature. β appeared approximately two hours after the solution-mediated transformation was initiated. It was difficult to singly grow the β crystals except through pseudo-β′→β solution-mediated transformation, because the growth rate of β was extremely low. Hence, the growth conditions of β were limited. The crystallized sample was examined with XRD and DSC. The data were compared to those of crystals obtained by melt crystallization and polymorphic transformation.

RESULTS

X-ray diffraction. XRD short-spacing patterns of four polymorphs of POS are shown in Figure 1. Table 1 summarizes d-values and relative intensities of the XRD short-spacing spectra. The XRD short-spacing spectra of α and β are almost identical to those of α and β_1 of POP and SOS (3), respectively. α has a single peak at 4.23 Å. β has one strong peak of 4.58 Å and medium peaks around 3.70 and 4.02 Å. However, the XRD short-spacing patterns of δ and pseudo-β′ differed somewhat from those of POP and SOS (3). δ has a strong peak at 3.89 Å and three medium peaks at 4.63,4.31 and 4.11 Å. No strong peak appeared around 4.72 Å, which was observed in γ of POP and SOS (3). Pseudo-β′ has two strong peaks at 4.13 and 3.85 Å.

The chainlength structure (15,16) was determined by comparing the long-spacing values with the length of glycerol residue and stearoyl, palmitoyl and oleoyl chains. The long-spacing value of α was 47.6 Å which corresponds to the double chainlength structure. The long-spacing values of the other three forms correspond to the triple chainlength structure.

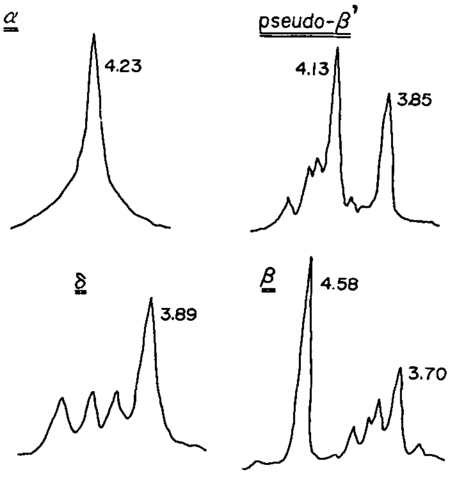

FIG. 1. X-ray diffraction short-spacing spectra of four polymorphs of POS.

TABLE 1

X-ray Diffraction Long-Spacing and Short-Spacing of Polymorphs of POS

Polymorph	Long-spacing (Å)	Short-spacing (Å)				
α	47.6	4.23 (vs)				
δ	70.6	4.63 (m)	4.31 (m)	4.11 (m)	3.89 (s)	
pseudo-β′	67.9	4.30 (w)	4.13 (s)	3.85 (s)		
β	64.0	4.58 (vs)	4.02 (w)	3.92 (m)	3.85 (m)	3.70 (s)

Crystallization. All of the four polymorphs were isolated by melt cooling or melt mediation. The rate of the melt crystallization will be reported in a subsequent paper (17).

α occurred by chilling the melt below its melting point. Pseudo-β′ was formed by melt cooling and melt mediation. The δ form was isolated only by the melt cooling method in a range of T_C between 24 and 25°C. An intermediate form, whose melting point lies between those of δ and pseudo-β′, was detected, but this form could not be isolated. β occurred both from solid-state transformation and melt-mediated crystallization. It is important to note that POS did not possess β_2, which is the second stable form in POP and SOS (3).

Thermal data. The DSC thermal data are shown in Table 2. We did not measure the enthalpy of fusion for α, because the fusion of α rapidly induced the crystallization of pseudo-β′. Instead, we measured the enthalpy of crystallization, ΔH_C, of α. Figure 2 displays the melting curves of the four polymorphs of POS. The melting point of α is 19.5°C. The fusion of α was soon followed by crystallization of pseudo-β′ which melts at 31.6°C (Fig. 2a). The melting points of δ and pseudo-β′ are almost the same as those of γ and pseudo-β′ of POP (3). The δ form transformed to an intermediate form, shown by an arrow in Figure 2b, and pseudo-β′ at the same time. The melting point of β in POS, 35.5°C, is lower than that of β_1 of POP, 36.7°C (Fig. 2c) (3).

TABLE 2

Thermal Data of POS

Polymorph	Temperature (°C)	ΔH_f[a] (KJ/mol)
α	19.5	41.2[b]
δ	28.3	89.6
Intermediate	29.8	—[c]
Pseudo-β′	31.6	119.2
β	35.5	147.8

[a] Experimental errors: temperature, +1.0°C for α and ±0.3°C for others; ΔH_f ±7 KJ/mol for β, ±3 KJ/mol for others.

[b] Enthalpy of crystallization was measured on α.

[c] Enthalpy of fusion is not available.

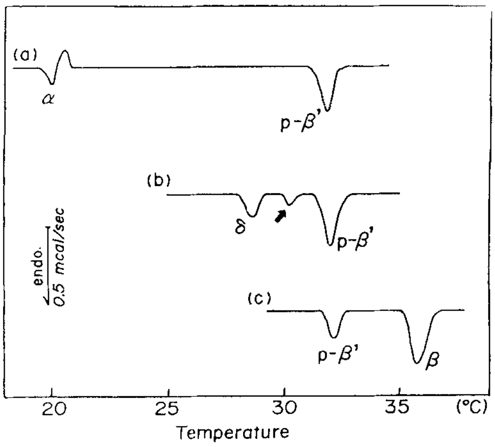

FIG. 2. DSC heating thermograms of (a) α→pseudo-β′ transformation; (b) δ→pseudo-β′ transformation; and (c) pseudo-β′→β transformation. Heating rate is 1° C/min.

Transformation rate. The transformation rates from metastable to more stable forms were precisely measured at different temperatures by using the XRD short- and long-spacings and DSC melting peaks as indicators.

Table 3 summarizes the transformation rate, which was defined as a duration during which the single melting peak of the initial polymorph completely converted into the single melting peak of the next stable form at a constant temperature in the DSC patterns. All transformations were irreversible, implying a monotropic nature of polymorphism. There are two pathways of polymorphic transformations in POS: α→pseudo-β′→β and δ→pseudo-β′→β. α directly transformed to pseudo-β′, not through the δ form. This tendency was often observed in saturated mono-acid TAGs, and not observed in POP and SOS (3). In saturated mono-acid TAGs (7), the transformation occurs between the double chainlength structure, whereas the conversion from α to the other two forms in POS is from double to triple chainlength structures. The transformation rate from δ to the intermediate form could not be measured precisely, because the δ form transformed concurrently to the intermediate form and the pseudo-β′ form. Hence, the identification of this intermediate form was quite difficult. Pseudo-β′ directly transformed to the most stable form, which is almost identical to β_1 of POP and SOS (3). It appears that, in all pathways, the transformation needed higher thermal energy and took longer until the polymorphic form approached the most stable form, β. Particularly, the pseudo-β′→β transformation was significantly delayed, *e.g.* over 2.5 days at 30°C.

Solubility data. Solubility curves of the β_1 form of POP and SOS, and of β of POS in tetradecane are shown in Figure 3, and numerical data are displayed in Table 4. Solubilities of POP, SOS and POS increased with increasing temperature. The solubilities as expressed by molar fraction and 1/T (K^{-1}) did not follow the Van't Hoff equation in the three TAGs. The differences in the saturation temperatures between the β_1 forms of POP and SOS were 5.4∼5.5°C (5). Interestingly, the solubility of β of POS lies in-between those of the β_1 forms of POP and SOS below 13°C, but it became highest above that temperature. It was impossible to measure the solubility of other polymorphic forms, since the solution did not reach the equilibrium with the metastable forms due to the solution-mediated transformation to the more stable form.

Solvent crystallization. Figure 4 shows an optical photograph of a single crystal of β in POS crystallized via solution-mediated transformation from pseudo-β′ in acetonitrile solution. The interplanar angles of the rhombic crystals are 123° and 57°, which are nearly the same as those of β_1 of POP and SOS (5), and of β of trilaurin (18).

TABLE 3

Rate of Polymorphic Transformation of POS in Solid State

POS	α → pseudo-β′ 3 hr (18°C)	pseudo-β′ → β 2.5 day (3°C)
	δ → pseudo-β′ 1 day (25°C)	

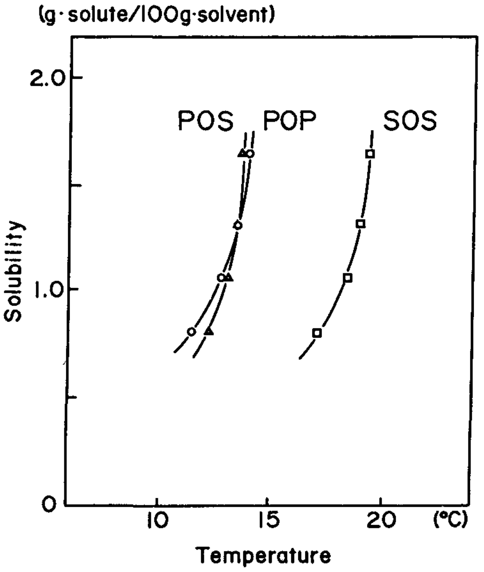

FIG. 3. Solubility of β form of POS, β_1 forms of POP and SOS in tetradecane solutions at different temperatures.

TABLE 4

Solubility Data of β_1 and β of POP, SOS and POS in Tetradecane

g solute / 100 g solvent	$T_s{}^a$(POP)	T_s(SOS)	T_s(POS)
1.65	13.9	19.3	13.3
1.30	13.6	19.0	13.2
1.05	12.9	18.3	13.0
0.80	11.5	17.0	11.9

$^a T_s$, saturation temperature (°C).

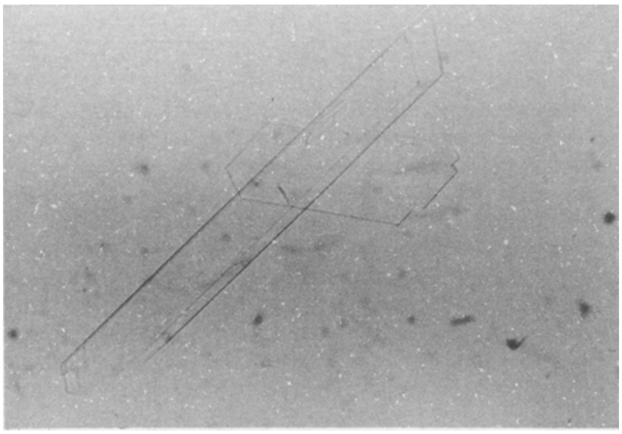

FIG. 4. Single crystals of β form of POS in acetonitrile solvent.

DISCUSSION

Nomenclature and independent polymorphs. In the nomenclature of the polymorphs of POS, we have used Larsson's method based on the subcell packing and melting temperature: α has hexagonal packing (H) and the lowest melting point, β′ has orthorhombic perpendicular packing ($O_\perp$) and β has triclinic parallel structure ($T_{//}$). In addition, the polymorphic form that was newly found in the present study was named in accordance with its structure and stability. In POS, we obtained four polymorphs, named α, δ, pseudo-β′ and β.

The α form was named based on a single XRD short-spacing peak of 4.23 Å, corresponding to hexagonal subcell packing. α first crystallized by chilling the melt and exhibited the lowest melting point. α is the least stable form.

δ was obtained only by a simple melt cooling method in a range of 24~25°C. In POP and SOS, the polymorphic form whose melting point lies between α and pseudo-β′ was γ. However, there are three major dissimilarities between γ of POP and SOS, and δ of POS. In the first, the XRD short spacing of δ of POS has no peak of 4.70 Å, which was the very strong peak in γ of POP and SOS. Also, three peaks of 4.63, 4.31 and 4.11 Å of δ of POS are not observed in γ of POP and SOS, although the peaks at 3.88–3.89 Å are commonly observed in the three forms. Secondly, δ was only crystallized by simple melt cooling in a narrow range of temperature, but not by the α-melt-mediated crystallization such as γ of POP and SOS. Lastly, δ was not formed by the solid-state transformation from the α form. This behavior differs from that of γ forms in POP and SOS. Therefore, we conclude that δ of POS was not the γ form that commonly occurred in POP, SOS, AOA and BOB.

Pseudo-β′ was named like in POP and SOS. "Pseudo-" means a certain deviation from the ordinary β′ form of saturated mono-acid TAG, which is packed according to $O_\perp$ subcell in a double-chainlength structure (19). In POS, pseudo-β′ predominantly crystallized in comparison with those of POP and SOS, because pseudo-β′ was formed not only by the α-melt-mediated transformation, but also by the solid-state transformation from the α and δ forms.

We defined the β form, having a peak at 4.58 Å corresponding to $T_{//}$ subcell packing. β was obtained by solvent crystallization, melt-mediated transformation and solid-state transformation from pseudo-β′. Simple melt cooling did not form β. β was the most stable form, exhibiting the same XRD short-spacing patterns as β_1 of POP and SOS (3). Importantly, POS did not possess β_2, which is the second stable form in POP and SOS (3).

Table 5 displays the nomenclature for the polymorphs of POS as reported in previous literature (20–22). A comparison with earlier reports was primarily based on XRD long- and short-spacings and on melting points. The present study shows a good agreement with previous reports except for the δ form, which was detectable as Form III from thermal analysis by Landmann *et al.* (22).

Polymorphic structure and phase transition. It is rather difficult to decide the precise polymorphic structure based

TABLE 5

Nomenclature for the Polymorphs of POS

Present	α	δ	Pseudo-β′	β	
Lutton	α-2		β′-2, β′-3	β-3	Ref. 20
Lavery	α-2		β′-3	β-3	Ref. 21
Landmann *et al.*	IV	III	II	I	Ref. 22

on the data obtained from the powder sample. Hence, we comparatively discuss properties of the four polymorphic structures of POS with those of POP and SOS (3).

Figure 5 shows the XRD long-spacing values of each polymorph in POP, SOS and POS (3). The long spacing of the α form in POS was 47.6 Å. This value corresponds to the double chainlength structure, in which palmitoyl and oleoyl chains are packed together in the same lamellae. The long-spacing value of α of POS is between those of the α forms of POP and SOS. As to the subcell structure, the α form is packed according to the same hexagonal type as POP and SOS (3), because a single peak at 4.23 Å was observed in the XRD short spacing. Hence, the zigzag planes of hydrocarbons are arranged in rotationally disordered orientation similar to α of mono-acid TAG (7).

The δ form reveals 70.6 Å values in the XRD long spacing, which corresponds to the triple chainlength structure and is almost equal to γ of SOS (3). In the triple chainlength structure, saturated acyl chains and oleoyl chains are separated, and a distinct oleoyl chain lamellae is packed between two saturated chain lamella. The δ form of POS may reveal normal orientation of the molecules with respect to the lamella plane, like γ of POP and SOS. However, the XRD short-spacing spectra for δ of POS indicate that the oleoyl chain as well as palmitoyl and stearoyl chains might be arranged in a different manner from γ of POP and SOS. In POP and SOS, α converted to γ both in solid-state and melt-mediated transformations. However, the α form in POS directly transformed to the pseudo-β′ form, not to δ. This again indicates the deviation of the structure of δ of POS from γ of POP and SOS.

The long-spacing value for pseudo-β′ of POS is 68 Å, corresponding to the triple chainlength structure. This value is a bit shorter than that of pseudo-β′ of SOS, 70 Å (Fig. 5). It is notable that the two pseudo-β′ forms of POP are both double chainlength structures (3). In the XRD short-spacing spectra, pseudo-β′ of POS has two strong peaks at 4.13 and 3.85 Å, which indicate the existence of orthorhombic perpendicular ($O_\perp$) subcell packing. Interestingly, the short-spacing pattern of Form IV in cocoa butter (8) quite resembles the pseudo-β′ of POS. This is because POS is the major component of cocoa butter. The pseudo-β′ form of POS directly transforms to the most stable β form in the solid state.

The triple chainlength structure was also observed in the β form of POS. The XRD short-spacing spectra of β reveal one strong peak at 4.58 Å, which indicates the triclinic parallel ($T_{/\!/}$) subcell packing of saturated acyl moieties. In addition, some medium strength peaks at 3.92, 3.85 and 3.70 Å are observed. As a whole, the β form of POS corresponds to the β_1 form of POP and SOS. The crystal habit of the single crystal of β also resembles the β_1 of POP and SOS. The β_2 form of POS was not detected in the two crystallization modes of simple melt cooling and α melt-mediated crystallization. In addition, the solid-state transformation from pseudo-β′ and solvent crystallization did not form β_2. Hence, we conclude that β_2, observed in POP and SOS, is not the distinct polymorph of POS, although there is no clear reason for that.

Thermal property. The melting points and enthalpies of fusion of each polymorph in POP, POS and SOS, determined by DSC, are shown in Figure 6 (3). In the α form, POS melts at 19.5°C and exhibits an intermediate value between POP and SOS. However, the melting point of pseudo-β′ of POS is almost the same as that of POP. Curiously, the melting point of β of POS, 35.5°C, is lower than β_1 of POP, 36.7°C. This means that the relationship of the thermodynamic stability of the most stable form is dependent on temperature. In the solubility measurement of β_1 of POP and β of POS, the conversion of the two solubility values of POP and POS occurred at 13.5°C, below which POS β is more stable than POP β_1. However, an opposite case was observed above 13.5°C. This tendency was also observed in fully saturated acid TAG. For example, the melting points of β of 1,3-*rac*-palmitoyl-stearoyl-2-palmitoylglycerol (PPS) (23) and 1,3-*rac*-palmitoyl-stearoyl-2-stearoylglycerol (PSS) (23) are 61.3 and 64.4°C, respectively, and they are lower than that of tripalmitin (PPP) (24), 66.4°C.

As for the α form, we could not measure the enthalpy of fusion, as explained above. So, we substituted it with the enthalpy of crystallization, ΔH_C. The ΔH_C for α of POS is smaller than those of POP and SOS. This may be caused by the weaker interaction in POS than in POP and

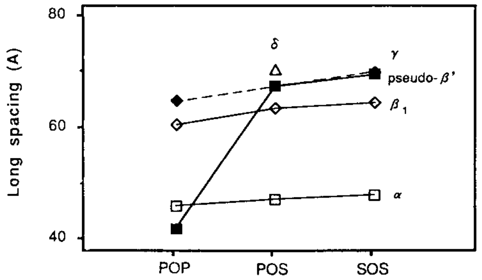

FIG. 5. X-ray diffraction long-spacing values of the polymorphs of POP, POS and SOS.

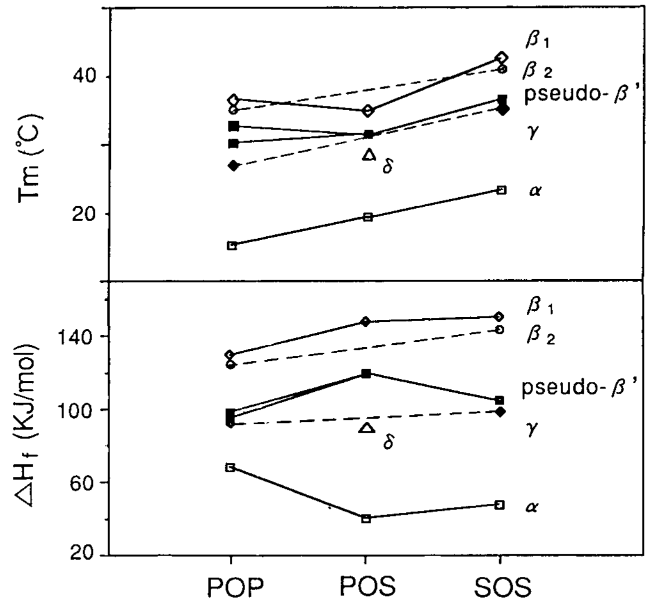

FIG. 6. Melting temperature (T_m) and enthalpy of fusion (ΔH_f) of the polymorphs of POP, POS and SOS. Enthalpy of crystallization was measured for α in the three triacylglycerols.

SOS at the lamella-lamella interfaces and adjacent acyl chains in α. Conversely, the ΔH_f of pseudo-β' POS is largest, and ΔH_f of β of POS is close to that of SOS, β_1. In fully saturated acid TAGs, ΔH_f for β of PPS (182.6 KJ/mol) (25) is larger than 1,3-distearoyl-2-palmitoylglycerol (SPS) (174.6 KJ/mol) (25). So, the difference in the acyl chainlengths at the *sn*-1,3-positions might contribute to the stabilization of the CH_3 end packing in the pseudo-β' and β modifications.

To conclude, the polymorphic behavior of POS differs somewhat from those of POP and SOS. In particular, no γ and β_2 were observed in POS, although these two forms occurred as the metastable forms in POP and SOS. Instead, a completely specific δ form was observed. This may be caused either by the chainlength differences of saturated acid moieties or by the POS sample itself, which may involve two optical isomers. The specific lattice packing may be unstabilized due to racemization. The present POS samples, obtained from both cocoa butter and synthesized by enzymatic interesterification are thought to be the racemic mixture. So, it is required to further investigate the polymorphism of stereospecifically numbered 1-palmitoyl-2-oleoyl-3-stearoyl glycerol.

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