Dynamic Crystallization of Cocoa Butter. II. Morphological, Thermal, and Chemical Characteristics During Crystal Growth

Siree Chaiseri[1] and Paul S. Dimick*

Department of Food Science, The Pennsylvania State University, University Park, Pennsylvania 16802

ABSTRACT: After an induction period, crystallization of cocoa butter under dynamic conditions at 26.5°C occurs in two stages, primary and secondary. The primary stage involves nucleation, crystal growth, aggregation, and sintering. Crystals formed during the primary stage were slightly or non-birefringent, and had long, irregular-shaped filaments. The secondary stage was initiated by the formation of spherulites. Total crystallization time may depend upon the crystal growth rate in the primary stage and the time that cocoa butters take to form the spherulitic crystals in the secondary stage. After the spherulitic crystals formed, the crystal growth rates were rapid. Cocoa butters crystallized into two fractions during the primary and secondary stages. The low-melting fractions had onset melting temperatures similar to those of polymorphs IV and V of cocoa butter. The high-melting fractions, which were observed at the latter stages of crystallization, had differential scanning calorimetry endotherms with peak maxima at approximately 34–36°C (Form VI). The concentrations of 1,3-stearoyl-2-oleoylglycerol (SOS) in the crystals during growth were higher than those in the original cocoa butter. As crystallization progressed, crystals increased in their proportions of SOS in the triacylglycerol fraction. Concentrations of the C_{18} free fatty acids were lower during early crystallization as compared to the original cocoa butter.

JAOCS 72, 1497–1504 (1995).

KEY WORDS: Chemical composition, cocoa butter, crystal growth, morphology, thermal properties.

Crystallization of cocoa butter is important to process control and final product quality in chocolate manufacture. Cocoa butters have different rates of solidification and polymorphic transition. The cause of the differences is believed to be the variation in composition. Effects of triacylglycerol composition on solidification behavior, and hardness of the final product have been investigated (1,2). Minor components, such as glycolipids, phospholipids, and saturated triacylglycerols, could play an important role. Davis and Dimick (3) reported that cocoa butter seed crystals that formed during early crystallization stages contained high concentrations of glycolipids (11.1%), phospholipids (6.6%), and saturated triacylglycerols (67.7%). Cocoa butters that contain higher tristearin seem to crystallize at a faster rate (4). Manning and Dimick (5) illustrated that the "bow-tie" or filamentous tubule-shaped crystals formed during the early stages of static crystallization of cocoa butter contained higher 1,3-stearoyl-2-oleoylglycerol (SOS) than did the original cocoa butter. The purpose of this study was to investigate changes in the thermal behavior, simple lipid composition, and morphology of cocoa butter crystals during growth under dynamic conditions. Crystal morphologies of six cocoa butters were observed by light and polarized-light microscopy. Chemical composition studies were carried out on cocoa butters from the Ivory Coast and Ecuador, which exhibited rapid and slow crystal growth rates, respectively. Components that crystallized at various growth stages of both cocoa butters were analyzed in comparison to their respective cocoa butters.

MATERIALS AND METHODS

Samples and crystal morphology. Sample preparation and dynamic crystallization studies of six cocoa butter samples from Malaysia, the Ivory Coast, Ghana, Ecuador, the Dominican Republic, and Brazil (Bahia) were carried out under the same procedures as described by Chaiseri and Dimick (6). Crystallization studies of each cocoa butter were performed in duplicate and plotted from the average crystallization times when the samples reached specific Δ absorbances, i.e., 0.0, 0.1, 0.2, 0.4, 0.6, 0.8, ..., 2.8 (Fig. 1). Crystal morphologies of six cocoa butters were observed under a light microscope equipped with a removable polarized lens. During dynamic crystallization, samples were taken from a Brabender cup (Brabender Instrument, Inc., South Hackensack, NJ) at various stages, placed on glass microslides at room temperature (*ca.* 25°C), and covered with glass slips. Progress in crystallization was monitored with a Hitachi spectrophotometer model 100-40 (Hitachi Ltd., Tokyo, Japan). Crystal sizes were determined by comparison with an optical micrometer graduated in 0.01-mm divisions. Photographs were taken with an Olympus-OMI camera body (Olympus Corp., Woodbury, NY) attached to the microscopy with MTV-3 and an OM-mount photomicroadapter.

[1]Current address: Department of Food Science and Technology, Kasetsart University, Chatuchak, Bangkok 10900, Thailand.

*To whom correspondence should be addressed at Department of Food Science, 116 Borland Laboratory, The Pennsylvania State University, University Park, PA 16802.

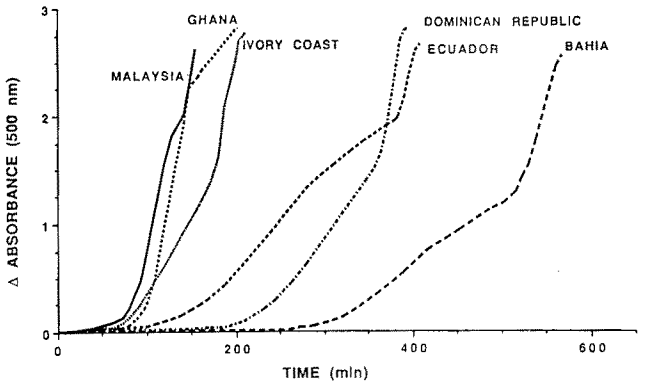

FIG. 1. Crystallization curves of six cocoa butters crystallized under dynamic conditions at 26.5°C.

Crystal isolation and analyses. Crystals of Ivory Coast and Ecuadorian cocoa butters at various growth stages were isolated for compositional analyses. Crystals were isolated when the Δ absorbances from the spectrophotometer reached 0.02, 0.5, 1.0, 1.5, and 20. The Δ absorbance is defined as follows:

$$\Delta Abs = Abs_t - Abs_{to}, \text{ where } Abs_t \quad [1]$$

is the absorbance of the sample at the time of study, and Abs_{to} is the absorbance of cocoa butter melt when the temperature has reached the crystallization temperature. When the dynamic crystallization of the cocoa butter at 26.5°C reached the desired Δ absorbance, the samples were transferred into wide-mouth, 250-mL polyallomer Nalgene centrifuge bottles (Nalge Co., Rochester, NY). The crystals, isolated at the different growth stages, were obtained by centrifugation at 18,600 × *g* for 8 min in a Beckman J2-21 centrifuge equipped with a JA-14 rotor (Beckman Instruments, Inc., Palo Alto, CA). After centrifugation, the liquid cocoa butter was discarded, and the crystal mass was spread between layers of Whatman No. 1. filter papers and hand-pressed to remove the contaminating cocoa butter melt. The pressing process was repeated twice, once before and once after a 5-min incubation at 27°C in a Precision Scientific incubator (Chicago, IL). The samples were immediately analyzed for their thermal behavior by differential scanning calorimetry.

Thermal analysis was conducted on a model DSC-4 (Perkin-Elmer, Norwalk, CT) equipped with an Intracooler I Freon refrigeration unit. Gallium (99.999% purity; Aldrich Chemical Co., Milwaukee, WI) was used as a standard for instrument calibration. The cocoa butter crystals were immediately quench-cooled on dry ice to prevent polymorphic transition before thermal analyses.

Chemical compositional analyses of Ivory Coast and Ecuadorian cocoa butter crystals, isolated at various stages of crystallization, were carried out according to the methods described previously (6). The major lipid classes—simple lipids, glycolipid, and phospholipids—were separated by silicic acid column chromatography. The simple lipid fraction of cocoa butter and their seed crystals was analyzed by high-temperature capillary gas chromatography (CGC) (6). Triacylglycerols were separated by high-performance liquid chromatography on a 25-cm Absorbosphere C-18 reverse-phase column (Alltech Associates, Deerfield, IL). The minor simple lipids (free fatty acids, mono- and diacylglycerols, and sterols) were quantitated by high-temperature CGC in the same manner as the total simple lipid profiles. Fatty acid compositions of the free fatty acid and diacylglycerol fractions were analyzed separately as fatty acid methyl esters. Lipid classes were purified by thin-layer chromatography.

Statistical analyses. Samples were analyzed in three replicates with duplication for each replicate. Each replicate was a combination of seed crystals from two isolations. Seed crystals of each sample were isolated from seven batches. Data were analyzed by using the Statistical Analysis System (SAS). The experiment was under the nested design with the model as follows:

$$Y_{ij} = \mu + \alpha_i + b_{j(i)} + e_{ij} \quad [2]$$

where μ = overall mean, $\alpha_i = i^{th}$ stage of crystallization (Δ absorbance) effect, $b_{j(i)} = j^{th}$ isolation effect. Analysis of variance was calculated with the General Linear Model. Multiple comparison with the least significant difference was applied to separate the means of $\alpha = 0.05$.

RESULTS AND DISCUSSION

Crystal growth and morphology. Samples used in this study were selected based on their crystallization behavior. The crystallization curves show the nucleation and crystal growth rates of the respective samples (see Figs. 3–8, later in paper). Cocoa butters with short nucleation times had rapid crystal growth rates, whereas cocoa butters with long nucleation times had slow crystal growth rates. Cocoa butters from Malaysia, the Ivory Coast, and Ghana had short induction times and rapid growth rates (Fig. 1). Cocoa butters from the Dominican Republic and Bahia had long induction times and slow growth rates. The crystallization characteristics of the Ecuadorian sample deviated from those of the other samples. Ecuadorian butter had a short induction time but had a slow growth rate. Schenkel (7) observed similar phenomena in some cocoa butters after seeding. In his study, a few cocoa butters started to crystallize rapidly onto the seeds prepared from the finely grated β-form of cocoa butter. These seeded cocoa butters, however, had slow crystal growth rates. Crystallization of cocoa butter can be divided into three stages (Fig. 2). The primary crystallization stage takes place after an induction period. The secondary crystallization stage is initiated at the inflection point after the induction period. The crystallization curves of cocoa butter samples did not always show a clear division between the primary and the secondary stages. When the two stages are not apparent, it could be that crystallization in the secondary phase occurs while crystallization in the primary stage is still progressing. In rapid-crystallizing samples, both primary and secondary crystallization

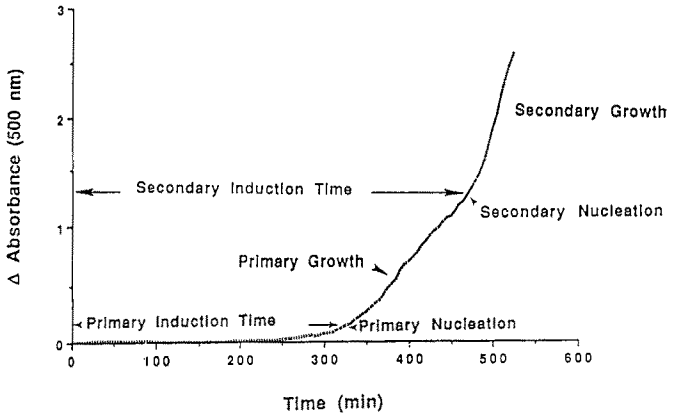

FIG. 2. Crystallization curves of cocoa butter, illustrating the induction period, nucleation, and the two stages of crystallization.

stages progressed at high rates, making it difficult to differentiate between the primary and secondary phases. It was evident, based on Δ absorbance, that crystallization in the secondary stage was more rapid than during the primary stage. Crystallization curves in these studies were constructed based on the light-scattering properties of the crystals, not the direct percent crystallinity of the samples; therefore, the increase in absorbency values may not indicate the formation of more of the same crystal type. It could be the result of the formation of crystals that were different in either structure or composition from those of the previously existing crystals.

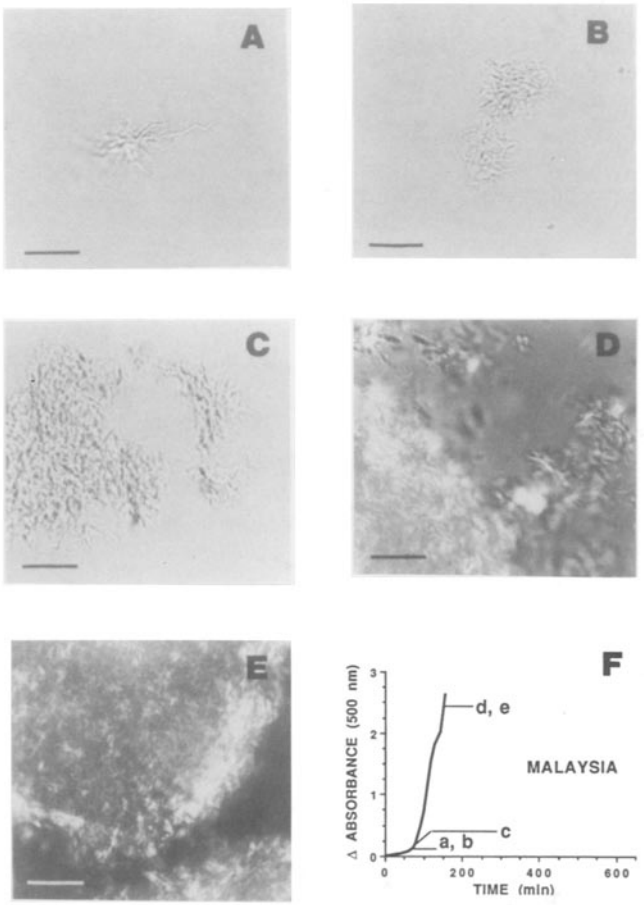

FIG. 3. Micrographs (A–E) illustrating the dynamic crystallization of Malaysian cocoa butter at 26.5°C (bars = 20 μm); crystallization growth curve (F) (lower case letters indicate sampling points).

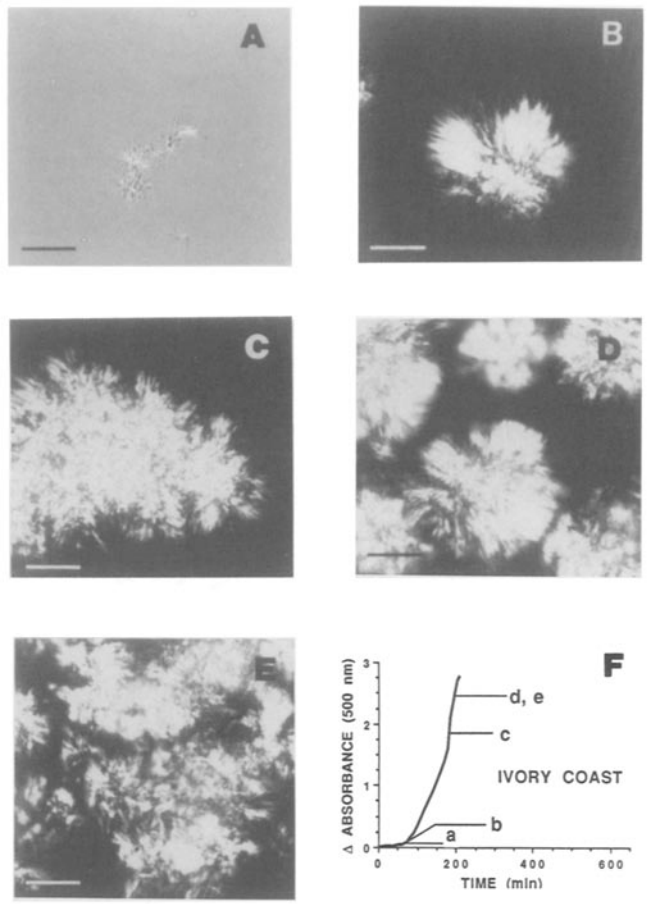

FIG. 4. Micrographs (A–E) illustrating the dynamic crystallization of Ivory Coast cocoa butter at 26.5°C (bars = 20 μm); crystallization growth curve (F) (lower case letters indicate sampling points).

Morphological studies of cocoa butter crystals indicated that, when isolated at Δ absorbance of 0.01, few crystals were present, and they ranged from 5 to 20 μm. The number of crystals with similar size increased when Δ absorbance reached 0.02. Morphologies of the crystals isolated at Δ absorbance = 0.02 are illustrated in Figures 3A–8A. These crystals are referred to as "seed crystals," and exhibit minor variations in their morphologies, but they share some common features, i.e., tubular and slight or nonbirefringence. Ivory Coast and Dominican Republic seed crystals showed slight birefringence at the crystal core and appeared to have a "bowtie" structure, as reported by Manning and Dimick (5). These seed crystals were irregular in shape and were constructed with long tubular filaments, which are not observed with pure triacylglycerols. The factors that affect the crystal morphol-

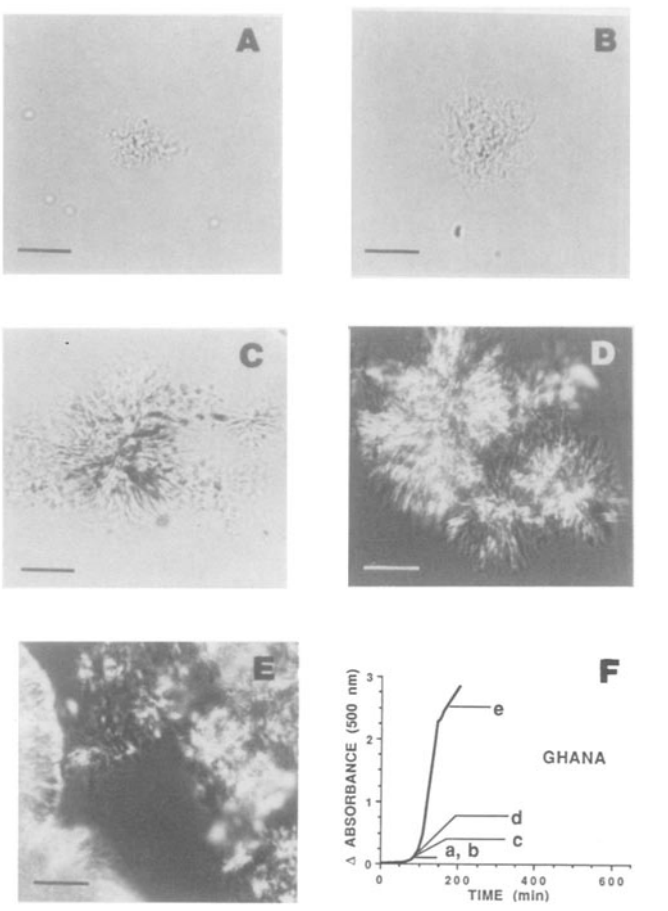

FIG. 5. Micrographs (A–E) illustrating the dynamic crystallization of Ghanaian cocoa butter at 26.5°C (bars = 20 μm); crystallization growth curve (F) (lower case letters indicate sampling points).

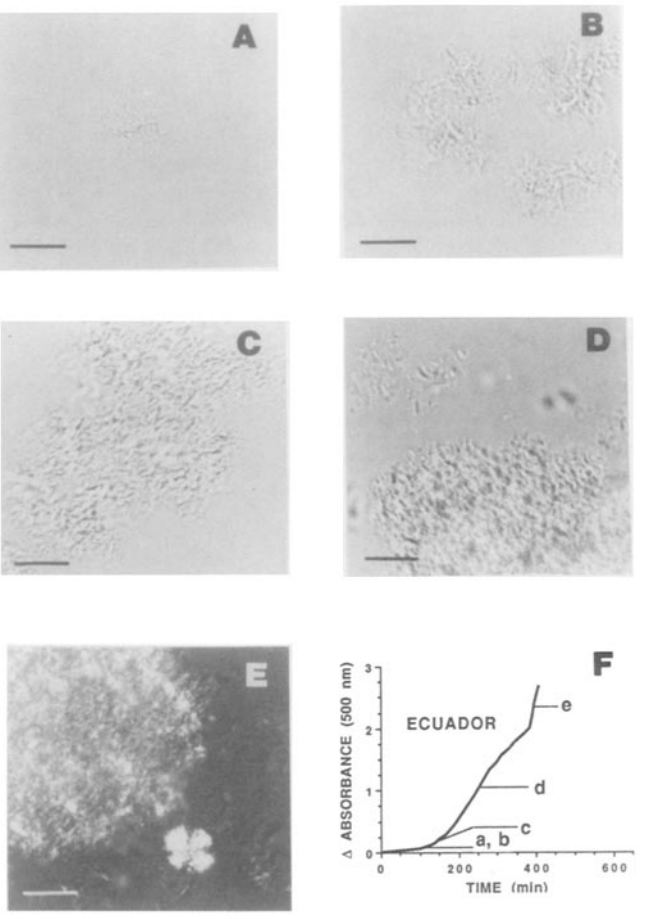

FIG. 6. Micrographs (A–E) illustrating the dynamic crystallization of Ecuadorian cocoa butter at 26.5°C (bars = 20 μm); crystallization growth curve (F) (lower case letters indicate sampling points).

ogy are not known. However, the irregular shape of the tubular filaments may be the effect of polar lipids, such as glycolipids, phospholipids, and lipoproteins, that cocrystallize with the triacylglycerols (3).

Shortly after nucleation in the primary stage, crystal growth became predominant (Fig. 3B,C, Fig. 8B,C). The phenomena that occurred during the primary growth stage were the growing of existing crystals, agglomerating of the crystals, and the possible sintering of the agglomerated crystals. Aggregation of fat crystals due to van der Waals forces is common when fats crystallize under mild agitation. Aggregated, slight, or no birefringent crystals started growing and concurrently sintering into large masses, which were clearly observed in the slow-growth samples (Fig. 5C, Fig. 7C, Fig. 8C).

The secondary stage was characterized by the formation of birefringent spherulites. In this stage, a number of small spherulites formed throughout the crystallization process, resulting in a rapid growth rate. The small spherulitic crystals can be observed from micrographs D in Figures 3–8. The change in crystal morphologies of the crystals in the secondary growth stage from the crystals in the primary growth stage possibly occurred after most impurities had crystallized during the primary stages, leaving the molten cocoa butter a purer system. It also could be due to the polymorphic transition to the more stable polymorphs, in which the triacylglycerol molecules are more tightly packed. Tightly packed triacylglycerols allow less polar impurities to fit into the crystal lattices. It is believed that secondary nuclei are generated by the collision among the existing crystals and between the crystals and the vessel. Secondary nuclei also could be produced from collisions of the spherulitic crystals. Other possibilities that cause secondary nucleation are the growth of the dendritic crystals and the shearing of dendrites or the ordered layers from the growing crystals by flowing fluids (8).

Rapid-growth cocoa butters either had rapid growth rates in the primary stage or reached the secondary stage early. Ivory Coast and Ghanaian cocoa butters, which were the rapid-growth samples, formed spherulites at the early stages of crystallization. Crystals of the Ivory Coast cocoa butter exhibited birefringent spherulitic structures when Δ absorbance reached 0.04. Ghanaian cocoa butter started to form large spherulites from the aggregated mass as early as Δ absorbance = 0.06. The primary crystal rate was rapid in Malaysian cocoa

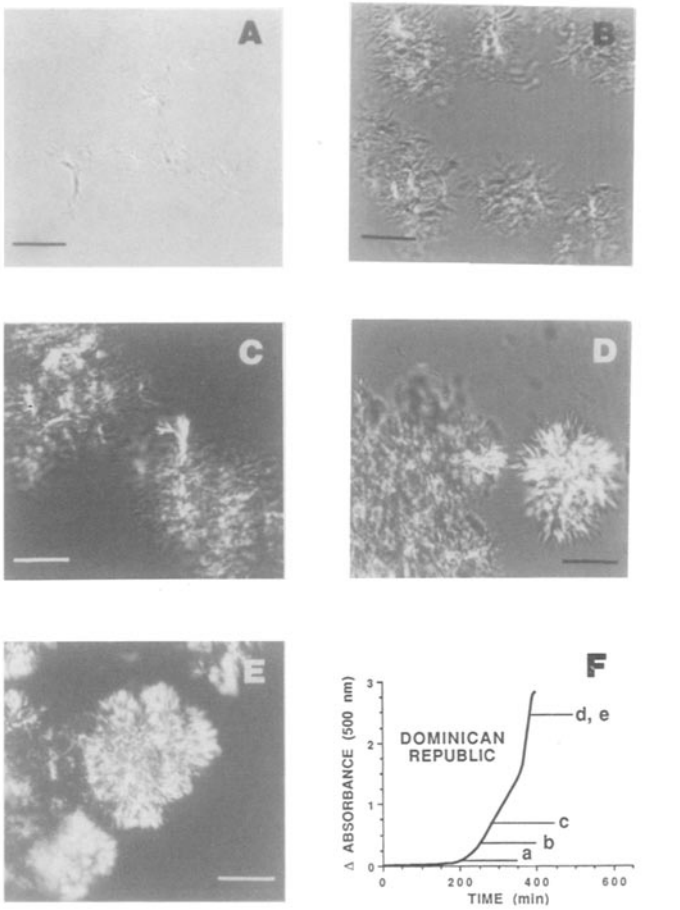

FIG. 7. Micrographs (A–E) illustrating the dynamic crystallization of the *Dominican Republic cocoa butter* at 26.5°C (bars = 20 μm); crystallization growth curve (F) (lower case letters indicate sampling points).

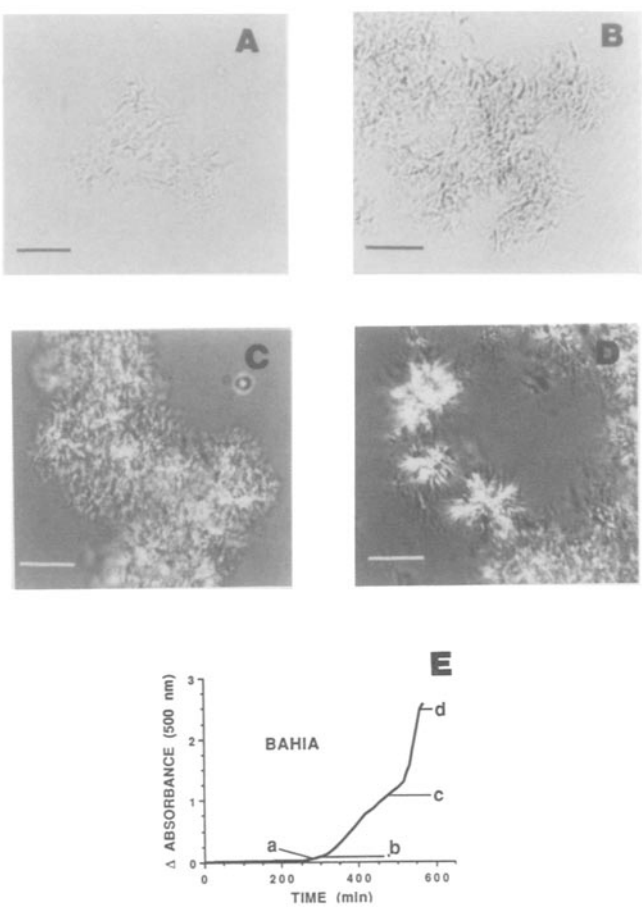

FIG. 8. Micrographs (A–D) illustrating the dynamic crystallization of Bahian (Brazil) cocoa butter at 26.5°C (bars = 20 μm); crystallization growth curve (E) (lower case letters indicate sampling points).

butter, although the secondary stage was not reached until Δ absorbance was 2.0.

Primary growth rates were slow, in the slow crystal-growth cocoa butters, and the formation of spherulites was prolonged. In the slow-growth cocoa butters from Ecuador, the Dominican Republic and Bahia, spherulitic crystals formed when Δ absorbance was approximately 1.1–1.2. The formation of spherulites was concomitant with increasing crystallization rate. This suggests that total crystallization time may depend upon the induction time of the spherulites in the secondary stage in addition to the crystal growth rate in the primary stage.

Thermal analyses. Crystals from Ivory Coast and Ecuadorian cocoa butters at various crystallization stages were isolated for thermal and chemical analyses. Ivory Coast and Ecuadorian cocoa butters were rapid-growth and slow-growth samples, respectively. Figure 9 presents the thermograms of the Ivory Coast samples during crystallization at 26.5°C at various growth stages (Δ absorbance 0.02–3.0). The lowest-melting endotherm, representing polymorphs I–III, was the result of quenching the residual cocoa butter melt associated with the crystals. The endotherms of the crystal phase increased in peak maxima from approximately 28–29 to 34.5°C, indicating polymorphic transition from IV–V to VI for cocoa butter. Studies on Ecuadorian cocoa butter revealed similar results (Fig. 10). The endotherms of the solid phase were observed at the early stage when Δ absorbance was 0.02. The peak maxima of the isolated crystals of Ecuadorian samples during the early stages of crystallization were approximately 29–30°C, which were similar to the crystals isolated from the Ivory Coast samples. This indicates that the majority of the crystals that formed in the early stages of crystal growth were polymorph form IV–V. Polymorphic transition to form V–VI was observed by the shift of peak maxima during the latter stages of growth, and this was concurrent with the formation of spherulites in Ecuadorian cocoa butter. There have been reports on polymorphism and morphology of pure triacylglycerol and fat crystals (9–11). However, in this study, whether the polymorphic transition to forms V–VI is the cause of spherulite formation is not conclusive because the Ivory Coast sample exhibited spherulitic morphology at early stages, but showed the polymorphic transition at the later stages of crystallization. The high-melting fraction (35–36°C) of the Ecuadorian samples could be observed in the later stages of growth. This high-melting fraction has a melting point of form VI and could be a result of fractional crystal-

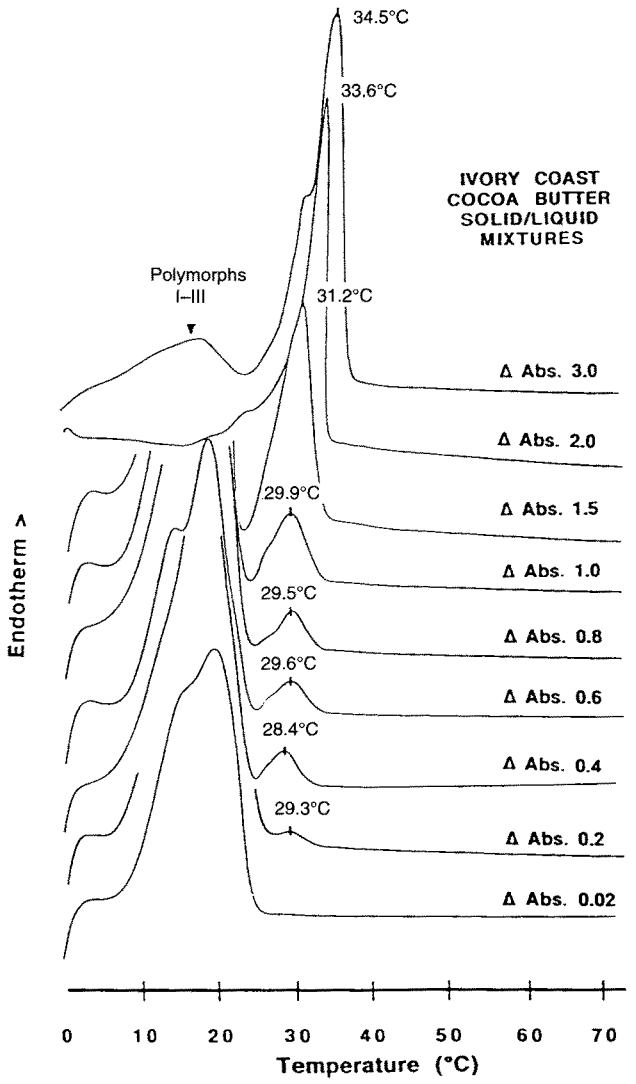

FIG. 9. Differential scanning calorimetry thermograms of mixtures of solid and liquid phases of Ivory Coast cocoa butter sampled at various growth stages. Abs., absorbance.

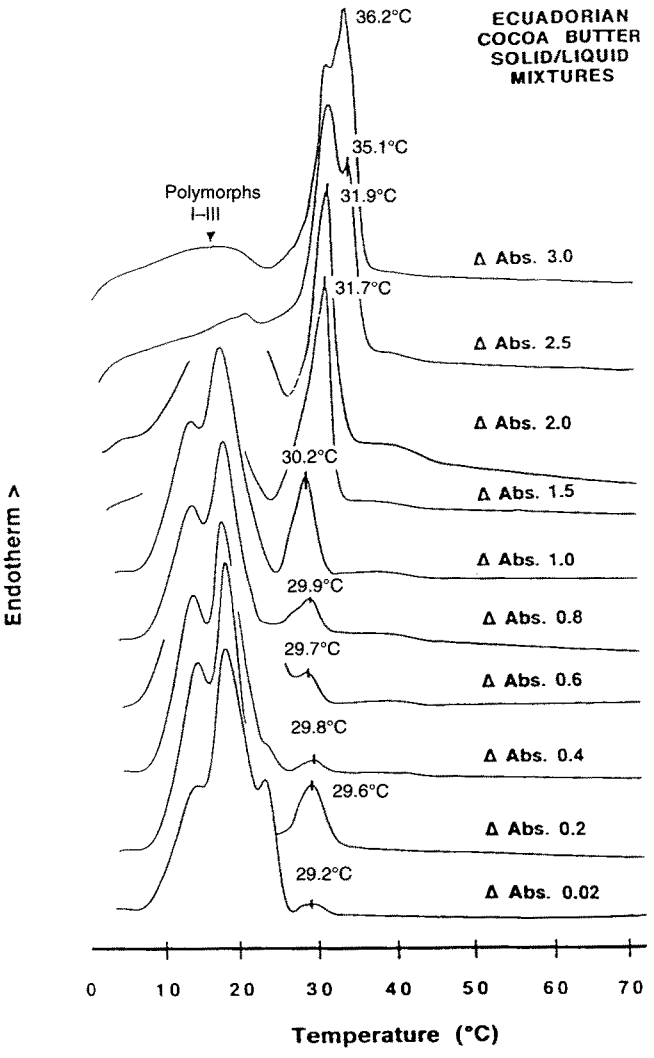

FIG. 10. Differential scanning calorimetry thermograms of mixtures of solid and liquid phases of Ecuadorian cocoa butter sampled at various growth stages. Abs., absorbance.

lization or segregation of some components in the existing solid phase to the purer state. The Ecuadorian sample took longer to solidify when compared to the Ivory Coast cocoa butter; hence, the Ecuadorian butter required a longer time for fractionation or segregation.

Chemical composition. Composition of the crystals isolated from the Ivory Coast and Ecuadorian samples at various growth stages were analyzed in comparison to those of the original cocoa butters. The composition of the crystals was that of the solid phase after the contaminating cocoa butter melt had been removed. At the initial stages of crystallization, polar lipids crystallized at rapid rates and were isolated in high concentrations with the crystals. When Δ absorbance reached 0.5, the percentages of glycolipids and phospholipids associated with the solid phase decreased significantly and remained constant throughout the remaining crystallization process. Throughout the crystallization process of both cocoa butters, concentrations of minor simple lipids were constant at approximately 2% of the total simple lipid fraction. Concentrations of the unsaturated C_{18} free fatty acids of the growing crystals were lower than those of their respective cocoa butters (Tables 1 and 2). The unsaturated free fatty acid content is undoubtedly high because these acids do not crystallize under the study conditions and remain in the liquid state. Sterols, on the other hand, crystallized out during growth, resulting in higher concentrations of stigmasterol and β-sitosterol as compared to the original cocoa butters. The composition of the free fatty acid fraction indicated that stearic acid crystallized consistently during crystal growth, whereas oleic, linoleic, and linolenic acids remained in the liquid phase. The diacylglycerol fractions of both samples showed similar fatty acid distributions. During crystallization, more of the saturated fatty acid-containing diacylglycerols solidified, leaving the highly unsaturated diacylglycerols in the liquid phase.

TABLE 1
Simple Lipid Distribution Within Minor Simple Lipid Fractions of Ivory Coast Cocoa Butter Crystals at Various Stages as Indicated by Increases in Spectrophotometric Absorbance at 500 nm

	Content[a] (wt%)											
Δ Absorbance	$C_{14:0}$	$C_{16:0}$	$C_{18:U}$	$C_{18:0}$	MG	Campesterol	Stigmasterol	β-Sitosterol	DG-32	DG-34	DG-36	DG-38
0.02	2.4 B	14.5	10.6 A	13.9	1.8	0.7	2.1 A	4.0 A	2.0	19.1 AB	28.1	0.6
0.5	2.8 AB	13.7	9.5 A	15.9	1.7	0.8	2.1 A	3.6 ABC	2.0	19.7 AB	27.4	0.7
1.0	3.2 AB	14.3	9.8 A	13.5	1.9	0.7	2.0 AB	3.6 ABC	2.1	20.3 AB	26.4	0.7
1.5	3.1 A	14.8	9.3 A	10.0	1.8	0.8	2.1 A	3.7 AB	2.2	21.5 A	30.4	0.4
2.0	2.2 B	14.2	9.7 A	13.8	1.9	0.7	1.9 AB	3.4 CD	2.2	20.6 AB	28.9	0.5
Cocoa butter	2.5 AB	14.7	14.7 B	14.3	1.2	0.7	1.8 B	3.2 D	1.5	18.1 B	26.9	0.4

[a]Means within the same column with the same uppercase letter are not different at $\alpha = 0.05$; MG, monoacylglycerol; DG, diacylglycerol.

TABLE 2
Simple Lipid Distribution Within Minor Simple Lipid Fractions of Ecuadorian Cocoa Butter Crystals at Various Growth Stages Indicated by Increase in Spectrophotometric Absorbance at 500 nm

	Content[a] (wt%)											
Δ Absorbance	$C_{14:0}$	$C_{16:0}$	$C_{18:U}$	$C_{18:0}$	MG	Campesterol	Stigmasterol	5-Sitosterol	DG-32	DG-34	DG-36	DG-38
0.02	2.9 A	12.1	7.9 CD	10.3 B	1.8 A	0.7 A	1.7 A	3.4 A	1.9 AB	24.6 A	32.5 AB	0.4
0.5	2.9 A	13.0	7.8 CD	13.2 A	1.9 A	0.6 AB	1.6 AB	3.2 AB	2.2 AB	22.6 B	30.1 CD	0.8
1.0	2.1 B	11.5	6.9 D	11.3 AB	1.9 A	0.6 AB	1.7 A	3.1 AB	2.3 AB	24.7 A	33.3 A	0.7
1.5	2.3 AB	13.2	8.9 C	12.9 A	1.6 A	0.6 AB	1.6 AB	3.2 AB	2.2 AB	22.1 B	30.9 BC	0.5
2.0	2.4 AB	11.9	11.9 B	13.6 A	1.7 A	0.5 B	1.4 C	2.8 B	1.8 B	21.7 B	29.8 CD	0.6
Cocoa butter	2.9 A	12.1	13.7 A	13.3 A	1.1 B	0.6 AB	1.5 BC	3.0 B	2.2 A	20.8 B	28.5 D	0.3

[a]Means within the same column that does not have the uppercase letter are not different at $\alpha = 0.05$. Abbreviations as in Table 1.

TABLE 3
Triacylglycerol Composition of Ivory Coast Cocoa Butter Crystals at Various Growth Stages Indicated by Increases in Spectrophotometric Absorbance at 500 nm

	Triacylglycerol[a] (wt%)														
Δ Absorbance	PLO	PLP	OOO	SLO	POO	PLS	POP	SOO	SLS	POS	PPS	SOS	PSS	SOA	SSS
0.02	0.8	1.6 AB	0.8 A	0.2	1.8	3.3 AB	14.3 AB	2.1 AB	1.6	43.8 A	0.9	26.0 A	O.9 A	1.0	0.8 AB
0.5	0.7	1.4 AC	0.4 B	trace	1.9	3.5 AB	13.2 BC	2.3 B	1.7	44.3 A	0.9	27.2 AB	1.1 A	0.8	0.8 AB
1.0	0.7	1.5 ABC	0.5 AB	trace	1.7	3.2 AB	13.4 C	2.0 AB	1.6	43.6 A	1.0	27.8 BC	1.2 A	1.0	0.9 A
1.5	0.6	1.4 C	0.6 AB	0.3	1.5	2.9 A	13.1 C	1.8 A	1.5	44.3 A	0.8	28.7 BC	1.0 A	0.9	0.8 AB
2.0	0.6	1.5 AC	0.6 AB	0.1	1.5	2.9 A	12.4 C	2.2 AB	1.4	44.4 A	1.0	29.0 C	1.0 A	0.9	0.7 AB
Cocoa butter	0.7	1.7 C	0.4 B	0.1	1.8	3.7 B	15.0 A	2.3 B	1.7	46.3 B	0.8	24.1 D	0.4 B	0.8	0.4 B

[a]Means within the same column with the same uppercase letter are not different at $\alpha = 0.05$; P = palmitate; O = oleate; S = stearate; L = linoleate; A = arachidonate.

TABLE 4
Triacylglycerol Composition of Ecuadorian Cocoa Butter Crystals at Various Growth Stages Indicated by Increases in Spectrophotometric Absorbance at 500 nm.

	Triacylglycerol[a] (wt%)														
Δ Absorbance	PLO	PLP	OOO	SLO	POO	PLS	POP	SOO	SLS	POS	PPS	SOS	PSS	SOA	SSS
0.02	0.6	1.5	0.5	trace	2.4	3.3	13.4	3.4	1.6 A	44.7	0.8 C	25.6 BC	0.8 B	0.8	0.7 A
0.5	0.7	1.5	0.5	trace	2.4	3.0	13.2	3.1	1.3 B	44.6	1.0 ABC	26.0 AB	1.3 A	0.8	0.9 A
1.0	0.7	1.5	0.5	trace	2.3	3.0	13.4	3.1	1.4 AB	44.0	1.1 AB	25.9 ABC	1.5 A	0.8	0.9 A
1.5	0.7	1.5	0.6	0.2	2.1	2.9	12.9	3.1	1.2 B	44.8	1.2 A	26.5 AB	1.4 A	0.8	0.9 A
2.0	0.6	1.4	0.4	trace	2.2	3.0	13.0	3.1	1.4 AB	44.8	0.9 BC	26.8 A	1.0 B	0.8	0.7 A
Cocoa butter	0.5	1.6	0.7	0.1	2.7	3.1	14.1	3.3	1.6 A	45.4	0.8 C	24.8 C	0.4 C	0.8	0.3 B

[a]Means within the same column that does not have the uppercase letter are not different at $\alpha = 0.05$. Abbreviations as in Table 3.

During crystal growth, the concentrations of PLP, OOO, PLS, and 1-stearoyl-2,3-oleoylglycerol (SOO) of the Ivory Coast butter triacylglycerols varied significantly (Table 3). Trisaturated triacylglycerols, PSS and SSS, were constant and significantly higher in the crystals during growth than in the original cocoa butter. Concentrations of 1-palmitoyl-2,3-oleoylglycerol (POO) and SOO of the crystals remained constant during crystallization. During crystallization of the Ivory Coast sample (Δ absorbances = 0.02–2.0), the SOS concentration in the crystals was higher than in the original cocoa butter and increased as crystallization progressed. The triacylglycerol composition of the Ecuadorian sample showed similar trends (Table 4). The POO and SOO contents of the Ecuadorian cocoa butter remained the same throughout crys-

tallization. The SOS concentration of the Ecuadorian cocoa butter crystals during growth increased to 26.8%, as compared to 29.0% in the Ivory Coast sample. In the Ecuadorian samples, the presence of the high-melting fraction (35–36°C) may be the result of the segregation of components, such as trisaturated triacylglycerols from the *sn*-2-oleodisaturated triacylglycerol-rich solid phase. This high-melting fraction could also be a result of recrystallization of SOS into a purer state as observed by formation of the SOS-rich, high-melting crystals by Manning and Dimick (5).

It could be anticipated that the crystals that formed at the end of the crystallization of the Ivory Coast cocoa butter would have a different triacylglycerol composition than the crystals that formed during the early stages. This is because the solid phase contained a higher SOS concentration than did the original cocoa butter. Composition of the remaining liquid phase, therefore, would be rich in the other unsaturated triacylglycerols. There was no conclusive evidence that, besides the initial concentrations of POO, SOO, POS, and SOS in the original cocoa butter, there were any specific compounds responsible for the differences in crystal growth rate. SOS rapidly crystallized in a higher proportion in cocoa butters with a rapid crystal growth rate than presented in the original cocoa butter. The slow-growth samples did not show this characteristic.

REFERENCES

1. Lehrian, D.W., P.G. Keeney, and D.R. Butler, *J. Am. Oil Chem. Soc. 57*:66 (1980).
2. Chaiseri, S., and P.S. Dimick, *Ibid. 66*:1771–1776 (1989).
3. Davis, T.R., and P.S. Dimick, *Ibid 66*:1494–1498 (1989).
4. Kattenberg, H.R., *Proceed. Ann. Prod. Conf. 35*:50–54 (1989).
5. Manning, D.M., and P.S. Dimick, *Food Microstructure 4*:249–265 (1985).
6. Chaiseri, S., and P.S. Dimick, *J. Am. Oil Chem Soc. 72*:1491–1496 (1995).
7 Schenkel, J., *Review for Chocolate, Confectionery and Bakery 8*:3–6 (1983).
8. Garside, J., *Food Structure and Behavior*, Academic Press, New York, 1987, p. 35.
9. deMan, J.M., A.N. Mostafa, and A.K. Smith, *Food Structure 4*:233–239 (1985).
10. Hicklin, J.D., G.G. Jewell, and J.F. Heathcock, *Food Microstructure 4*:241–248 (1985).
11. Chawla, P., J.M. deMan, and A.K. Smith, *Food Structure 9*:329–332 (1990).

[Received February 22, 1995; accepted August 17, 1995]