Effects of Hydrophobic Emulsifier Additives on Crystallization Behavior of Palm Mid Fraction in Oil-in-Water Emulsion

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ABSTRACT: Ultrasonic velocity measurements and X-ray diffraction were employed to monitor the crystallization behavior of palm mid fraction (PMF) in oil-in-water emulsions (20 vol%). Three hydrophobic emulsifiers—sucrose oligoesters (SOE) containing palmitic acid (P-170) and stearic acid (S-170) moieties and a polyglycerine ester (DAS-750) containing a stearic acid moiety—were added to PMF in an attempt to increase the rate and extent of crystallization of PMF, which are otherwise suppressed owing to emulsification of the oil phase into many droplets. The results revealed that the hydrophobic emulsifiers accelerate the nucleation of PMF in the emulsion system, while retarding the rate of crystal growth. As a result, the crystallization temperature (T_c) of PMF increased with increasing concentrations of the hydrophobic emulsifiers. The effects of the three additives were different; in particular the addition of DAS-750 remarkably enhanced crystallization at low concentrations. By adding the emulsifiers at higher concentrations, the polymorphic behavior of PMF crystallization was also modified to different degrees, depending on the type of emulsifier. With addition of SOE, PMF crystallized predominantly in the β′ form; with addition of DAS-750, the extent of β′ nucleation was reduced by comparison with that observed with SOE. The results were explained in terms of adsorption of the hydrophobic emulsifier additives at the oil–water interface, which provides a template for acceleration of surface heterogeneous nucleation of PMF in the emulsion system.

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KEY WORDS: Fat crystallization, heterogeneous nucleation, hydrophobic emulsifiers, O/W emulsion, palm oil, polymorphism.

Crystallization of solid fats in oil-in-water (O/W) emulsion systems has captured the interest of many researchers owing to its importance in coagulation processes of emulsions in chilled states, de-emulsifying of whipped creams, freezing of ice creams, etc. (1–4). The production, stability, and quality of food products containing emulsified fat are influenced by crystallization of the oil phase (5), and hence many researchers have dealt with the different factors affecting the crystallization, e.g., cooling rate, thermal treatment, impurities, type of emulsifier, etc. (6–10). We have recently studied the fundamental mechanisms of fat crystallization accelerated by hydrophobic additives placed in the oil phase using *n*-hexadecane as a model system (11–15). It was obvious that the addition of highly hydrophobic emulsifiers having high melting points accelerates the crystallization of *n*-hexadecane in O/W

emulsions, as evidenced by the increase of the crystallization temperature (T_c) from 3°C without additives to 13°C with sucrose oligoesters (11,12) and to 8°C with polyglycerine esters (13). The mechanisms of acceleration of nucleation, which did not occur in the bulk state, were interpreted by taking into account heterogeneous nucleation of *n*-hexadecane, which was induced by a template formed by the addition of the hydrophobic emulsifiers into *n*-hexadecane (15).

Based on the experimental findings obtained using the model system represented by *n*-hexadecane, which does not exhibit polymorphism, we have undertaken studies of the crystallization of edible oils in O/W emulsions. In the present work, we deal with the palm mid fraction (PMF), which exhibits polymorphism in a multicomponent fat system. The crystallization behavior of PMF in emulsions is important from an industrial point of view, since palm oil is now one of the major oils used in many food applications. It represents about 23% of the world output of the major vegetable oils and fats (16). In addition, PMF, a fraction of palm oil having melting points in between those of palm stearin and palm olein (17), has been employed in vegetable-fat-based creams.

In the present work, we studied the crystallization behavior of PMF in O/W emulsions, examining the two main mechanisms of crystallization, heterogeneous nucleation and crystal growth, in a separate manner. The polymorphic crystallization of PMF was also examined, since the polymorphic properties of the fat crystals affect the various physical properties of food fats (18). Ultrasonic velocity measurements were used to monitor the crystallization process, together with X-ray diffraction (XRD). Sucrose oligoesters (SOE) and a polyglycerine ester (PGE) were chosen as the additives, since their molecular and dispersion properties have been studied and their effects on the crystallization of *n*-hexadecane have also been elucidated in the bulk and emulsion states (14,15).

MATERIALS AND METHODS

PMF (hard type) was provided by Fuji Oil Ltd. (Izumisano, Japan). The fatty acid composition of PMF and the main triacylglycerol components are summarized in Table 1. The O/W emulsion was prepared as follows. A mixture of distilled water and Tween 20 (2.0 wt% with respect to the total amount of oil and water phase) was mixed with PMF in a ratio of 80:20 (vol/vol). A high-speed mixer (4000 rpm) was used to mix the mixture components for 5 min prior to homogenization. Homogenization was performed by passing the mixture through a microfluidizer four times at a pressure of 8.5

TABLE 1
Fatty Acid and Major Triacylglycerol (TAG) Compositions of Palm Mid Fraction

Fatty acid	%	Major TAG[a]	%
M (myristic)	0.8	POP	64.0
P (palmitic)	56.1	POS	13.3
S (stearic)	6.1	PLP	6.3
O (oleic)	33.5	Others	16.4
L (linoleic)	2.7		
Li (linolenic)	0.5		
B (behenic)	0.1		

[a]POP = 1,3-dipalmitoyl-2-oleoyl-*sn*-glycerol, POS = 1,3-*rac*-palmitoyl-stearoyl-2-oleoyl-glycerol, PLP = 1,3-dipalmitoyl-2-linoleoyl-*sn*-glycerol.

kg/cm². The temperature of the mixture was kept above 6°C to avoid PMF crystallization.

Highly hydrophobic SOE emulsifiers in which the fatty acid moieties are palmitic acid (P-170) and stearic acid (S-170) were purchased from Mitsubishi Kagaku Foods Corporation (Tokyo, Japan), and a polyglycerine-ester containing stearic acid (DAS-750) was supplied by Sakamoto Pharmaceuticals (Osaka, Japan). The hydrophilic–lipophilic balance (HLB) values of these hydrophobic emulsifiers were in the range of 2–4, and they were added to the PMF prior to emulsification. The concentrations of the additives ranged from 0.1 to 1 wt% with respect to the oil phase. A laser particle size analyzer (SALD-2000 J; Shimadzu, Kyoto, Japan) was used to measure the particle size distribution of the emulsion droplets, and the measurements were performed soon after the emulsion was prepared. The average droplet diameter was calculated to be 0.8 ± 0.2 μm.

The ultrasonic velocity equipment employed to monitor the fat crystallization has been described elsewhere (10). Briefly, the sample was introduced into a brass cell equipped with two quartz X-cut transducers, having a base frequency of 2 MHz, placed 2.8 cm apart. A pulse generator (Iwatsu, PG-230, Tokyo, Japan) and a function generator (Iwatsu, FG-350) were employed to generate and adjust the electrical pulse, respectively. The electrical pulse changes to an ultrasonic wave after passing through one transducer, and then it converts back to an electric pulse after passing through the sample to the second transducer. An oscilloscope (Sony-Tektronix, TDS340AP, Tokyo, Japan) was used to monitor both the original and the final electric pulse as a function of the ultrasonic velocity. The output for pulse generation was 20 V, and the accuracy in the ultrasonic measurements was 1 m/s. The prepared emulsion was placed in the sample cell, which was held in a temperature-controlled water bath at 60°C; an interval of 30 min was required to ensure the thermal equilibration of the sample cell at the programmed temperature. The average of three measurements at each temperature was taken.

The polymorphic behavior was observed by a time-resolved X-ray diffraction (XRD) method. A RINT-TTR diffractometer (Rigaku, Tokyo, Japan), with a rotator-anode emitting Cu -Kα (wavelength 0.154 nm) radiation and a Ni filter [8.4 kW (42 kV, 200 mA)] was employed. It has a vertical goniometer in which the liquid sample was mounted on the X-ray diffrac-

tion glass plate, placed in a horizontal positions, and cooled by using a temperature-controlled sample holder.

RESULTS AND DISCUSSION

Figure 1 illustrates the temperature variation of the ultrasonic velocity (*V*) of PMF in the O/W emulsion during the heating and cooling processes. The sample was cooled from 60 to –5°C and was heated back up to 60°C. The arrow in Figure 1 points to the crystallization temperature (T_c). As can be seen from the cooling curve, *V* increased during the cooling from 60 to 40°C due to changes in the adiabatic compressibility of the emulsion (19). Upon cooling below 40°C, *V* decreased due to the contribution of the water structure. At 12°C, *V* suddenly increased due to the crystallization of PMF, i.e., T_c = 12°C. On further cooling, the value of *V* again dropped below 6°C due to the contribution of the water phase. During the heating process from –5°C, *V* increased gradually over the temperature interval from –5 to 21°C due to the contribution of the water phase and then started to decrease due to the melting of the PMF, which was completed at 30°C. The final values of the ultrasonic velocity were larger than those at the beginning of the thermal cycle owing to coalescence of the oil droplets.

Figure 2 shows the effects of the addition of different amounts of S-170 on the T_c of PMF in the O/W emulsion during cooling from 30 to 0.5°C. A shift of T_c to higher values was observed, its magnitude depending on the amount of the addition. For example, T_c increased from 12 to 15°C with the addition of 0.25 wt% of S-170, further increased to 16°C with the addition of 0.5 wt%, and finally reached 18°C at the maximal amount of S-170 added (0.75–1 wt%). Figure 3 shows the variation in T_c with various concentrations of P-170, S-170, and DAS-750 ranging from 0.1 to 1 wt%. The addition of all three hydrophobic emulsifiers increased T_c, but the effects of DAS-750 were different from those of S-170 and P-170. T_c increased to 15°C at a concentration of DAS-750 as low as 0.1 wt%, and no further increase in T_c was observed with increasing amount of the additive up to 1 wt%. By contrast, P-170 and S-170 increased T_c in two stages: a first in-
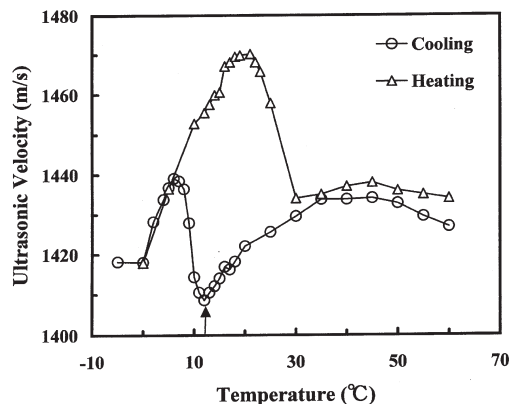

FIG. 1. Temperature variation of ultrasonic velocity (*V*) of palm mid fraction (PMF)/water emulsion during cooling and heating processes. The arrow indicates the crystallization temperature (T_c).
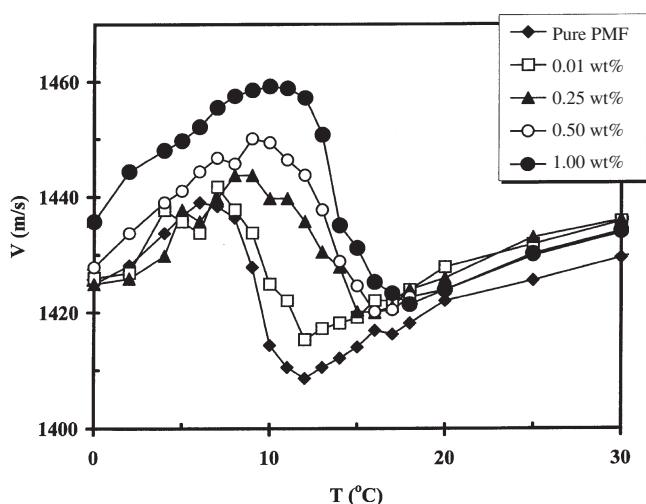
FIG. 2. Effects of the additive S-170 at differed concentrations on temperature variation of ultrasonic velocity (V) of PMF/water emulsion during cooling process. See Figure 1 for abbreviation.

crease up to $T_c = 15°C$ was observed at concentrations of 0.1 and 0.25 wt%, and a further increase up to 18°C occurred at concentrations of 0.5 and 0.75 wt%.

In order to examine the variation in the extent of crystallization of PMF in the O/W emulsion resulting from the presence of the additives, isothermal crystallization was performed with and without the additives. Figure 4 shows the variation in the V values of PMF without additives during isothermal crystallization at 5, 10, and 15°C. The V value increased rapidly at 5°C within 200 min and then became steady after reaching its maximal value. By contrast, the V value increased gradually over 600 min at 10°C. The V values at 5°C were higher than those at 10°C at an early stage of the isothermal crystalliz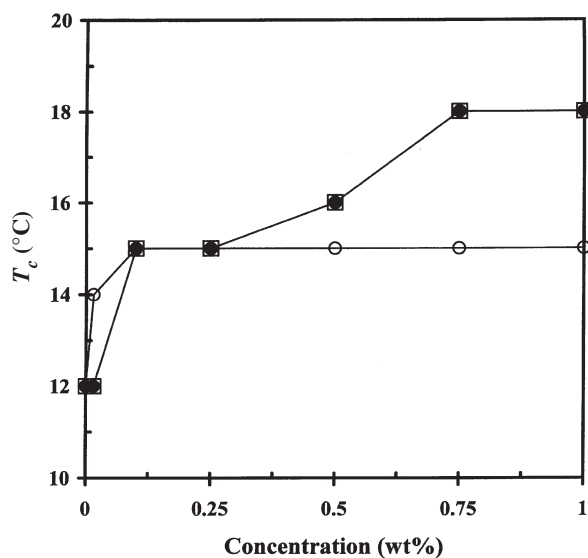ation. No significant increase, however, was observed at 15°C, because the crystallization in the O/W emulsion occurs below that temperature. The results of Figure 4 reflect the effect of temperature on the extent of crystallization of PMF with time. Figure 5 shows a comparison of the isothermal crystallization at 10°C between the pure emulsion and that with 1.0 wt% S-170. The pure emulsion reached a maximal V value at a later time than the emulsion containing S-170. In addition, the rate of increase of V in the early stages of the isothermal crystallization and the maximal V value reached in the final stage were both larger for the emulsion containing S-170 than for the pure emulsion. This result indicates that the extent of crystallization of PMF in the O/W emulsion was increased by the addition of S-170.

For the direct measurement of crystal growth rate (20), which is a prerequisite for the separation of the nucleation and crystal growth processes, liquid PMF was seeded with PMF crystals (~10 wt%). The melt was cooled to 25°C, where PMF was supercooled to some extent, and put in the cell employed for the ultrasonic measurements. The seed crystals were added at 25°C. Three bulk samples were tested, which included one sample with no additives, while the other two samples contained 0.5 and 1 wt% S-170. Figure 6 shows that in the case of the sample with no additives, the ultrasonic pulse disappeared after 410 min owing to scattering of the ultrasonic waves by the crystallized oil. In the case of the sample containing 0.5 wt% S-170 the V value of PMF also increased as a function of time, but the extent of the increase was reduced compared with that for pure PMF. With the addition of 1 wt% S-170, no increase in V was observed during 800 min of isothermal crystallization. The results presented in Figure 6 clearly show that S-170 retarded the crystal growth rate, similarly to its effects on n-hexadecane (15).

Figure 7 shows *in situ* XRD observations of the PMF emulsion without additives, with 1 wt% of S-170, and with 1 wt% DAS-750. The temperature of the samples was decreased rapidly from 30 to 20°C, and then slowly from 20 to 7°C at a constant rate of 2°C/min. Figure 7A clearly shows that the pure emulsion crystallized at 13°C in the α form and that the β′ form

FIG. 3. Variations in crystallization temperature (T_c) of PMF/water emulsions at different concentrations of three hydrophobic emulsifiers: □, S-170; ●, P-170; ○, DAS-750. See Figure 1 for abbreviation.
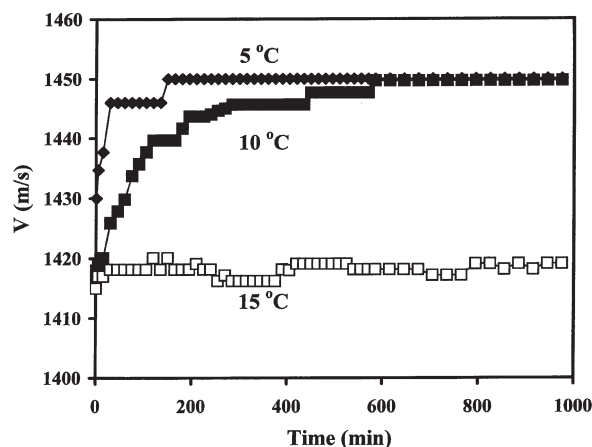

FIG. 4. Time variation of ultrasonic velocity of pure PMF/water emulsion during isothermal crystallization at 5, 10, and 15°C. See Figure 1 for abbreviation.
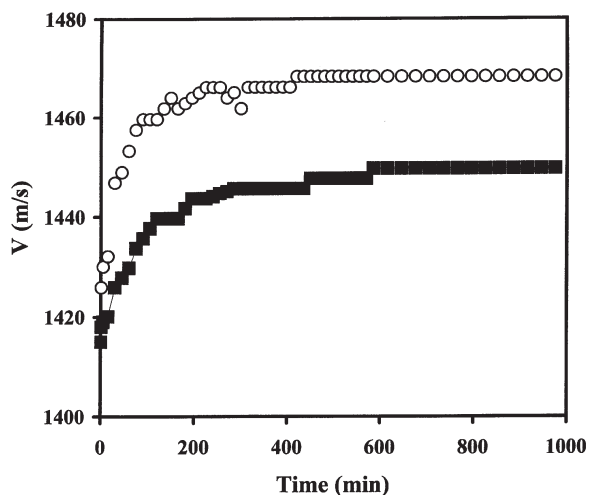
FIG. 5. Time variation of ultrasonic velocity of PMF/water emulsion with and without addition of S-170 during isothermal crystallization at 10°C. ■, No additives; ○, with S-170 (1.0 wt%). See Figure 1 for abbreviation.

appeared at 9°C. At 7°C, the amount of α was more than that of β'. With the addition of S-170 (1 wt%), as shown in Figure 7B, PMF began to crystallize at 17°C in the β' form. On further cooling, the amount of β' increased, and few indications of α crystallization were observed. Eventually, the β' form was predominant at 7°C. However, with the addition of DAS-750 (1 wt%), as shown in Figure 7C, the sample started to crystallize at 17°C in the β' form, at 13°C the α form started to crystallize rapidly, and at 7°C the amount of α was more than that of β'. The results shown in Figure 7 clearly indicate that the polymorphic behavior of PMF was modified by the addition of the two hydrophobic emulsifiers in a different manner: with the addition of S-170, PMF preferentially crystallized in the β' form, whereas with the addition of DAS-750, it also crystallized the β', form, but the rate of growth of the β' crystals was less. In both cases, the α form crystallized below its melting point (13°C). The results will
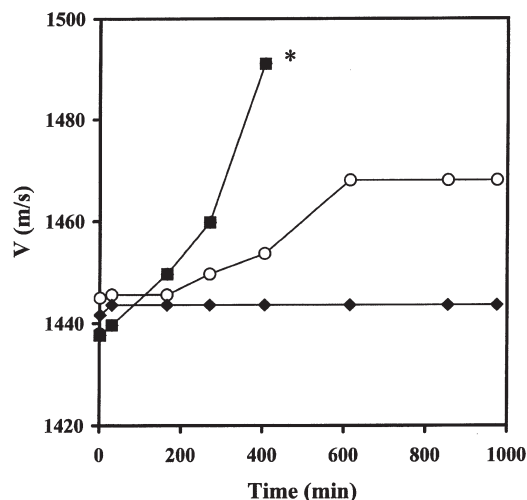
be discussed later by taking into account the competitive crystallization of the α and β' forms.

In summary, the effects of the addition of hydrophobic emulsifiers on the nucleation process of fat in O/W emulsions have been considered within the framework of heterogeneous nucleation (5,11–15). Because nucleation occurs through the catalytic action of the additives that are added in a crystallizing medium, nucleation of an emulsion may be homogeneous rather than heterogeneous in nature when no additives are present in the oil phase (21,22). Then, heterogeneous nucleation is induced to occur when catalytic effects are operative at the oil–water interface or in the oil phase due to the presence of additives. Although no molecular-level information about the ability of Tween 20 to act as a template for heterogeneous nucleation at the oil–water interface is available, this possibility must be considered. McClements *et al.* (23) indicated that Tween 40 and Tween 60 accelerate crystallization in emulsions because films formed at the oil–water interface act as templates. It was also
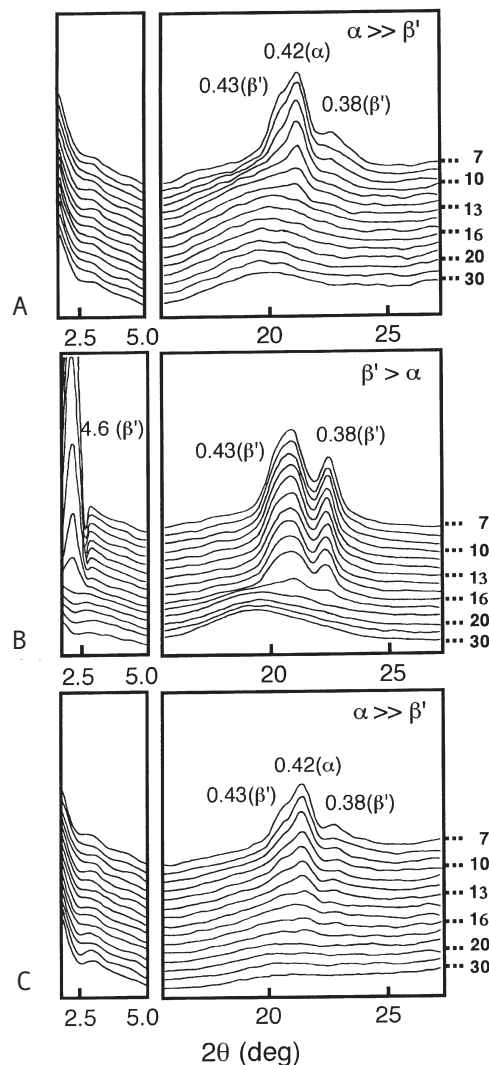

FIG. 6. Variation of ultrasonic velocity of bulk PMF seeded with PMF crystals during isothermal crystallization at 25°C. ■, No additives; ○, with S-170 (0.5 wt%), ◆, with S-170 (1.0 wt%). See Figure 1 for abbreviation. *, Signal disappeared.

FIG. 7. Short- and long-spacing X-ray diffraction spectra of PMF/water emulsions during cooling from 30 to 5°C. (A) Pure PMF emulsion; (B) S-170; (C) with DAS-750 (1 wt%). See Figure 1 for abbreviation.

mentioned in a study done by Skoda and Van den Tempel (1) that an adsorbed layer of emulsifier molecules accelerates the nucleation process. In the case of the crystallization of *n*-hexadecane (11–15), additives were reported to cause surface heterogeneous nucleation. It was also reported that the existence of reverse micelles in the oil phase enhanced the crystallization of *n*-hexadecane at higher temperatures when SOE were added at higher concentrations (15).

As an application to real food fats, the same method that was employed in the previous work with *n*-hexadecane was performed with PMF. The two SOE (P-170, S-170) would be expected to accelerate the nucleation of PMF droplets because they have higher melting points than that of PMF, which means that, upon cooling, the emulsifiers would crystallize before the oil. These emulsifiers would then have the ability to have the same roles as catalytic impurities in the bulk system, and, thus, nucleation of the oil phase would be accelerated. This type of acceleration of nucleation was observed in the emulsion system, not in the bulk system.

Surface heterogeneous nucleation and formation of reversed micelles. Figure 8 depicts the mechanism of surface heterogeneous nucleation. It shows that some additive particles are adsorbed onto the oil–water interface. These particles crystallize first, forming templates, and accelerate the nucleation of fat crystals at higher temperatures. Another possibility is the formation of reverse micelles in the oil phase, which may also act as templates. Although the SOE applied in the present work are highly hydrophobic, they have very limited solubility in the oil phase as monomers owing to the repulsive interactions between their sucrose units and oils (24). Heterogeneous nucleation is dependent on the level of impurities in the oil. Hence, at lower levels of concentration, all the impurities are incorporated at the oil–water interface and participate in performing surface heterogeneous nucleation. It has been reported that SOE are not solubilized in the oil phase and tend

FIG. 8. Molecular model of interface heterogeneous nucleation and reverse micelle formation oil-in-water emulsions with sucrose oligoester additives.

to form molecular aggregates such as inverse micelles even at low concentrations (25,26). The acceleration of fat crystallization by reverse micelles was also indicated by the presence of minor amphiphilic components of phospholipids in cocoa butter (27,28) and mono- and diglycerides in triglycerides (1). As a result, T_c of PMF increased in two stages, as shown in Figure 3. The effect of DAS-750 on nucleation was limited; i.e., it can modify the nucleation at the interface only, not in the oil phase, and, beyond a concentration of 0.1 wt%, independently solidifies with no effects on the oil phase.

With regard to the polymorphic forms of PMF, the results indicated that the additive type and amount and the cooling temperature influenced the preferential formation of the α or the β′ form of PMF, e.g., with S-170, β′ grew predominantly, whereas both forms grew in the case of DAS-750, with α actually growing more than β′.

When no template film is present, the polymorphic crystallization of fat is basically explained by the effects of supercooling and the rate of nucleation. When the rates of nucleation of the two polymorphs are of the same order, the polymorphic form having a higher value of supercooling crystallizes much more easily. The rates of nucleation of α and β′ differ, however, with α crystallizing much more rapidly than β′, as observed in tripalmitin (29). Therefore, upon simple cooling of the liquid, α nucleates as soon as the temperature reaches its melting point, even though supercooling with respect to β′ is much larger than α. That is, although β′ possesses the higher supercooling value compared with α, nucleation of α would be preferable below its melting temperature.

The α and β′ forms of PMF melt around 14 and 30°C, respectively. The increase in T_c due to the heterogeneous nucleation caused by the addition of S-170 or DAS at a level of 1 wt% exceeded the melting point of the α form. On cooling of the O/W emulsion containing S-170, the β′ form crystallized and no large amount of the α crystals was grew until the temperature reached the melting point of the α form, as shown in Figure 7b. By contrast, the addition of DAS-750 increased T_c by at most 3°C as measured by the ultrasonic technique. In this case, XRD measurements showed that the β′ form was the first to crystallize during the cooling process, although nucleation of β′ was minimized. However, on further cooling, α grew more than β′. Therefore, the effect of supercooling does not explain the preferential crystallization of β′ with S-170. Instead, one may postulate that the degree of β′ nucleation is controlled by the nature of the acyl chain packing of templates and the shape of their polar head group. For example, S-170 is characterized by a rigid polar head group and more tightly packed acyl chains than those of DAS-750. This may result in preferential nucleation of the β′ form by the template films formed by S-170, as compared to DAS-750. Further research is needed to address this question.

Much work will be required to elucidate the mechanism of PMF crystallization in an O/W emulsion and the effects of particle size, emulsifier type and amount, and cooling rate. Synchrotron radiation X-ray diffraction is an important technique with which it will be easier to monitor the crystalliza-
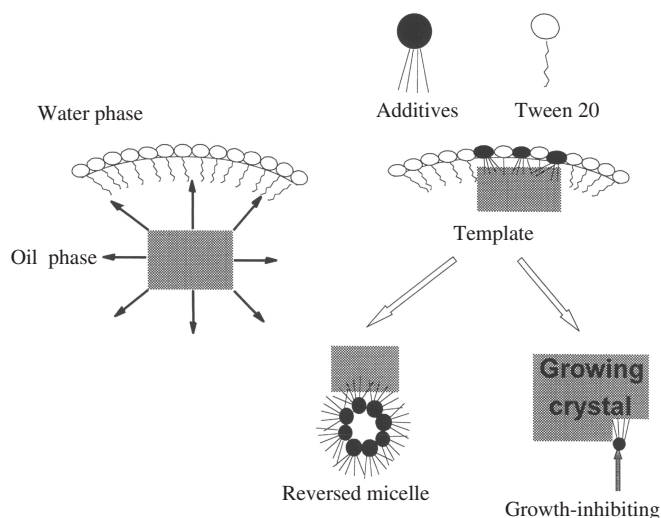
tion process *in situ* and elucidate more clearly the main trends of crystallization, involving polymorphic structure determination. This work is in progress.

ACKNOWLEDGMENT

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