Stabilization of Water-in-Oil Emulsions by Submicrocrystalline α-Form Fat Particles

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ABSTRACT: The results presented in this study confirm previous knowledge and stress the need for both hydrophobic emulsifiers and submicronial fat particles to stabilize water-in-vegetable oil emulsions. It was demonstrated that polyglycerol polyricinoleate (PGPR) is superior to glycerol monooleate and/or lecithin, but is incapable of stabilizing these fluid emulsions for sufficient storage periods. Fluid emulsions, unlike margarine, exhibit high droplet mobility and are susceptible to flocculation and coalescence. It was also demonstrated that submicronial α-form crystals of hydrogenated fat can be obtained in the oil phase by the flash-cooling process. The crystals are homogeneously almost mono-dispersed and exhibit insufficient stability against flocculation and phase separation. The use of an emulsifier (PGPR) in the fat crystallization process was very helpful in decreasing the aggregation and flocculation processes. The α-form (mixed with β′-form) submicronial crystals can stabilize water-in-oil emulsions only in the presence of food emulsifiers, provided the concentration of tristearin is limited to 1.0–2.0 wt% (to prevent phase separation and high viscosity) and the PGPR is added at sufficient concentrations (PGPR/tristearin ratio of 2.0 or more). Ideally stable (for over 6–8 wk) fluid emulsions can be formed in systems composed of fat submicrocrystalline hydrophilic particles and food-grade emulsifiers. These water-in-oil emulsions can serve as the basic preparation for any food-grade water-in-oil-in-water double emulsion.

JAOCS 75, 1825–1831 (1998).

KEY WORDS: Differential scanning calorimetry, α-form of tristearin, Pickering stabilization, polyglycerol polyricinoleate, polymorphism, solid particle stabilization, steric stabilization, submicronial fat crystals, water-in-oil emulsions, X-ray.

Margarine is a water-in-oil (W/O) emulsion stabilized by a blend of food emulsifiers, lecithin and monoglyceride stearate, and fat crystals. The precise role of the emulsifiers and the fat particles has never been fully clarified. Johansson and Bergenståhl (1–10), in their recent studies, tried "to fill some parts of the fat colloid puzzle concerning emulsifier adsorption to fat, crystal adsorption to the oil/water interface and fat crystal interaction in oils." They linked the information regarding adsorption to the stability of emulsions as a function of emulsifier and fat crystal content, and the structures formed by fat crystals. Figure 1 shows only the two-dimensional picture of a three-dimensional structure.

From this schematic picture (Fig. 1), it is clear that the fat particles play an important role in the Pickering stabilization mechanism, while the emulsifiers are the molecular bridges and molecular wetting agents facilitating such adsorption. Johansson and Bergenståhl (1–10) left many questions, such as the influence of physical parameters (temperature, mode of addition, stirring, cooling rates) and morphology of crystals (size, polymorphism), open. However, their work opened a new channel for investigators searching for methods to stabilize food W/O emulsions and for those exploring new methods to stabilize double water-in-oil-in-water (W/O/W) emulsions.

Many attempts have been made to stabilize the inner W/O emulsion in W/O/W double emulsions with monomeric emulsifiers (11–15) (with a strong tendency to desorb and migrate to the external interface) and with polymeric (16–20), naturally occurring amphiphilic molecules (21–24), such as proteins (25). Certain proteins, in spite of being quite hydrophilic, can complex with monomeric emulsifiers and adsorb onto the W/O interface. The thick film, which is formed onto the water droplets, contributes somewhat to the stability, but mainly to the release patterns of electrolytes and other addenda to the outer aqueous phase. Proteins and hydrocolloids are too hydrophilic to act as good steric stabilizers in W/O interfaces (26,27). The only synthetic polymer that is permitted

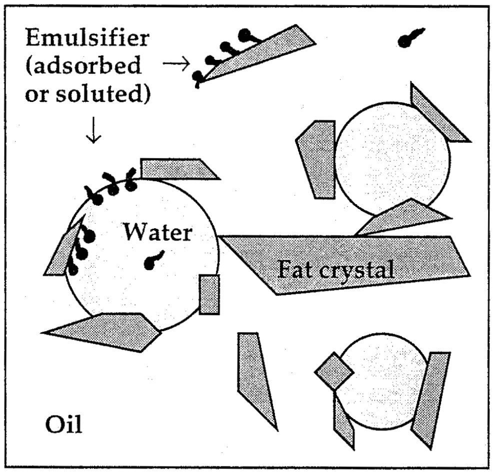

FIG. 1. A schematic picture of colloidal margarine structure. Adapted from Reference 7.

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in certain food systems is polyglycerol polyricinoleate (PGPR), which is also used for this stabilization (28).

Johansson and Bergenståhl's work has motivated us to try and make double emulsions with a combination of food emulsifiers and fat particles. It should be stressed, however, that double emulsions, unlike margarine, must be totally fluid and pourable. Therefore, votation and cooling methods that are employed in margarine technology cannot be exercised in our preparations.

This article reports some results of our attempts to form microcrystalline fat particles of a selected polymorphic form, with proper hydrophilicity, and to adsorb them onto water-oil interfaces in the presence and absence of PGPR.

EXPERIMENTAL PROCEDURES

Materials. The water phase was composed of double distilled water and of 0.2 M NaCl aqueous solutions. The oil phases were of deodorized and winterized soybean oil (Etz-Hazayit, Israel).

Three types of hydrogenated fats were used in the preparation of the microcrystalline fat particles: fully hydrogenated (IV < 1) tristearin (TS) (Akodur S), fully hydrogenated palmstearin (Cessa powder, IV < 1), and fully hydrogenated palm oil. All samples were purchased from Karlshamns (Karlshamn, Sweden).

The emulsifiers were: commercial grade deoiled, microfine powdered soy lecithin (Sternwet P) from Stern-Chemi, Hamburg, Germany; sorbitan monooleate (Span 80) from Sigma Chemicals, St. Louis, MO; ethoxylated sorbitan monooleate (Tween 80) from ICI, Middlesbrough, Cleveland, United Kingdom; and polyglycerol polyricinoleate (PGPR, S-100) from Croda Chemicals Ltd. (Goole, North Humberside, England).

All the emulsions that had to be studied for storage stability contained 0.005 wt% sodium azide as preservative.

Analytical methods. Size distribution of fat microcrystals dispersed in an oil phase was measured by Zetamaster (model ZEM 5002; Malvern, Malvern-Worcestershire, United Kingdom) and by a laser sizer (model CIS-1; Galai, Migdal Haemek, Israel).

Size distribution of the W/O emulsions was measured by the laser sizer and by light microscope (Nikon F, Tokyo, Japan).

Viscosity measurements were carried out on a Brookfield viscometer, model DV-I and DV-II cone and plate (Brookfield, Stoughton, MA). The polymorphic structures of the fat crystals were determined by X-ray diffraction (X-ray Philips PW-1820 diffractometer with CuK_α radiation) and differential scanning calorimetry (DSC, Mettler TA 4000 equipped with TC 11TA processor and DSC 30 low-temperature cell, Mettler, Greifensee-Zürich, Switzerland).

The DSC measurement profiles were performed mostly in 40 μL aluminum pans (using a Mettler M3 microbalance) in which 5–15 mg samples were weighed, cooled to −150°C, aged for a given time (to allow total crystallization of the fat particles within the oil phase), and reheated gradually to room temperature for further analysis (X-ray, microscope) and further use in the preparation of emulsions.

Flash-crystallization procedure. The main procedure used to obtain microcrystalline fat particles was based on weighing a given amount of commercial fat crystals (0.5–2.0 wt%) into liquid soybean oil and heating the mixture to 80°C, until a totally clear oil solution was obtained (the heating was done with nitrogen blanketing to avoid oxidation). The solution was flash-cooled (in liquid nitrogen) to approximately −150°C and aged for a few minutes to allow full recrystallization of the fat crystals within the oil. The newly formed dispersion of fat particles within the oil phase was brought gradually (80°C/min) to room temperature. Samples were withdrawn to evaluate concentration of fat crystals within the oil phase (by centrifugation), to determine the polymorphic forms of the fat that are present in the dispersion (by X-ray and DSC), and to determine viscosity of the dispersion. In certain cases the dispersions were made with fat crystals (TS, palm stearin, hydrogenated palm oil) and, in other cases, in the presence of food emulsifiers that were added together with the fat in the premolten stage.

Preparation of W/O emulsions. The dispersions of fat particles in oil were used as the continuous oil dispersion phase. Water (at 25–30 wt%) was added dropwise to the oil dispersions (at room temperature) while stirring. The crude emulsions were further homogenized in an Ultra Turrax T-25 homogenizer (Janke and Kunkel, Germany) at 8000-24000 rpm for 15 min or microfluidized in a microfluidizer Microfluidics Corp. (Newton, MA) only one pass at 5000 psi.

Samples were withdrawn for evaluation of particle size distribution, viscosity, and DSC measurements. Storage stability was determined (coalescence, aggregation and creaming) with time.

RESULTS AND DISCUSSION

Stabilization of W/O emulsions with glycerol monooleate (GMO) and lecithin. Table 1 summarizes the results of several attempts to stabilize 10–20 wt% W/O emulsions at room temperature with mechanical homogenization and without votation in the presence of blends of 4 wt% emulsifiers of deoiled lecithin and GMO in different ratios. GMO was selected since it was demonstrated by Bergenståhl that for liq-

TABLE 1
Stability Evaluation of 4 wt% Lecithin/GMO at Different Ratios in Stabilized Water-in-Oil Emulsions[a]

Lecithin/GMO ratio	Time (min) for 50% separation of water			
	φ = 0.1	φ = 0.15	φ = 0.20	φ = 0.25
0.5	2	8	10	50
1.0	2	100	200	1500
2.2	5	20	50	100
3.0	<5	<5	10	50
7.0	<5	<5	<5	<5

[a]GMO, glycerol monooleate; φ, weight fraction of water component.

uid W/O emulsions it performed better than glycerol monosterate. This fact was reconfirmed in our studies. It can be clearly seen that only the emulsion with 25 wt% water and lecithin/GMO ratio of 1 is stable for a minimum of 1500 min at room temperature.

These findings were the basis for our further studies.

Stability of W/O emulsions with GMO, lecithin, and TS. Similar emulsions were made with GMO and lecithin (at 4 wt% and 1:1 ratio) in the presence of 0–2 wt% commercial tristearin particles (used directly from the jar without any pretreatment or recrystallization).

The TS was dispersed in the oil phase by ball-mill. The particle size of the TS was reduced to 1–5 μm in the oil phase prior to being used in the emulsion.

The water phase was homogenized for 2–15 min in the TS-oil dispersion. In Figure 2 we can see the distribution of the TS particles in the oil phase prior to the addition of water and distribution of the W/O droplets after homogenization by Ultra Turrax. More than 80% of the TS particles, in the oil phase and prior to the addition of water, were in the range of 0.5 to 1.0 μm. After adding 25 wt% water the majority of the droplets was in the range of 0.5–1.0 μm after 15 min of homogenization, but additional population of 10–40 μm was detected. Close examination under a light microscope revealed that most probably this population (10–40 μm) is not composed of W/O droplets, but rather of fat particles that have aggregated during the emulsification process to large crystals. It is also possible that the fat goes through a crystal growth process. We did not investigate further the nature of these crystal clusters.

It must be noted that all the emulsions separated into two phases within 10–20 min from the time of preparation (using Ultra Turrax homogenizer).

Figure 3 (photomicrographs) demonstrates the droplet size of the W/O emulsions prepared with 2–6 wt% TS. The TS is mostly located at the W/O interface or nearby, and only minor amounts are seen in the continuous phase. The figures are not very conclusive and it is, therefore, hard to claim that all the TS is located at the interface, due mainly to the fact that the particle size distribution (PSD) of the TS particles in the oil phase did not differ much from the water droplet size distribution.

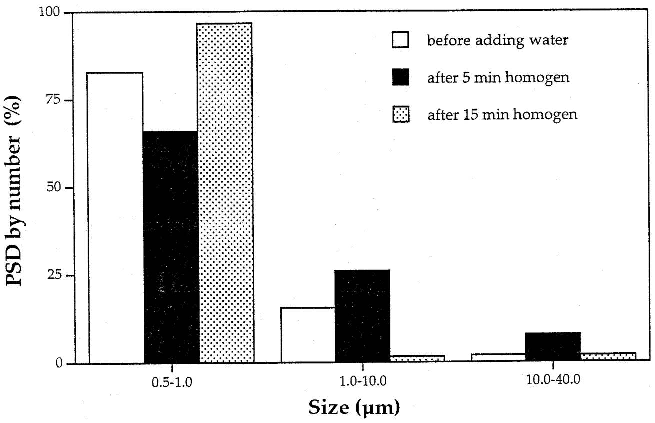

FIG. 2. Particle size distribution (by number %) of the tristearin particles in the oil phase dispersion before adding 25 wt% water, during the homogenization and the addition of water, and after 15 min of homogenization.

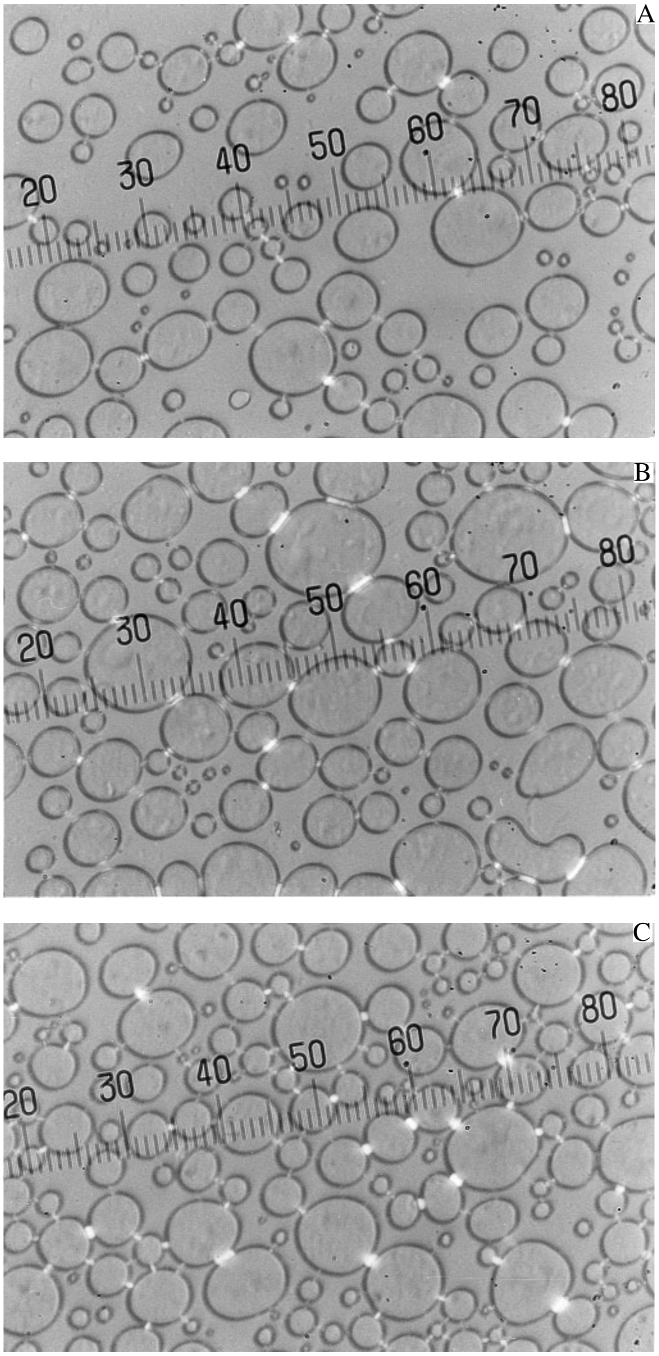

FIG. 3. Photomicrographs of a water-in-oil emulsion containing 25 wt% water + 2 wt% lecithin + 2 wt% glycerol monooleate and different amounts of tristearin: (A) 2, (B) 4, and (C) 6 wt% of tristearin. Magnification ×2000.

Emulsions prepared with lecithin/GMO and flash-cooled TS particles. Figure 4 shows that emulsions with TS particles prepared by flash-cooling consist of droplets smaller than

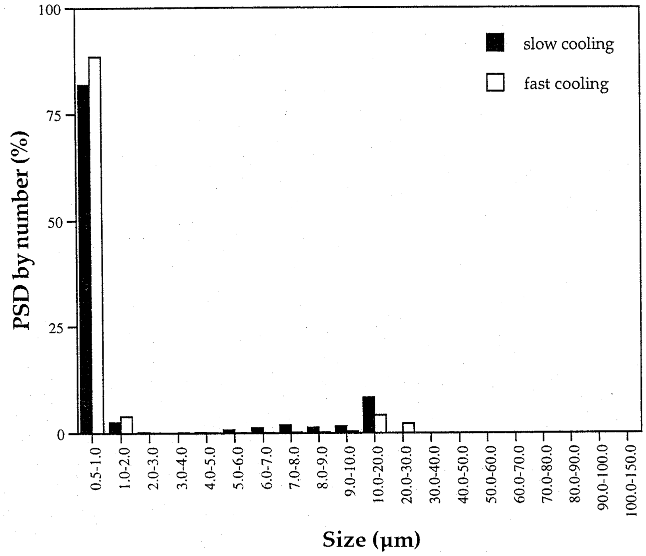

FIG. 4. Particle size distribution (PSD) (by number %) of 2 wt% tristearin dispersed in the oil phase containing 0.2 wt% polyglycerol polyricinolate.

those made by mechanical size reduction of the TS. Two similar populations of sizes were seen in those sets of experiments. The emulsions suffered less from aggregation and seemed to have fewer stability problems.

Formation of submicronial particles in the oil phase by flash-cooling. It is obvious that the size, morphology, and shape of the fat crystals play a key role in the stabilization of W/O emulsions. It was expected that submicron particles (less than 0.1 μm), with narrow size distribution and as spherical as possible in shape, would need to be obtained in the oil phase in order to achieve good anchoring, with good wetting, at the water interface. In addition, the aim was to obtain particles with smooth morphology. Johansson and Bergenståhl also stressed the fact that α-form fat crystals are significantly more hydrophilic than β′ and β-form crystals and, therefore, will better wet the water interface and tend to anchor better at the W/O interface than β-form crystals. They did not attempt to use α-form crystals in real emulsion systems, and their studies were based on interfacial tension measurements of water-oil films in the presence of emulsifiers, and different polymorphic forms of fat crystals. The effect of particle size was also not studied.

We tried to crystallize α-form tristearin microcrystals in the oil phase prior to making the emulsions and to study their effect on the stability of emulsions in the presence and absence of monomeric emulsifiers.

Two types of flash-cooling were tested: (i) flash-cooling of the crystallization cell with the molten mixture of TS and oil (or TS, oil, and emulsifiers) in liquid nitrogen, followed by a short aging period and gradual reheating to room temperature; and (ii) direct pouring of the two- or three-component molten mixture into a liquid nitrogen medium and evaporation of the liquid nitrogen. The TS concentrations in the oil phase were of 0.5–4.0 wt%. All our attempts to crystallize the TS in submicronial sizes and narrow distribution in the absence of emulsifiers failed. In all the experiments the TS particles aggregated, flocculated, and grew to sizes above 2 μm with a wide range of size distribution. All our attempts to make emulsions with these particles led to very unstable emulsions.

Therefore, it was concluded that it is essential to have sufficient amounts of emulsifier in the oil phase to guarantee surface adsorption of the emulsifier onto the fat particles in order to reduce flocculation and growth processes and to stabilize the dispersions.

Out of the two sets of emulsifiers, GMO/lecithin and PGPR, it was decided to concentrate on PGPR, since the dispersions seemed to have narrower size distribution and the W/O emulsions made of PGPR + TS seemed to have longer shelf-life and better stability.

Table 2 shows a summary of the results obtained from dispersions made with 1 wt% PGPR and 0.5–4.0 wt% TS. It can be clearly seen that the TS particles obtained by this method were by far smaller than the particles obtained by any milling process (Fig. 5). At a 1:1 ratio the average size of the TS particles was in the range of 300 nm. More than 79% of the particles were below 0.5 μm. At a PGPR/TS ratio of 2:1 the par-

TABLE 2
Particle Size Distribution of TS Flash-Crystallized in Soy Oil in the Presence of PGPR[a]

PGPR (wt%)	TS (wt%)	PGPR/TS ratio (w/w)	Average size of TS particles (nm)	% Particles <0.5 μm	% Particles <1.0 μm
0.5	0.5	1	386	100	100
	1.0	0.5	443	100	100
1	0.5	2	302	97	100
	1.0	1	300	79	98
1	2.0	0.5	956	0	23
	4.0	0.25	1858	0	0
2	0.5	4	280	92	100
	1.0	2	837	0	90

[a] TS, tristearin; PGPR, polyglycerol polyricinoleate.

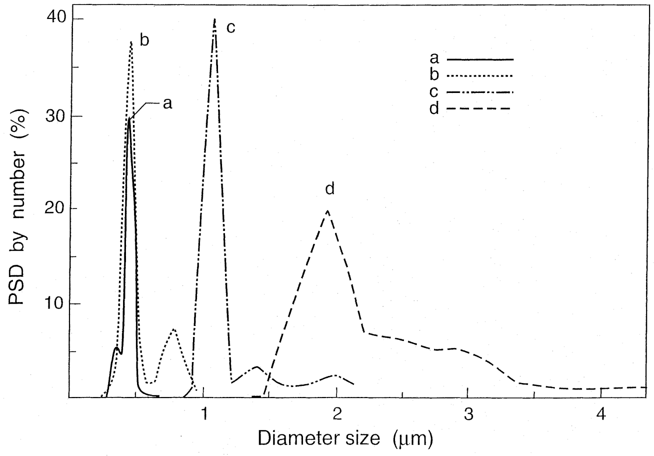

FIG. 5. PSD (by number %) of 2 wt% tristearin of tristearin particles dispersed in the oil phase at different ratio of tristearin/polyglycerol polyricinoleate: (a) 0.5, (b) 1.0, (c) 2.0, and (d) 4.0. See Figure 4 for abbreviation.

ticles were even smaller and more monodispersed; over 97.4% of them were smaller than 0.5 μm.

When the PGPR concentration was increased to 2 wt% and the ratio of PGPR/TS was kept constant at 1.0 (less TS and more PGPR) the particles were even smaller (284 nm), and over 92% were of less than 0.5 μm.

From all these experiments it seems that the best results are obtained when TS is kept at 0.5 wt% and the PGPR is at a similar concentration. At high TS levels the PGPR is not sufficient to cover the particles and protect them from aggregation and growth. At high PGPR levels the added value of the emulsifier is minor, mainly due to the increase in viscosity. The particles are somewhat larger, but significantly more monodispersed. It was also demonstrated that direct cooling by liquid nitrogen is more efficient than indirect cooling, mainly because of a better and more efficient heat transfer. The liquid nitrogen evaporates without affecting the size and/or the morphology of the crystals.

The crystalline form. Fat particles were dispersed in the soy oil and, therefore, it was difficult to quantitatively determine the amount of each polymorphic form present in the oil and to study the stability of these forms to solution-mediated transformations. DSC and X-ray measurements were done on each sample during each crystallization process. The amounts of each polymorph were evaluated from the melting enthalpy peaks. Because of the excess of oil in each sample, the melting peaks were shifted to a lower temperature. The polymorphs could be detected during a heating cycle only. Two procedures were tested and compared: (i) slow-cooling (10°C/min) from melt to 30°C, followed by 2 h aging process and moderate heating (10°C/min) to the melting points of the fat polymorphs (the M_1-cycle); and (ii) flash-cooling process at 50°C/min from the melt (100°C) to −150°C, followed by 2 h aging and moderate heating (10°C/min) to the melting points of the fat crystals (the M_3-cycle).

From Table 3 one can see that the slow-cooling process leads to the formation of only 27 wt% of α-form and up to 62% of β-form, while in the flash-cooling process (M3) over 63% of α-form, 32 wt% of β′-form, and only minor amounts of β-form were crystallized. These results are expected from flash-cooling. The addition of PGPR (in great excess of up to 9 wt%) did not significantly change the crystallization picture. Slow-cooling led to exactly the same polymorphic internal distribution (30 wt% of α-form and 58 wt% of β-form) while the flash-crystallization was somewhat different. Only 30 wt% α-form was obtained, and the rest was β′-form. These results clearly demonstrate that the PGPR adsorbs onto the fat nuclei while forming and enhancing the formation of the β′-form. Flash-cooling does not allow formation of any β-form in the presence or in the absence of the emulsifier. The role of PGPR is, therefore, mostly to prevent aggregation of the α or β′ crystals in the oil phase rather than to control the formation of the adequate crystalline form. It seems that more α-form crystals can be obtained in the absence of emulsifier, but it does not guarantee the stabilization of the fat crystals in the dispersion and, therefore, the combination of the two is better.

W/O emulsions with PGPR. PGPR is known to sterically stabilize W/O emulsions. Water (25 wt%) was emulsified in soy oil in the presence of 0.2 wt% PGPR. The emulsions were prepared in two modes: (i) fast-cooling of the oil phase to −150°C to *in situ* crystallize TS, followed by emulsification to which the water was added; and (ii) slow natural cooling (80–20°C) followed by room-temperature emulsification. The fast-cooling was beneficial even if TS was not present in the emulsion. Almost one population of droplets in the range of 0.5 to 2.0 μm (total of 95%) was formed (less than 5% of large particles were detected) in comparison to the formation of two populations almost similar in distribution formed when slow-cooling was employed (Fig. 6). The first population was

TABLE 3
Polymeric Transformations of TS Crystals in the Absence and Presence of PGPR in Two Modes of Crystallization

PGPR (wt%)	Oil (wt%)	Method[a]	Peak temperature (°C)	Crystallographic modification	Peak (%)
0	100	M_1	54.3	α	27
		(slow-cooling)	62.2	β′	10
			69.1	β	62
		M_2	53.1	α	63
		(flash-cooling)	62.5	β′	32
9	91	M_1	53.2	α	30
		(slow-cooling)	63.4	β′	11
			69.2	β	58
		M_2	52.6	α	30
		(flash-cooling)	62.7	β′	70

[a] M_1, Method 1: from melt to 30°C, slow-cooling at ambient conditions, and aging of samples at 30°C for 2 h. The analysis of the polymorphic structures that were formed was done by heating the dispersion to 100°C at 10°C/min. This crystallization–melting cycle was termed M_1. M_2, Method 2: From melt (100°C) to −150°C at flash-cooling of 50°C/min, and aging of the samples at −150°C for 2 h, with reheating process (for analysis) to 100°C at 10°C/min. For other abbreviations see Table 2.

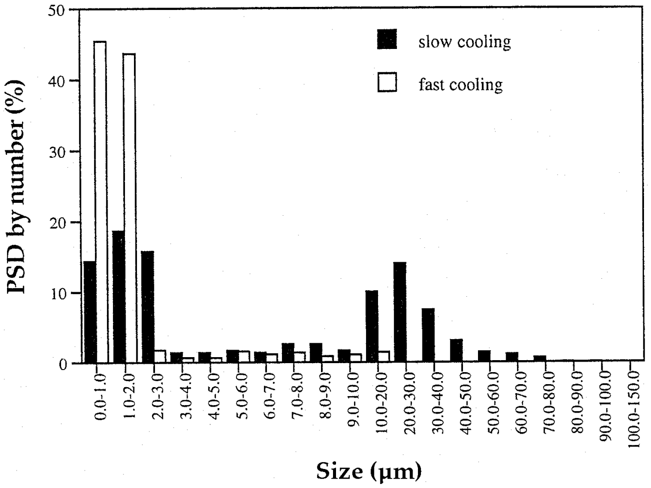

FIG. 6. PSD (by number %) of a water-in-oil emulsion containing 25 wt% water + 0.2 wt% polyglycerol polyricinoleate + 2 wt% tristearin at two different cooling rates (fast and slow). See Figure 4 for abbreviation.

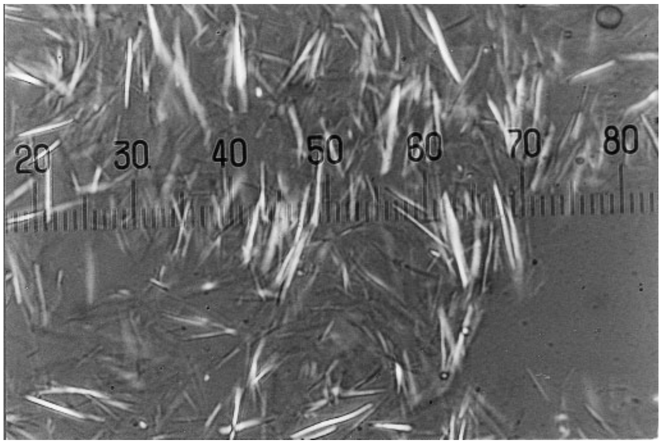

FIG. 7. Photomicrographs of tristearin crystals in the oil phase as obtained after fast-cooling (50°C). Magnification ×2000.

of droplets ranging from 0.2 to 3.0 μm (total of 53%), and the second population ranged from 10–50 μm (total of 47%). The soy oil segregated at the cooling process and small amounts of saturated fat crystallized within the oil. These crystals participated in the emulsification process and contributed to the stabilization of the emulsion (first population of droplets). The second population seems to have contributed to the destabilization of the emulsion. The second population (from the fast cooling process) was found to be needle-like crystals of saturated fat, and was dendritic in its morphology (see Fig. 7).

W/O emulsion with PGPR and TS. All attempts to stabilize W/O emulsions with TS alone failed, even if the TS dispersions in oil were prepared by flash-cooling. However, when PGPR was present with TS, the emulsions turned out to be more stable and small in droplet size.

Emulsions prepared with 0.2 wt% PGPR and 2.0 wt% TS and cooled in the slow mode (80 to 20°C at 2.0°C/min) were nonstable despite the fact that the droplets were small in size (80% in the range of 0.5–2.0 μm), while emulsions prepared with oil phase, in which TS was fast-cooled, were dramatically more stable at a similar size range of distribution. Here, again, the second population of particles practically did not exist if fast-cooling was employed, while emulsions prepared with slow-cooling showed presence of the second crystal population. The two emulsions were examined again after six weeks. The fast-cooling emulsion showed no dramatic change in the droplet size distribution and exhibited no flocculation or coalescence, while the slow-cooled emulsion separated after less than 2 d (Fig. 8).

Similar emulsions were prepared with other PGPR/TS ratios. Figure 9 shows its stability as a function of time, in which 0.2 wt% PGPR was used with 1.0% TS. This clearly indicates that the emulsifier is not sufficient and coalescence occurs with time.

A comparison of the emulsification systems with various PGPR/TS ratios and different levels of TS (water/TS ratios of 25:0.5 to 25:6) stresses the need for high PGPR levels at high TS levels and high PGPR ratios at any given TS concentration. These results are in good agreement with the results obtained in the oil dispersion systems, indicating, again, that the best emulsions will be achieved by combining submicronial fat crystalline particles of the α or β′ form and sufficient amounts of PGPR.

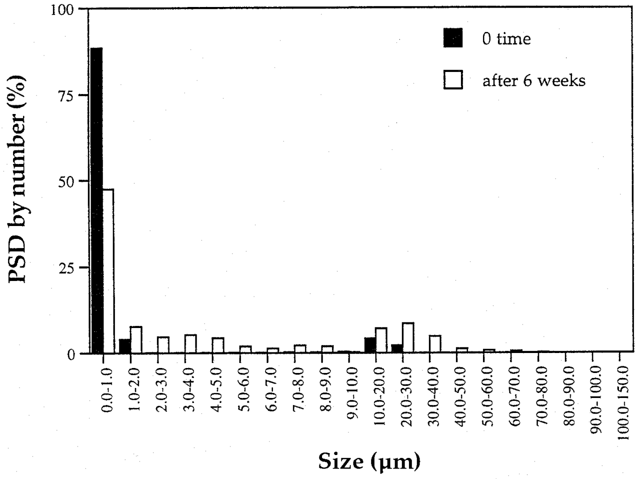

FIG. 8. PSD (by number %) of a water-in-oil emulsion containing 25 wt% water + 0.2 wt% polyglycerol polyricinoleate + 2 wt% tristearin immediately after preparation and after 6 wk incubation at room temperature. See Figure 4 for abbreviation.

Other fat crystals. Fat crystals from two other sources were examined. The fat submicronial particles were prepared as a dispersion in the oil phase by flash-cooling in the presence of PGPR. The emulsions were composed of 25 wt% water, 0.2% PGPR and 2% TG. Palm stearin crystallizes almost exclusively in the β′-form, and so does hydrogenated palm oil. The droplet size distribution was not affected much by the type and size of the microcrystalline fat particles (all three fat dispersions were in the range of 250–300 nm). None of the emulsion droplets exceeded 1.0 μm, and all three emul-

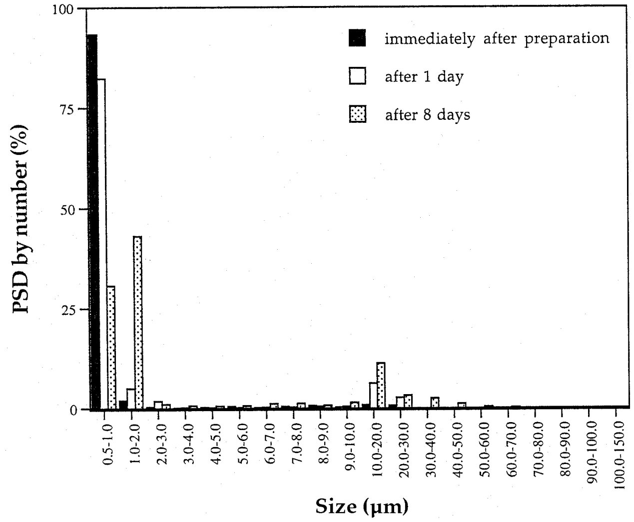

FIG. 9. PSD (by number %) of a water-in-oil emulsion containing 0.2 wt% polyglycerol polyricinoleate and 1 wt% tristearin immediately after preparation; and after incubation at room temperature: 1 d and 8 d. See Figure 4 for abbreviation.

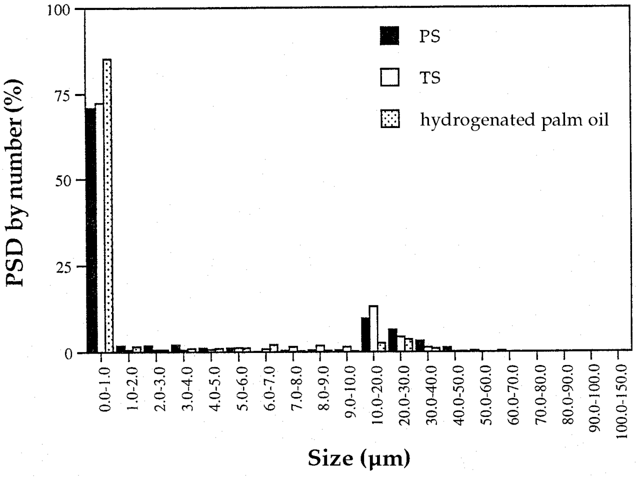

FIG. 10. PSD (by number %) of a water-in-oil emulsion containing 25 wt% water, 0.2 wt% polyglycerol polyricinoleate, and 2 wt% of palm stearin, tristearin, and hydrogenated palm oil, immediately after preparation. See Figure 4 for abbreviation.

sions remained stable after a few weeks of aging. It seems that there are minor advantages to emulsions prepared with hydrogenated palm oil over PS and TS immediately after preparation, but the differences are not very pronounced (Fig. 10).

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[Received April 2, 1998; accepted July 25, 1998]