

# Isothermal Crystallization of Tripalmitin in Sesame Oil

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**ABSTRACT:** Crystallization of tripalmitin (TP) in sesame oil was investigated under isothermal conditions at a cooling rate similar to the one achieved in industrial crystallizers (1 K/min). The results obtained indicated that, at TP concentrations <0.98%, triacylglycerides of sesame oil developed mixed crystals with TP. However, at concentrations within the interval of 0.98 to 3.44%, tripalmitin crystallized independently from sesame oil. Within this concentration interval, discontinuities were observed in the behavior of the induction time of TP crystallization ( $T_i$ ) in sesame oil as evidenced by differential scanning calorimetry, polarized microscopy studies, and determination of the Avrami index ( $n$ ). In general, the discontinuities in  $T_i$  were associated with different polymorph states developed by TP in sesame oil as a function of its concentration and crystallization temperature. Thus, TP crystals obtained at temperatures above 296 K with 1.80 and 2.62% TP solutions had  $n$  values close to 3 and developed lamellar-shaped crystals that are characteristic of  $\beta$  tripalmitin. In contrast, the crystals obtained at temperatures of 296 K and below with 1.80% and 2.62% TP solutions provided  $n$  values close to 3. Axialite-shaped  $\beta'$  TP crystals were obtained under these conditions. For the 0.98% TP solution, simultaneous production of  $\alpha$  and  $\beta'$  crystals occurred below 291 K. However, at temperatures above 291 K, a crystallization process with  $n = 3$  was obtained, and it developed a different polymorph state, i.e.,  $\beta$ , with lamellar-shaped TP crystals. *JAACS* 74, 69–76 (1997).

**KEY WORDS:** Avrami equation, crystallization, polymorphism, sesame oil, tripalmitin.

In the oil/fat industry, triacylglyceride crystallization is a process utilized to achieve any of the following objectives: (i) to eliminate small quantities of high-melting compounds from an oil so it remains clear at low ambient temperature (i.e., winterization); (ii) to obtain oil/fat fractions with particular temperatures for phase changes (e.g., solid→liquid, liquid→solid); and (iii) to develop or modify the texture of food systems. However, fats and oils are mixtures of different triacylglycerides, and consequently, they do not have specific melting and solidification temperatures. Rather, fats and oils show melting/solidification temperature profiles.

When oils are cooled, the triacylglyceride family with the highest melting temperature crystallizes and develops a solid

in a liquid phase (1–3). Eventually, after a sufficient crystallization time, a system with a fractal organization is developed (4). Furthermore, triacylglyceride crystallization is characterized by the development of polymorphic crystalline states with different physical properties (3,5,6) (i.e., crystal size, melting temperature). These two properties have a profound effect in the textural properties of food systems, such as butter and margarine (4,7).

Saturated monoacid triacylglycerides can form three types of polymorphic crystals, namely the  $\alpha$ -form with the lowest melting temperature, the  $\beta'$ -form with an intermediate melting temperature, and the  $\beta$ -form with the highest melting temperature. The crystallization/melting behavior of tripalmitin (TP), in pure form and in binary mixtures with other triacylglycerides, has been studied by differential scanning calorimetry (DSC) (8), nuclear magnetic resonance, X-ray diffraction (5, 9), and polarizing microscopy (6). TP is the triacylglyceride with the highest melting temperature in palm oil and represents 5–11% of its composition (10,11). However, after dry fractionation, the solid fraction obtained (i.e., palm stearin) may contain, depending on the crystallization temperature, between 12–56% of TP (10). Thus, TP must have a significant effect on the crystallization kinetics and polymorphic behavior of palm oil and palm stearin. Nevertheless, to the best of our knowledge, there are no studies that investigate TP crystallization ( $T_i$ ) in mixtures with vegetable oils. The results obtained with this model system will support further investigations about the behavior of palm oil or its derivatives in mixtures with vegetable oils. In the near future, palm oil will be the most economical and abundant edible oil worldwide (12). Thus, there is a need to develop food systems that eventually support the expansion in the utilization of palm oil or its derivatives.

The aim of this study was to investigate the isothermal crystallization of TP in sesame seed oil by DSC, polarizing microscopy and crystallization curves determined by spectroscopy. Few studies regarding the physicochemical properties of sesame oil and/or its interactions with other lipid systems (i.e., TP and tristearin) have been published (13–15). Sesame seed (*Sesamum indicum* Linn.) oil has a high natural oxidative stability and unique flavor. Mexico is one of its major producers. Kamal-Eldin and Appelqvist (16,17) and Kamal-Eldin *et al.* (18) have investigated the fatty acid and triacylglyceride composition of sesame oil, as well as its concentration of sterols, tocopherols, and lignins.

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## EXPERIMENTAL PROCEDURES

$$\ln(x) = \Delta H_f/R (1/T_p - 1/T_s) \quad [1]$$

**Materials.** The same batch of whole-seed refined sesame oil was used in all experiments. The sesame oil was obtained from a local industry (Aceitera San Juan, Salvatierra, Gto. Mexico). TP was obtained from Sigma Chemical Co. (St. Louis, MO), and its purity (>99%) was confirmed by gas chromatography and DSC. For the gas chromatography analysis, a Supelco (Bellefonte, PA) glass column (2.6 m × 2.1 mm) packed with GP 10% SP 2330 on Chromosorb 100/120 was utilized.

**Chemical analysis.** The iodine and saponification values of sesame oil were determined by following AOAC procedures (19). Fatty acid composition was determined by gas chromatography, by following the methodology of Bannon *et al.* (20), in a Shimadzu chromatograph GC-9A (Shimadzu Corp., Kyoto, Japan) with flame-ionization detector. The temperature in the column was 200 and 215°C in the injection port, and helium was used as the carrier gas (20 mL/min). Fatty acid concentration was determined after normalization of chromatogram areas according to the method of Ackman and Sipos (21).

**DSC.** The equipment (Perkin-Elmer model DSC-7; Norwalk, CT) was calibrated with Indium and the baseline was obtained with an empty aluminum pan. For dynamic (i.e., nonisothermal) runs, ≈12 mg samples of TP or TP solution in sesame oil (0.00, 0.32, 0.98, 1.80, 2.62, and 3.44%, wt/vol) were sealed in sample pans and held at 353 K for 30 min before each DSC scan. The system was cooled at 10 K/min until a temperature of 243 K was achieved. After 2 min at this temperature, the melting curve was obtained by heating at 5 K/min until reaching 353 K. The temperature corresponding to the beginning of crystallization (i.e., temperature where the heat capacity of the sample had a significant departure from the baseline) and the maximum in the melting peak ( $T_s$ ) were calculated with the DSC-7 software library. The enthalpy of fusion of pure TP was determined in the same way.

The ideal behavior of TP in sesame oil was evaluated with the Hildebrand equation (22):

where  $\Delta H_f$  is the enthalpy of fusion per mole of pure TP,  $T_p$  and  $T_s$  are the melting temperature of TP in the pure state and in oil solutions, respectively (i.e., the maximum temperature in the DSC endotherm),  $R$  is the universal gas constant, and  $x$  is the mole fraction of TP. An average molecular weight for sesame oil triacylglycerides was calculated (877.65) from the sesame oil fatty acids composition (Table 1).

For isothermal runs, the TP solution was heated at 353 K for 30 min and then cooled (1.0 K/min) to a preset temperature (287–299 K) and held at that temperature for crystallization. After a time equivalent to achieve the minimum transmittance in the crystallization curves (see next section), the melting thermogram was obtained by heating at a rate of 1.0 K/min. The  $T_i$  was calculated as the period of time from the start of the isothermal process to the beginning of crystallization (i.e., time where the heat capacity of the sample had a significant departure from the baseline) (23) by using the DSC-7 software library.

**Crystallization curves.** Isothermal crystallization curves of TP solutions (0.00, 0.98, 1.80, and 2.62%, wt/vol) were obtained by measuring its transmittance (600 nm) as a function of time at constant temperature within 287 and 299 K. A double-beam spectrophotometer with data acquisition system (Shimadzu UV-2101PC; Shimadzu Corp.) and temperature control (Brookfield TC-500; Brookfield Instruments, Stoughton, MA) was utilized. After destroying the “memory” of crystallization of the solution (353 K for 30 min), the system was cooled at 1.0 K/min until the desired temperature was reached ( $\pm 0.2$  K). The transmittance of the solutions was recorded every 12 s. The spectrophotometer was calibrated with the liquid fraction obtained by filtration of sesame seed oil after storage at 4°C for 15 d and 1 h at  $-20^\circ\text{C}$ .

The fractional crystallization ( $F$ ) as a function of time ( $t$ ) was calculated as  $F = (T_i - T)/(T_i - T_f)$  where  $T_i$  is the transmittance of the oil solution at time zero,  $T$  is the transmittance at time  $t$ , and  $T_f$  is the minimum transmittance obtained during the crystallization process. From the Avrami equation:

**TABLE 1**  
Fatty Acid Profiles (% wt/vol) for Sesame Seed Oil Obtained in Three Different Studies

Acid	This study <sup>a</sup>	Toro-Vazquez and Gallegos-Infante (Ref. 15) <sup>a</sup>	Kamal-Eldin and Appelqvist (Ref. 16) <sup>a</sup>
Palmitic (16:0)	10.03 ± 0.21	9.50 ± 0.07	9.35 ± 0.23
Stearic (18:0)	5.71 ± 0.05	5.42 ± 0.05	6.10 ± 0.37
Palmitoleic (16:1)	0.28 ± 0.05	0.29 ± 0.04	0.18 ± 0.04
Oleic (18:1)	40.14 ± 0.20	39.70 ± 0.28	42.75 ± 1.14
Linoleic (18:2)	42.70 ± 0.12	43.75 ± 0.17	39.70 ± 1.28
Linolenic (18:3)	0.61 ± 0.15	0.60 ± 0.23	0.58 ± 0.04
<i>cis</i> -Vaccenic (18:1 Δ11)	n.d.	n.d.	0.85 ± 0.05
Arachidic (20:0)	n.d.	n.d.	0.30 ± 0
Unidentified	0.64 ± 0.15	0.50 ± 0.26	n.d.
Chemical indexes:			
Free fatty acids	0.20 ± 0.20	n.d.	n.d.
Saponification index	160.89 ± 2.51	n.d.	n.d.
Iodine index	87.56 ± 0.95	n.d.	n.d.

<sup>a</sup>Mean and SD ( $n = 4$ ); n.d. = not determined.

$$-\ln(1-F) = zt^n \quad [2]$$

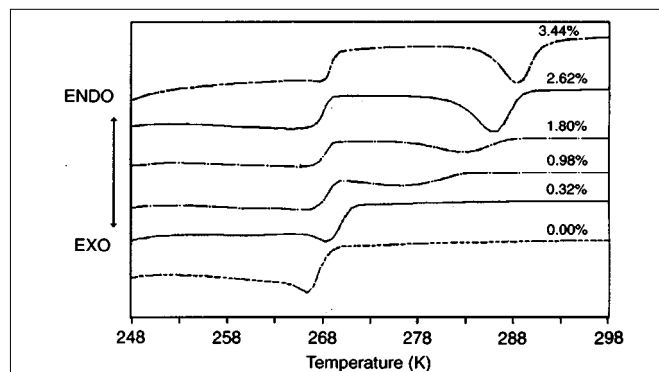
the index of crystallization reaction ( $n$ ) was calculated from the slope of the linear regression of  $\ln[-\ln(1-F)]$  vs.  $\ln(t)$ , using values of fractional crystallization within 0.25 and 0.75 (24). Since  $n$  has to be an integer number, the calculated value was rounded off to the nearest integer number. The  $n$  value describes the crystal growth mechanism, thus a crystallization process with  $n = 4$  follows a polyhedral crystal growth mechanism,  $n = 3$  represents a plate-like crystal growth mechanism, and  $n = 2$  indicates linear crystal growth (23). The rate constant of spherulite crystallization,  $z$ , depends on the magnitude of  $n$  and is a function of both nucleation rate and linear growth rate (23).

**Microscopy studies.** Crystal morphology was studied under isothermal conditions (287–299 K) with a polarized microscope with camera (model BX60F/PMC35; Olympus Optical Co., Ltd., Tokyo, Japan). The objective magnification was 20 $\times$ , and the ocular magnification was 10 $\times$ . Temperature control was achieved with a specially built platen that was equipped with a heating/cooling system (Brookfield model TC-500; Brookfield Instruments). A small volume ( $\approx 4 \mu\text{L}$ ) of TP oil solution was dropped on a glass slide, and after placing a cover slip, the system was heated to 353 K for 30 min and then cooled (1.0 K/min) until the desired temperature was reached. After induction of nucleation, pictures of the crystals were taken as a function of time.

## RESULTS

The fatty acids profile of sesame oil is shown in Table 1. In general, sesame oil composition was in close agreement with the results obtained by Toro-Vazquez and Gallegos-Infante (15) and Kamal-Eldin and Appelqvist (16). However, the latter authors (16) obtained slightly higher concentrations of stearic and oleic acid and lower concentrations of palmitic, palmitoleic, and linoleic acid than obtained in this study and by Toro-Vazquez and Gallegos-Infante (15). These differences can be explained by considering that Kamal-Eldin and Appelqvist (16) utilized unrefined sesame oil from species grown in the Sudan, while in Reference 15 and in this study, a refined sesame oil extracted from species grown in Mexico was used.

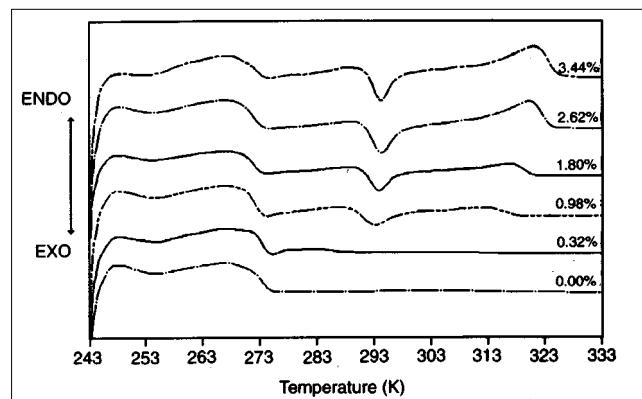
Sesame seed oil showed a high degree of unsaturation, and thus the onset of crystallization occurred at low temperature (270.5 K, Fig. 1). The crystallization temperature was lower than that determined by Toro-Vazquez and Gallegos-Infante (277.6 K) (15) from turbidity measurements and a cooling rate of 1.0 K/min. This divergence in crystallization temperatures could not be explained on the basis of significant differences in fatty acid composition (Table 1). Furthermore, when the onset of crystallization was determined from turbidity measurements and a cooling rate of 1.0 K/min as reported earlier (15), a temperature of 271.2 K was obtained. This value was in agreement with the one determined by DSC (Fig. 1). As has been reported in crystallization studies with palm oil



**FIG. 1.** Dynamic differential scanning calorimetry cooling (10 K/min) experiments for sesame oil (0.00%) and tripalmitin solutions in sesame oil at different concentrations (0.32, 0.98, 1.80, 2.62, and 3.44 wt/vol). ENDO, endothermic; EXO, exothermic.

(25), differences in crystallization temperature among different batches of oil from the same source might be associated with variations in the concentration of diacylglycerides and/or free fatty acids. However, the effect of these components on sesame oil crystallization was not studied in this investigation nor in our previous study (15).

The cooling and heating thermograms for sesame oil, pure TP, and TP-sesame oil solutions are shown in Figures 1 to 3. Sesame oil showed a broad crystallization peak with a maximum at 266.2 K (Fig. 1), two overlapping melting peaks with maxima at 248.5 and 268.5 K, and completion of melting at 275.8 K (Fig. 2). These results contrast with those reported by Hannewijk and Haighton (13) who, with differential thermal analysis, found two melting peaks in sesame oil at  $\approx 255.2$  and  $\approx 262.2$  K and the end of melting at  $\approx 273.2$  K. This difference can be explained by considering the distinct thermal history of the oil used in each study. We melted (5 K/min) refined sesame oil that was cooled down to 243 K at a rate of 10 K/min, while Hannewijk and Haighton (13) melted (1.8 K/min) unrefined sesame oil that had been gradually crystallized (2 d) to 203 K.



**FIG. 2.** Dynamic differential scanning calorimetry heating (5 K/min) experiments for sesame oil (0.00%) and tripalmitin solutions in sesame oil at different concentrations (0.32, 0.98, 1.80, 2.62, and 3.44 wt/vol). See Figure 1 for abbreviations.

The crystallization profile of TP (10 K/min) showed a single exothermic peak at 317.9 K, and the melting thermogram (5 K/min) showed an endotherm peak around 332 K, an exothermic peak at  $\approx 332$  K, followed by an endothermic peak with a maximum at 342.1 K (Fig. 3). This calorimetric behavior of TP has been previously observed by Norton *et al.* (5) at cooling/heating rates of 0.5 K/min and 1 K/min. Through X-ray diffraction analysis, these authors associated the first endothermic peak to melting of TP in the  $\alpha$  form, the exothermic peak to the polymorphic transformation  $\alpha$ -melt  $\rightarrow$   $\beta$ -crystallization, and the second endothermic peak to the melting of TP in the  $\beta$  form (5). Within this framework, it was established that the fusion temperature of TP was 342 K with a  $\Delta H_f$  for TP of 185.37 J/g. The magnitude of the values calculated were somehow different from the ones determined by Norton *et al.* (5) at a heating rate of 0.125 K/min ( $\Delta H_f = 204.37$  J/g and melting temperature of 339.7 K). However, the shape and behavior (i.e.,  $\alpha$  to  $\beta$  polymorphic transformation of TP) of melting curves obtained by DSC are strongly dependent on the scan rate utilized for cooling/heating (5).

When TP was present in the sesame oil, a distinct peak was observed in the cooling thermograms. The position of the exothermic peak shifted to lower temperature and broadened as the TP concentration was decreased in the sesame oil (Fig. 1). For the melting thermograms of TP–sesame oil solutions (Fig. 2), the peaks corresponding to  $\alpha$  melting, polymorphic transformation  $\alpha$ -melt  $\rightarrow$   $\beta$ -crystallization, and  $\beta$  melting of TP were present. As observed in the cooling thermograms (Fig. 1) for TP crystallization, melting peaks shifted to lower temperature and broadened as TP concentration decreased in sesame oil (Fig. 2). Thus, sesame oil solubilized TP, and this effect was more evident as the TP concentration decreased in the system.

To evaluate this effect, we utilized the Hildebrand solubility equation (Fig. 4). This equation states that, for an ideal solution, the logarithm of the molar fraction of a solid (i.e., TP) in a solvent (i.e., sesame oil) is proportional to the reciprocal of the solid melting temperature. An excellent linearity be-

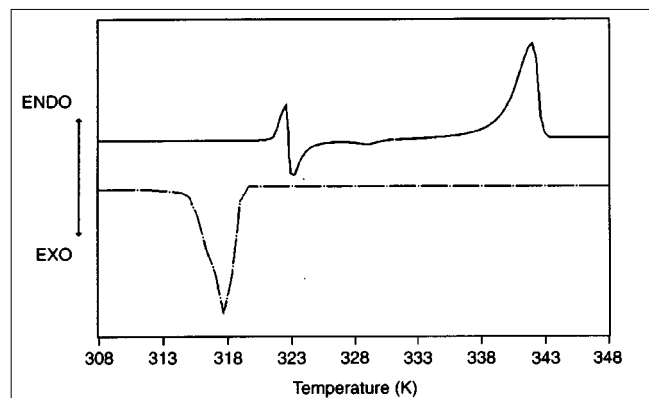


FIG. 3. Melting profile (solid line, 5 K/min) and crystallization process (dotted line, 10 K/min) for pure tripalmitin. See Figure 1 for abbreviations.

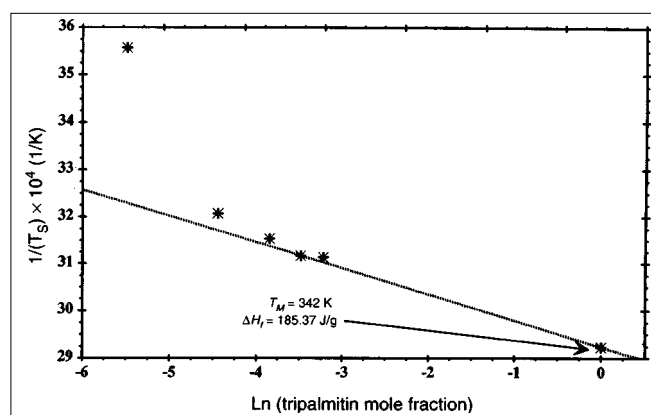


FIG. 4. Solubility of tripalmitin in sesame oil. Experimental data fitted according to the Hildebrand equation. The arrow indicates the fusion temperature ( $T_M$ ) and  $\Delta H_f$  for pure tripalmitin (molecular weight = 807.34) utilized in the equation.  $T_s$  is the melting peak temperature for tripalmitin in the sesame oil solutions.

tween 0.98 and 3.44% of TP was obtained (i.e., ideal solution behavior). However, at 0.32% TP, a significant deviation from ideality was observed (i.e., TP melted at lower temperatures than predicted) (Fig. 4). These results suggest that mixed crystal formation occurred at TP concentrations  $< 0.98\%$ . A high-melting temperature triacylglyceride fraction of sesame oil could co-crystallize with TP and depress the melting point below the value predicted for pure TP (Fig. 4).

From the above results, three TP concentrations within the interval of ideal solution behavior (0.98, 1.80, and 2.62%) were selected to investigate tripalmitin crystallization in sesame oil by using the Avrami model and DSC studies. Thus, the index of crystallization reaction ( $n$ ) according to the Avrami equation (Equation 2) was determined from crystallization curves obtained by transmittance. In all cases, the regression coefficient of the plot of  $\text{Ln}[-\text{Ln}(1 - F)]$  vs.  $\text{Ln}(t)$  was greater than 0.9998 (data not shown). The values of  $n$  as a function of crystallization temperature are shown in Table 2. The corresponding DSC isothermal crystallization curves showed a single exotherm peak that broadened as the temperature of crystallization increased. As an example, Figure 5 shows the DSC thermograms for the 2.62% TP solution at different crystallization temperatures. Considering that no exothermic peak was observed in sesame oil that was subjected to the same temperature conditions, the exothermic peak obtained in TP sesame oil solutions was associated just with tripalmitin crystallization. Besides, after separation of the crystals developed at different temperatures (0.98% at 298 K, 1.80% at 294 K, and 2.62% at 296 K), the only fatty acid utilized from the oil phase as a function of crystallization time was palmitic acid (data not shown). Therefore,  $n$  values described the crystal growth mechanism followed by TP in sesame oil. The results shown in Table 2 indicate that TP crystallized in sesame oil by following different mechanisms for crystal growth as a function of crystallization temperature. Thus, in the 0.98% TP solution, the crystallization of TP followed a polyhedral crystal growth mechanism at 287 K and a

**TABLE 2**  
Index of the Crystallization Reaction ( $n$ ) According to the Avrami Equation for the Three Concentrations of Tripalmitin in Sesame Oil at Different Crystallization Temperatures<sup>a</sup>

Temperature (K)	Tripalmitin concentration (% wt/vol)		
	0.98	1.80	2.62
285	— <sup>a</sup>	— <sup>a</sup>	— <sup>a</sup>
287	4.14 (4.0)	— <sup>a</sup>	— <sup>a</sup>
289	3.28 (3.0)	— <sup>a</sup>	— <sup>a</sup>
291	3.23 (3.0)	— <sup>a</sup>	— <sup>a</sup>
293	3.35 (3.0)	— <sup>a</sup>	— <sup>a</sup>
294	3.39 (3.0)	2.79 (3.0)	— <sup>a</sup>
294.5	n.d. <sup>c</sup>	n.d.	3.47 (3.0)
295	3.20 (3.0)	2.46 (2.0)	n.d.
295.5	n.d.	n.d.	3.38 (3.0)
296	n.d.	3.39 (3.0)	2.46 (2.0)
297	n.d.	2.83 (3.0)	n.d.
297.5	n.d.	n.d.	2.67 (3.0)
298	n.d.	3.37 (3.0)	n.d.
298.5	n.d.	n.d.	2.64 (3.0)
299	n.d.	2.49 (2.0)	3.06 (3.0)

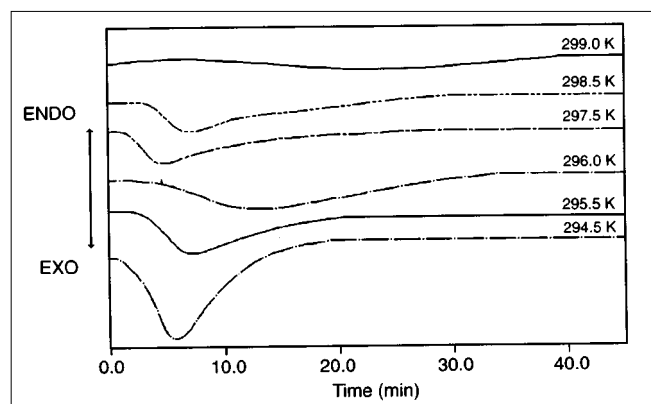
<sup>a</sup>Since  $n$  has to be an integer number, its value is rounded off to the nearest integer (value shown in parentheses).

<sup>b</sup>The system crystallized before reaching the isothermal temperature.

<sup>c</sup>n.d. = Not determined.

plate-like mechanism between 289 to 295 K (Table 2). Micrographs of crystals developed at different temperatures and TP concentrations, corresponding to values of  $n = 4$ ,  $n = 3$  and  $n = 2$ , are shown in Figure 6. It is important to point out that the value of  $n$  describes just the mechanism of crystal growth and it is not associated with crystal size or polymorphic form of the crystal.

From the cooling thermograms obtained (i.e., Fig. 5), we calculated the induction time ( $T_i$ ) for TP crystallization in sesame oil. A linear relationship between crystallization temperature and the logarithm of  $T_i$  was expected for each of the TP oil solutions. However, we observed discontinuities at  $\approx 290$  K with the 0.98% TP solution and at 296 K for 1.80% and 2.62% TP solutions (Fig. 7). These discontinuities may

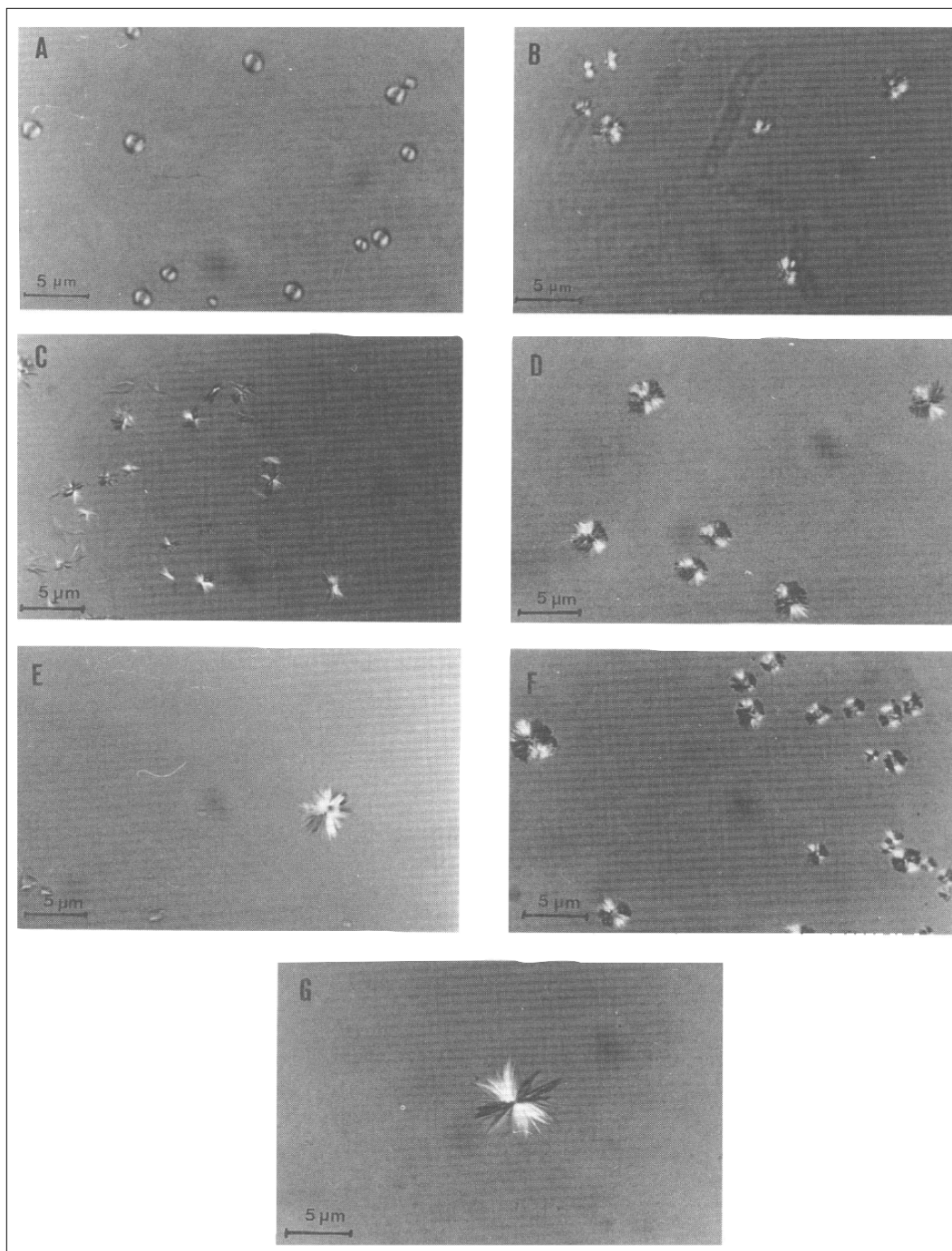


**FIG. 5.** Crystallization curves for the 2.62% tripalmitin solution in sesame oil at different crystallization temperatures. See Figure 1 for abbreviations.

be associated with different polymorphic states developed by TP as a function of crystallization temperature and concentration of TP in sesame oil. Kellens *et al.* (6) used a microscopic approach and have shown how the crystal morphology and the polymorphic form developed by pure TP depending on the isothermal temperature utilized or thermal history of the system. These authors have shown how the nucleation rate of pure TP, a value inversely associated with  $T_i$ , displays discontinuous behavior at temperatures where  $\beta$  crystallization becomes dominant (above 323 K) and  $\beta'$  crystallization is almost completely suppressed (6). On the other hand, Kawamura (23), in isothermal DSC studies with palm oil, reported a critical temperature of occurrence for  $\alpha$  crystals at 299 K. According to this author, the crystals developed in palm oil below 299 K were in the  $\alpha$  polymorph state (probably mixed with  $\beta'$ ), whereas those developed above 299 K were  $\beta$  crystals. Additional studies by Ng (26) reported a critical temperature of 297 K for palm oil and 306 K for palm stearin, which suggests that the critical temperature for polymorphic transformation depends on TP concentration in the oil. The results obtained indicate that in diluted TP solutions this discontinuity was also present, e.g., in sesame oil, TP crystallized in the  $\beta$  polymorph state at temperatures above 296 K, while below 296 K it crystallized in the  $\beta'$  polymorph state, probably mixed with  $\alpha$  crystals.

To further investigate the nature of the  $T_i$  discontinuities, the melting thermograms of crystals, produced at different temperatures with TP sesame oil solutions, were obtained. Figure 8 shows the melting thermograms of crystals produced with the 2.62% TP sesame oil solution. This melting profile was similar to the one obtained with the 1.80% TP solution (data not shown). Figure 9 shows the melting thermogram for the 0.98% TP oil solution. A single endothermic peak was obtained with 1.80 and 2.62% TP solutions (Fig. 8), while two endothermic peaks were observed with the 0.98% solution (Fig. 9). The discontinuity observed in the  $T_i$  of tripalmitin crystallization at 296 K (Fig. 7) was also evident in the melting behavior of crystals obtained with 1.80 and 2.62% TP oil solution (Fig. 8). These results indicate that different polymorph states were developed above and below 296 K. The crystals obtained at temperatures above 296 K with 1.80% and 2.62% TP solutions had  $n$  values close to 3 (Table 2), indicating a plate-like growth mechanism. The crystals obtained at such conditions (Fig. 6) showed a shape characteristic of  $\beta$  TP crystals when developed directly from its melt (6). At 296 K and below, the crystals obtained with 1.80 and 2.62% TP solutions provided  $n$  values close to 3 (Table 2). This plate-like growth mechanism was consistent with the axialite-shaped crystals obtained at such conditions (Fig. 6) and characteristic of  $\beta'$  TP crystals (6). These results confirmed that, at concentrations of 1.80 and 2.62%, TP crystallized in sesame oil in the  $\beta$  form at temperatures above 296 K, and in the  $\beta'$  form below this temperature.

For the melting thermograms of the crystals obtained at 287 K with the 0.98% TP oil solution (Fig. 9), we observed a low-melting peak around 301 K ( $n$  value of 4, Table 2). At



**FIG. 6.** Microphotographies of the crystals developed by tripalmitin in sesame oil. 0.98% tripalmitin crystallized at 287 K (A), 291 K (B), 295 K (C); 1.80% tripalmitin crystallized at 294 K (D), 295 K (E); 2.62% tripalmitin crystallized at 294.5 K (F), 297.5 K (G). Photographs were taken at 30 min after the induction time at the indicated temperature. The corresponding index of crystallization reaction ( $n$ ) is indicated in Table 2.

this crystallization temperature, fast nucleation with small spherulitic crystals was observed (Fig. 6), a behavior characteristic of TP in the  $\alpha$  form. This endothermic peak rapidly decreased in size while a higher-melting peak ( $\approx 315$  K) increased in size and broadened as crystallization temperature was raised from 287 to 291 K (Fig. 9). This behavior shows that, below 291 K, simultaneous production of  $\alpha$  and  $\beta'$  crys-

tals occurred in the 0.98% TP solution. When crystallization temperature was above 291 K, the higher melting peak showed a dramatic increase in its melting temperature ( $\approx 325$  K), indicating that a different polymorph state was developed, i.e.,  $\beta$ . Again, the  $n$  value of 3 was consistent with the lamellar-shaped crystals for the  $\beta$  TP form (6).

This study has shown that it is possible to develop a solid

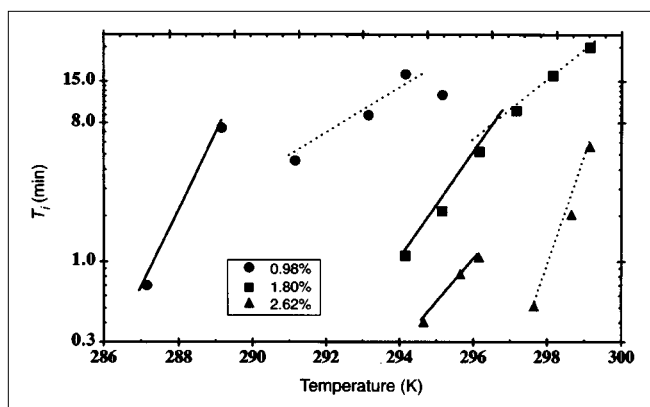


FIG. 7. Induction time ( $T_i$ ) for tripalmitin crystallization in sesame oil as a function of temperature and tripalmitin concentration (% wt/vol).

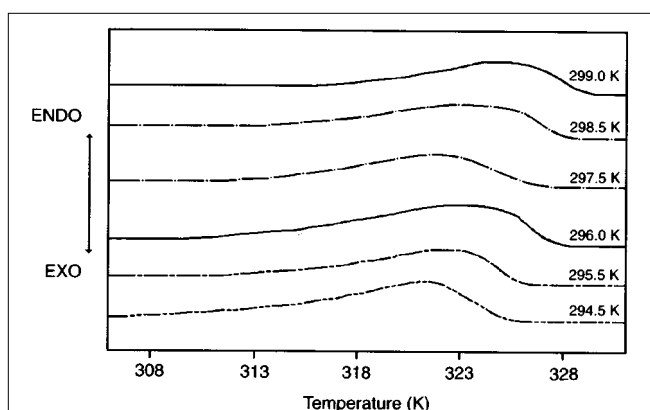


FIG. 8. Melting profile (1 K/min) of the crystals developed in the 2.62% tripalmitin sesame oil solution. The crystallization temperatures are indicated. See Figure 1 for abbreviations.

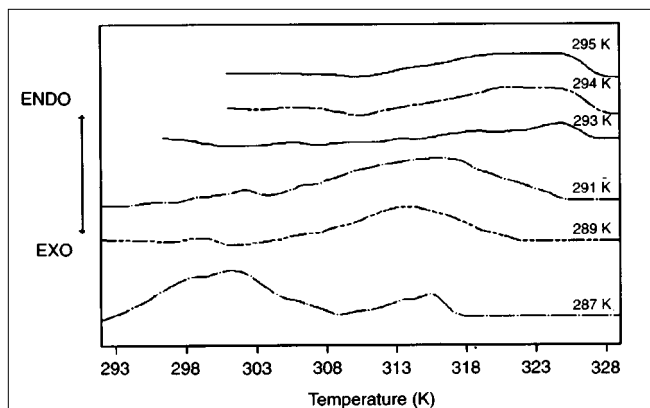


FIG. 9. Melting profile (1 K/min) of the crystals developed in the 0.98% tripalmitin sesame oil solution. The crystallization temperatures are indicated. See Figure 1 for abbreviations.

phase in sesame oil, through mixture with a lipid fraction or vegetable oil of high melting point (e.g., tristearin or palm oil). TP, the triacylglyceride with the highest melting temperature in palm oil and palm stearin (27), crystallized indepen-

dently of sesame oil at concentrations above 0.98% and developed polymorph states with different shapes and sizes as a function of its concentration in the system and the crystallization temperature. In addition to the melting/crystallization temperature of the crystals, shape, size, and, in general, the network of aggregated fat crystals that entrap oil determine the functionality (i.e., texture, spreadable) of oil/fat food systems (i.e., butter, vegetable creams, margarine). As a consequence, the rheology and fractal nature of fat crystal dispersions are currently receiving much attention. Ongoing research in our laboratory involves evaluating the rheology of crystal dispersions developed with TP–sesame oil and palm tristearin–sesame oil systems.

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