Effect of Temperature on Recrystallization Behavior of Cocoa Butter

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ABSTRACT: Crystallization of cocoa butter in the β phase directly from the melt is only possible by employing the memory effect of cocoa butter. Cocoa butter crystallized in the β phase, heated to the so-called maximal temperature (just above its melting end point), recrystallizes in the β phase after cooling to a crystallization temperature. The influence of the maximal and crystallization temperatures on the recrystallization behavior has been investigated for two cocoa butters. Rapid-starting recrystallization into the β(VI) phase and slow-starting recrystallization into the β(V) have been observed. It is concluded that rapid-starting recrystallization is induced by high-melting 1,3-distearoyl-2-oleoyl-glycerol (SOS)-rich crystals. The two β phases were identified by X-ray powder diffraction and melting ranges. However, the X-ray powder diffraction patterns for the β phases depended on the composition of the cocoa butter and on the crystallization method used. Therefore, it was not possible to take any particular β(VI) X-ray powder diffraction pattern as a standard for the β(VI) phase of all cocoa butters.

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KEY WORDS: Cocoa butter, crystallization, memory effect, seeding.

Crystallization is a critical point in making chocolate and confectioneries. Poorly crystallized chocolate results in the formation of fat bloom, a grayish-white film at the chocolate surface. The chocolate seems aged and musty, which results in an increase in customer complaints to chocolate manufacturers. To obtain quality products, understanding and total control of the cocoa butter solidification process is indispensable. However, the crystallization behavior of cocoa butter is very complex, as cocoa butter may crystallize in many different polymorphic phases.

Although this crystallization has been subject of thorough research for many years, no uniform nomenclature for the various phases of cocoa butter has been achieved. Vaeck (1) showed the existence of four phases and designated them by the Greek letters γ, α, β′, and β. Wille and Lutton (2) observed six different crystalline phases for cocoa butter, numbered with the Roman numbers I to VI. More recently, Van Malssen *et al.* (3) concluded from mechanically static solidification experiments that cocoa butter crystallizes in even more crystal modifications: a γ and an α phase, a β′ phase range, and two β phases were observed. In this chapter a combination of the nomenclature by Vaeck (1) and by Wille and Lutton (2) is used, resulting in the phases γ, α, β′, and two β phases: β(V) and β(VI). Each of the cocoa-butter phases has its own physical characteristics, such as diffraction properties, melting range, and relative stability.

Since each phase gives a characteristic pattern in X-ray powder diffraction (XRPD), this technique is very well suited for identification of cocoa-butter phases (4; Fig. 1). Furthermore, in time-resolved XRPD experiments, phase transitions can be observed and monitored (3,5).

The transitions from less stable to more stable phases are generally irreversible and depend on temperature and time (3;

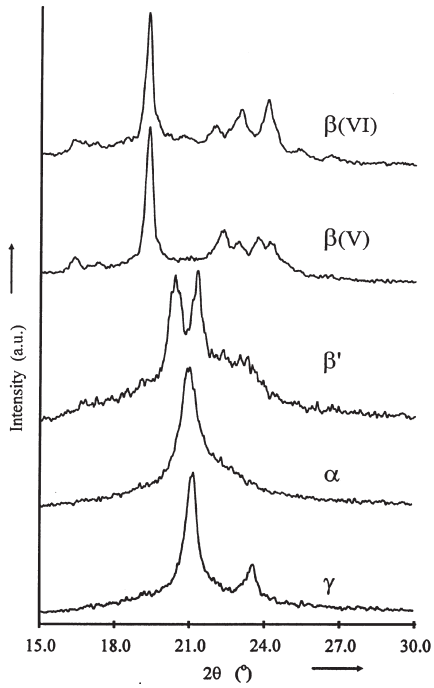

FIG. 1. Fingerprint region (λ = 1.5418 Å; *d*-spacing values 3.0 to 6.0 Å) of the X-ray powder diffraction (XRPD) pattern of various cocoa-butter phases. The γ, α, and β′ phases of Cameroon cocoa butter were measured after isothermal crystallization at –10.0, 0.0, and 20.0°C, respectively (3). The β(V) and β(VI) phases of B1 (Bahia, Brazil) cocoa butter were measured after isothermal crystallization at 22.0°C and from bulk material, respectively. These are the clearest XRPD patterns of the β(V) and β(VI) phases we have observed thus far.

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Fig. 2). All cocoa-butter phases except the two β phases may crystallize from totally molten cocoa butter. Although direct solidification of "form V" from the melt has been reported by Schlichter-Aronhime *et al.* (6), direct crystallization of β-cocoa butter under mechanically static conditions could not be confirmed by Van Malssen *et al.* (3,5) despite exhaustive cocoa-butter investigations. However, crystallization of cocoa butter in the β phase directly from the melt is possible *via* the "memory" of cocoa butter. When cocoa butter in the β phase is heated a few degrees above its melting end point (MEP), it still contains structural information. Upon cooling, the cocoa butter recrystallizes in the β phase. Recrystallization of cocoa butter *via* cocoa butter's memory has similarities with crystallization of cocoa butter induced by seeding. In both cases crystal-packing information is present in the melt, directing the crystallization. In the case of seeding, crystal-packing information is supplied by the addition of milled cocoa butter or pure triacylglycerols in the desired phase to the melt, whereas in the case of the memory effect, crystal-packing information remains present after melting. Both crystallization methods differ from crystallization from the memory-free melt, with or without tempering, where crystal nuclei are formed by primary nucleation during cooling of totally molten cocoa butter. Van Malssen *et al.* (7) studied cocoa-butter recrystallization and defined the β-memory point temperature (β-MPT) of a cocoa butter as the temperature at which cocoa butter in the β phase has to be heated to prevent cocoa butter recrystallization into the β phase within 45 min after cooling to 25°C. The β-MPT value of a cocoa butter is related to its composition. In particular, Van Malssen *et al.* (7) found a correlation between the β-MPT and the percentages of 1,3-distearoyl-2-oleoyl-glycerol (SOS) and stearic acid in the cocoa butter. Loisel *et al.* (8) doubted a correlation and stated that the β-MPT value corresponds to the trisaturated triacylglycerol content of cocoa butter.

To improve our understanding of the recrystallization of β-cocoa butter, we investigated the influence of the maximal temperature before cooling as well as the crystallization temperature on the recrystallization behavior of two different cocoa butters. The maximal temperature (T_{max}) is defined here as the temperature to which β-cocoa butter is heated before cooling to the crystallization temperature (T_{cryst}). Crystallization rate and recrystallized phase(s) of cocoa butter were determined for various combinations of T_{max} and T_{cryst}. However, the (recrystallized) phases β(V) and β(VI) have only small differences in the fingerprint region of the XRPD pattern (Fig. 1). To identify the recrystallized phases of cocoa butter and distinguish between the β(V) and β(VI) phase correctly or even quantify the β(V)/β(VI)-phase ratio, we compared XRPD patterns of cocoa butters in the β(V) and β(VI) phase with calculated patterns of various β(V)/β(VI) ratios. Finally, we considered cocoa-butter recrystallization in relation to its composition.

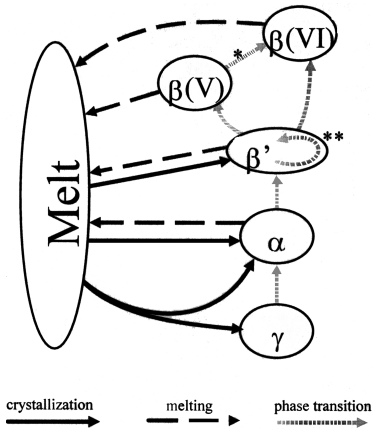

FIG. 2. Cocoa-butter phase-transition scheme (3) showing both isothermal and nonisothermal phase transitions. *This nonisothermal transition has been reported in the literature (2). **This nonisothermal transition has been reported in the literature (2) and has been observed in our experiments (Van Langevelde, A.J., and K.F. Van Malssen, unpublished data).

EXPERIMENTAL PROCEDURES

Samples, sample preparation, and equipment. XRPD patterns of cocoa butters of a previously used series of cocoa butters with various compositions (9; Table 1) were compared. Since these cocoa butters have been stored for more than 15 yr at ~5°C, they can be safely assumed to be in the stable β phase. For the (re)-crystallization experiments two different cocoa butters were used: one originating from Bahia, Brazil (B1) and one from Ghana (G1). Since the Brazilian cocoa butter from the series had deteriorated, a new sample (~2 yr old) was taken for B1. All cocoa butters were obtained from ADM Cocoa B.V. (Koog aan de Zaan, The Netherlands). Iodine values of all cocoa butters were determined using the Wijs method (10; IUPAC method 2.205, Table 2), the triglyceride compositions of B1 and G1 were determined by gas-liquid chromatography (GLC) (IUPAC method 2.323), and their fatty acid compositions by GLC *via* fatty acid methyl esters (IUPAC methods 2.301 and 2.302).

Samples for standard and real-time XRPD experiments were prepared by pressing cocoa butter in a temperature-controlled sample holder of $10 \times 15 \times 1$ mm^3 resulting in a flat-surface sample.

Standard XRPD measurements at controlled temperature were performed with a Philips PD1050 diffractometer (Philips

TABLE 1
Iodine Value of Cocoa Butters

Country of origin	New iodine value[a]	Old iodine value[b]
Brazil	40.3[c] (31.0)	40.8
Peru	36.6	36.2
Cameroon	36.0	36.6
Liberia	35.0	34.5
Congo	32.8	35.0
Sierra Leone	34.5	35.3
Ghana	31.0	35.2
Togo	35.2	33.0
Nigeria	31.2	35.2
Equatorial Guinea	36.5	37.0
Ivory Coast	32.5	34.7
Malaysia	33.3	33.9

[a]Determined in 1999.
[b]Determined in 1994 (9).
[c]New sample (see text).

TABLE 2
Iodine Values and Triglyceride and Fatty Acid Contents of the Two Cocoa Butters B1 and G1

	B1[a]	G1[b]
Iodine value	40.3	31.0
Triglyceride	(%)	(%)
C48	0.2	0.4
C50	16.7	16.6
C52	45.6	45.5
C54	35.9	34.7
C56	1.7	3.0
Fatty acid	(%)	(%)
$C_{16:0}$	23.4	26.5
$C_{16:1}$	0.5	0.8
$C_{18:0}$	31.3	36.0
$C_{18:1}$	37.8	33.0
$C_{18:2}$	4.5	2.0
$C_{18:3}$	0.2	0.1
$C_{20:0}$	1.2	1.2
$C_{20:1}$	0.0	0.0
$C_{22:0}$	0.9	0.1
Other	0.3	0.3

[a]Originating from Bahia, Brazil.
[b]Originating from Ghana.

Analytical, Almelo, The Netherlands) having Bragg-Brentano geometry and equipped with an Anton-Paar Low-Temperature camera. Step scans were made using Cu Kα radiation (λ = 1.5418 Å) from 15 to 30° 2θ, a step size of 0.02° 2θ, and a counting time of 2 s. Real-time XRPD measurements were performed with the temperature-controlled real-time X-ray powder diffractometer as described by Van Malssen *et al.* (5,11).

The β phases of cocoa butter. From the series of cocoa-butter samples, standard XRPD patterns were made at room temperature. From B1 and G1, standard XRPD patterns were made of the β(V) and β(VI) phases as recrystallized from the melt *via* the cocoa-butter memory effect. For this purpose, the cocoa-butter samples were heated to T_{max} and kept at this temperature for 5 min. Subsequently, the samples were cooled at 5°C min^{-1} to T_{cryst} and kept at this temperature for 2 h (Table 3). After 2 h standard XRPD patterns were made at T_{cryst}.

From these cocoa butters standard XRPD patterns also were measured of the β(V) and β(VI) phases as formed *via* phase transformation from β′. The β(V) phase was obtained by heating cocoa-butter samples at 60°C for 5 min, cooling at 5°C min^{-1} to 22°C and keeping them at this temperature for several weeks. Since the bulk was already in the most stable phase, it was used directly to obtain XRPD patterns of the β(VI) phase.

The XRPD patterns of 100% β(V) and 100% β(VI) B1 cocoa butter, as obtained *via* isothermal crystallization, were used to calculate XRPD patterns of various ratios of β(V) and β(VI).

Effect of T_{max} *and* T_{cryst} *on the recrystallization behavior.* Samples of cocoa butters B1 and G1 in the most stable phase were heated to T_{max} and kept at this temperature for 5 min. Subsequently, the samples were cooled at 5°C min^{-1} to T_{cryst} and kept at T_{cryst} for 2 h. T_{max} was chosen in the range from 34.0 to 38.0°C and T_{cryst} in the range from 17.0 to 28.0°C. At T_{cryst}, an XRPD pattern was made twice per minute with an exposure time (t_{exp}) of 15 s. XRPD patterns were analyzed using dynamic-difference functions (DDF) expressing the squared difference between various patterns (*j*) of the series (5). The recrystallization was characterized by a crystallization start point (CSP) and a crystallization end point (CEP). CSP is defined as the time (min) at which DDF(*j*,1) passes the 3% threshold, and CEP as the time (min) at which DDF(*j*,240) is 5%. The relative crystallization rate (CR) is calculated from these two parameters: CR = 100/(CEP – CSP).

TABLE 3
Temperatures Used to Obtain the β(V) and β(VI) Phases *via* Recrystallization from the Melt for the Two Different Cocoa Butters B1 and G1[a]

	β(V)		β(VI)	
	T_{max} (°C)	T_{cryst} (°C)	T_{max} (°C)	T_{cryst} (°C)
B1	37	19	34	25
G1	35	19	35	27

[a]For countries of origin see Table 2. See also Table 4 and Figure 4.

Determination of melting ranges. Melting ranges of B1 and G1 in the various β(V) and β(VI) phases were determined by heating samples at 0.5°C min^{-1} from T_{cryst} or 22.0°C (for bulk cocoa butter) to a final temperature of 40.0°C. During heating an XRPD pattern was made four times per minute with a t_{exp} of 15 s. The resulting XRPD-pattern series was analyzed using DDF (5). Melting ranges were characterized by a melting start point [MSP; DDF(*j*,1)] and a melting end point [MEP; DDF(*j,m*)].

RESULTS AND DISCUSSION

The β phases of cocoa butter. Since the cocoa butters of the series have been stored for a long period, they can be considered to be in the most stable β(VI) phase. Nevertheless, the XRPD patterns show some remarkable differences (Fig. 3). In the XRPD patterns of all the cocoa butters, the high-intensity diffraction peak (*d* = 4.57 Å) typical for the β phase can be observed, together with a complex group of smaller diffraction peaks at lower *d* values (between 3.5 and 4.0 Å). However, the intensities of these peaks do not increase from high to low *d* values for each cocoa butter as is commonly assumed for cocoa butter in the β(VI) phase (2,3,12,13; *c.f.* Fig. 1). Since cocoa butters of various origins have different X-ray diffraction characteristics, the XRPD patterns alone do not provide decisive evidence to classify a β phase as β(VI).

From comparison of the XRPD patterns of the cocoa-butter series with their iodine values, it appears that only cocoa butters with a high iodine value (≥36) give an XRPD pattern with a clear β(VI) character (Table 1; Fig. 3). In view of the intensity variation of the small group of diffraction peaks with *d* values between 3.5 and 4.0 Å, it is not possible to take any particular β(VI) XRPD pattern as a standard for the β(VI) phase of cocoa butter in general.

The X-ray diffraction characteristics of the β(V) and β(VI) phases also depend on the way they are crystallized (Fig. 4A,B; Table 3). If the phases of cocoa butter B1 are formed *via* isothermal phase transformation, the phases show distinct β(V) and

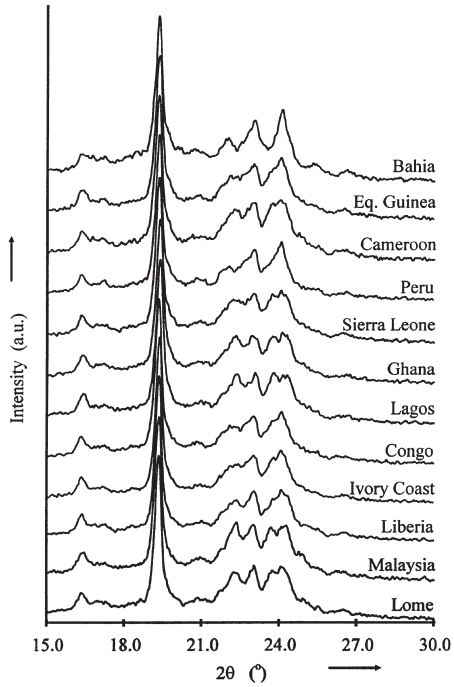

FIG. 3. XRPD patterns of bulk material of the cocoa-butter series (λ = 1.5418 Å; *d*-spacing values 3.0 to 6.0 Å).

β(VI) XRPD patterns. The β phases obtained by recrystallization *via* the memory effect have a lower signal-to-noise ratio and have broader diffraction peaks in the region of 3.5–4.0 Å. The XRPD patterns of the isothermally formed β(V) and β(VI) phases of G1 do not show such clear β(V) or β(VI) character.

From these observations one may conclude that cocoa butters with a high degree of unsaturation, which corresponds with the content of $C_{18:1}$ and $C_{18:2}$ (Table 2), have two distinguishable β phases. The two different β phases are not clearly observed in the cocoa butter originating from Ghana, which has an iodine value of 31.

For both cocoa butters the β(VI) phase melts at higher temperatures (~2°C) than the β(V) phase irrespective of the crystallization method (Table 4). Cocoa-butter phases obtained *via* isothermal crystallization melt at slightly higher temperatures than their corresponding phases obtained *via* recrystallization. Although there is no clear difference between the XRPD patterns of the β(V) and β(VI) phases of G1, two β phases exist as can be concluded from the melting ranges.

The small difference between the XRPD patterns of the β(V) and β(VI) phases makes it very difficult to quantify the ratio between β(V) and β(VI). A series of calibration XRPD patterns with various β(V)/β(VI) phase ratios should be made (14; Fig. 5). However, since the XRPD pattern of the β phases depends on the composition of the cocoa butters, a series of calibration XRPD patterns should be made for each cocoa butter under investigation. Furthermore, the crystallization method also should be taken into account because it affects the resulting XRPD pattern. But even for cocoa butters like B1 with distinct β(V) and β(VI) XRPD patterns, it is hard to determine the β(V)/β(VI) phase ratio from such a calibration pattern series with a reasonable accuracy. Therefore, in the recrystallization experiments cocoa-butter phases will be designated a β(V) or β(VI) phase only if it is absolutely clear from either the XRPD pattern or the melting range.

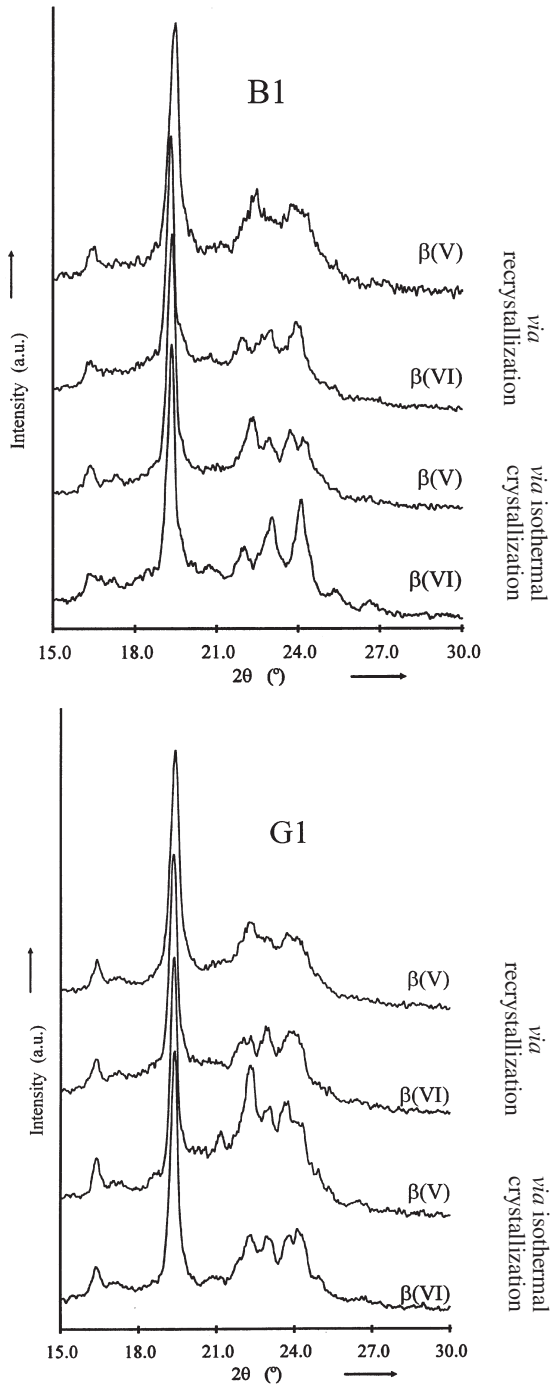

FIG. 4. XRPD patterns of the β(V) and β(VI) phases of cocoa butter (A) B1 and (B) G1. (λ = 1.5418 Å; *d*-spacing values 3.0 to 6.0 Å). The β(V) and β(VI) phases were crystallized *via* isothermal crystallization and *via* recrystallization (Tables 3 and 4). For abbreviations see Figure 1.

Effect of T_{max} *and* T_{cryst} *on recrystallization behavior.* CSP, CEP, and CR were determined for both cocoa butters B1 and G1 at various T_{max} and T_{cryst} values (Tables 5 and 6). T_{max} values

TABLE 4
Melting Start Points (MSP; °C) and Melting End Points (MEP; °C) of the β(V) and β(VI) Phases of Cocoa Butter obtained *via* Isothermal Crystallization and *via* Recrystallization[a]

	via recrystallization				*via* isothermal crystallization			
	β(V)		β(VI)		β(V)		β(VI)	
	MSP	MEP	MSP	MEP	MSP	MEP	MSP	MEP
B1	27.5	31.6	29.0	33.1	27.8	31.9	30.1	34.5
G1	28.0	32.5	31.5	34.8	28.5	33.0	31.1	35.4

[a]See Table 3, Figure 4.

were chosen slightly higher than the MEP values of the isothermally formed β(VI) phases (Table 4). For both cocoa butters recrystallization was much faster than crystallization at T_{cryst} from memory-free cocoa butter, especially at higher T_{cryst} values. In general, cocoa-butter recrystallization started later and took longer for increasing T_{max} values. Recrystallization was completed most rapidly at a T_{cryst} of 23°C and with the lowest T_{max} values for B1. For higher T_{max} values the optimal T_{cryst} value shifted to 19°C. For G1 at low T_{max} values the optimal T_{cryst} value was 21°C, but this optimum shifted to a lower value for higher T_{max} values. For lower T_{max} values recrystallization was observed even at a T_{cryst} of 26 to 27°C. CR values were slightly higher for B1 than for G1 at a T_{max} of 35°C.

Analysis of the standard XRPD patterns of each T_{max}–T_{cryst} combination for B1 (Table 5) shows that from the lower T_{max} values the cocoa butter recrystallized in the β(VI) phase, from higher T_{max} values in the β(V) phase, and from intermediate T_{max} values in both β phases. At the lowest T_{cryst} value used (17°C), crystallization of the α phase always was observed in the initial stage of the experiments, while in the case of higher T_{max} the β′ phase was observed simultaneously with the β phase (Fig. 6). However, in most cases unstable phase(s) rapidly disappeared when the β phase was formed.

Since the β(V) and β(VI) phases of G1 were not evidently distinguishable by their XRPD patterns alone, melting ranges of the crystallized cocoa butter were determined after each T_{max}–T_{cryst} experiment (Table 6). The presence of small amounts of metastable phases (α and/or β′) decreases the MSP value. Larger amounts of α and/or β′ decrease both the MSP and MEP values. For most T_{max}–T_{cryst} values (Table 7) cocoa butter recrystallized in the β(V) phase (maximal MEP ≈32.5°C). For a T_{max} value of 38°C, metastable phases (α and/or β′) were also observed for all T_{cryst} values, which was confirmed by the low MSP values. For lower T_{max} values, α crystallization occurred

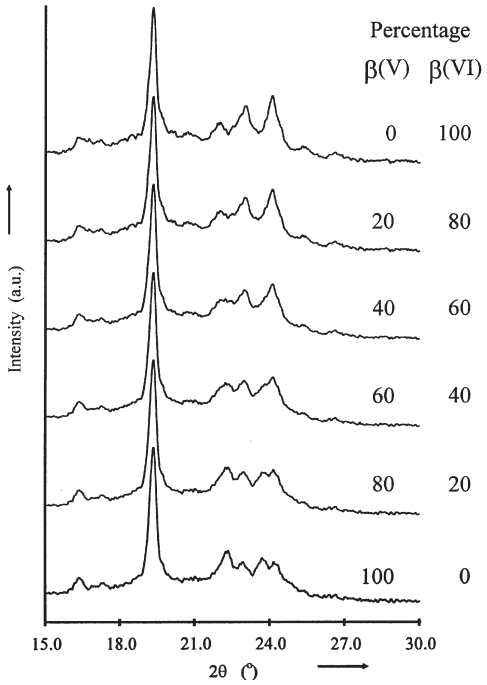

FIG. 5. XRPD patterns of various β(V)/β(VI) phase ratios calculated from 100% β(V) crystallized isothermally at 22.0°C and from 100% β(VI), bulk material (λ = 1.5418 Å; *d*-spacing values 3.0 to 6.0 Å). The cocoa butter (B1) used gives the most explicit (V) and (VI) XRPD patterns. For abbreviations see Figure 1.

TABLE 5
Recrystallization of B1 at T_{cryst} After Heating to T_{max}[a]

	T_{max} (°C)											
	34.0			35.0			36.0			37.0		
T_{cryst} (°C)	CSP (min)	CEP (min)	CR (min^{-1})	CSP (min)	CEP (min)	CR (min^{-1})	CSP (min)	CEP (min)	CR (min^{-1})	CSP (min)	CEP (min)	CR (min^{-1})
17.0	0.0	52.0 β(VI)[b]	1.92	1.5	36.0 β[b]	2.90	2.5	48.0 β[b]	2.20	5.0	50.0 β[b]	2.22
19.0	0.0	25.5 β(VI)	3.92	1.0	17.5 β	6.06	3.0	47.0 β	2.27	8.5	69.0 β(V)	1.65
21.0	0.0	21.5 β(VI)	4.65	2.0	15.5 β	7.41	6.0	43.5 β	2.67	22.0	90.5 β(V)	1.46
23.0	0.0	19.0 β(VI)	5.26	0.5	30.0 β	3.39	8.0	51.0 β	2.33	13.5	80.0 β(V)	1.50
25.0	1.5	25.0 β(VI)	4.26	2.0	62.0 β	1.67	15.0	96.5 β	1.23	30.5	101.5 β(V)	1.41
27.0	—	—		—	—		—	—		—	—	

[a]The phases after recrystallization were determined from their standard XRPD patterns.
[b]Besides β, metastable phases (α and/or β′) were observed during the experiment. CSP, crystallization start point; CEP, crystallization end point; CR, relative crystallization rate.

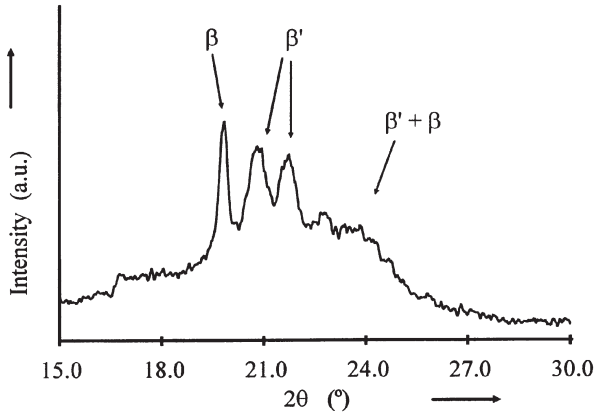

FIG. 6. XRPD pattern of various cocoa-butter phases simultaneously present after recrystallization (λ = 1.5418 Å; *d*-spacing values 3.0 to 6.0 Å). B1 after 5 min at T_{max} of 37°C and 2 h at T_{cryst} of 17°C.

only at lower T_{cryst} values, whereas for a T_{max} of 35°C no α crystallization was observed at all. Recrystallization of G1 in the β(VI) phase was observed only for T_{max} = 35°C and T_{cryst} = 27.0°C.

From all these experiments it is concluded that crystallization of cocoa butter directly in the β phase is enhanced if memory material is still present in the sample. Which phase and at which crystallization rate cocoa butter recrystallizes depends on T_{max}, T_{cryst}, and the composition of the cocoa butter. Since for higher T_{max} values the β(V) phase recrystallizes most rapidly at ~19°C and for lower T_{max} values the β(VI) phase at ~23°C, it is concluded that the optimal recrystallization rate of the β(V) phase is at ~19°C and for the β(VI) phase at ~23°C.

The memory effect of cocoa butter. In the T_{max}–T_{cryst} experiments carried out with B1, rapid-starting recrystallization (CSP < 2 min) was observed after heating to T_{max} values within a few degrees Celsius above the MEP. Heating to higher T_{max} values, especially in combination with increasing T_{cryst} values, leads to a progressively slower start of the recrystallization process. Furthermore, the rapid-starting recrystallization had an optimal T_{cryst} value of ~23°C and the slow-starting recrystallization an optimal T_{cryst} of ~19° C. In the case of G1, slow-starting recrystallization was generally observed, except for the lowest T_{max}–T_{cryst} combinations.

These observations can be explained by assuming that the rapid-starting recrystallization is induced by high-melting SOS-rich crystals. Cocoa butter is considered to be a conglomerate of crystals with individual triglyceride compositions. At lower T_{max} the concentration of SOS-rich crystals remaining in molten cocoa butter is sufficient to initiate a rapid-starting recrystallization, whereas at higher T_{max} values these crystals are molten and other higher-melting crystals will contribute to begin the (slower-starting) recrystallization process.

Crystals containing high concentrations of SOS play an important role in the crystallization of cocoa butter, which is supported by experimental results of others. Chaiseri and Dimick (15) showed that rapid-nucleating seed crystals contained higher concentrations of SOS than the original cocoa-butter samples, while slow-nucleating seed crystals showed no increased SOS concentration. Also, seeding of cocoa butter with pure SOS greatly accelerated the crystallization rate of cocoa butter, even more than milled cocoa butter did (16). In contrast, neither cocoa butter enriched with 1,2,3-tristearoyl-glycerol (SSS; 8) nor seeding of cocoa butter with SSS (16) led to an appreciable acceleration of cocoa-butter crystallization.

The interpretation of our results is also in agreement with the correlation found between the SOS concentration of 12 cocoa butters and the β-MPT values (7). Since the concentration of SOS present in the cocoa butter influences both the composition and the amount of high-melting SOS-rich crystals available at the various T_{max} values, it seems likely that the β-MPT will correspond to the T_{max} value at which the concentration of SOS in the high-melting seeds and their amount becomes too low to enable recrystallization within 45 min at a T_{cryst} of 25°C.

Generally, rapid-starting recrystallization induced by high-melting SOS-rich crystals resulted in the formation of the β(VI) phase, whereas slow-starting recrystallization resulted in the β(V) phase. This is most illustrative from the experiments involving B1. Therefore, which phase recrystallizes is related to the seed concentration and/or the seed composition. Hachiya *et al.* (17) concluded that the seed crystal does not completely determine the polymorphism of the bulk but serves as a crystallization accelerator only. They stated that the degree of supercooling determined the phase of the crystallized bulk. Since in the present study only high-melting SOS-rich seed crystals resulted in the recrystallization of the β(VI) phase, one may suppose that the recrystallized phase is also determined by the seed composition.

In the experiments with the cocoa butter G1, most of the T_{max}–T_{cryst} recrystallization started than in the corresponding experiments with the cocoa butter B1. During many T_{max}–T_{cryst} experiments with G1, metastable phases (α and β′) also were observed. For higher T_{max} values combined with lower T_{cryst} values, slow-starting recrystallization of the β(V) phase *via* the memory effect competed with memory-free isothermal crystallization of the α and β′ phases through primary nucleation. Therefore, it is concluded that recrystallization in

TABLE 6
Melting Ranges After Recrystallization of G1 at T_{cryst} After Heating to T_{max}[a]

	T_{max} (°C)							
	35.0		36.0		37.0		38.0	
T_{cryst} (°C)	MSP (°C)	MEP (°C)	MSP (°C)	MEP (°C)	MSP (°C)	MEP (°C)	MSP (°C)	MEP (°C)
17.0	27.6	32.5	22.8	29.3	23.3	28.0	23.4	28.1
19.0	28.0	32.5	27.8	31.4	24.0	30.0	24.1	29.0
21.0	28.3	32.6	28.4	32.6	24.8	31.3	24.7	29.5
23.0	29.0	32.5	29.0	32.8	29.7	32.4	26.1	32.1
25.0	29.6	33.1	29.6	33.1	29.9	32.8	—	—
26.0	29.9	33.5	29.9	33.8	—	—	—	—
27.0	31.5	34.8	—	—	—	—	—	—
28.0	—	—	—	—	—	—	—	—

[a]Compare with Table 7. For abbreviations see Tables 2 and 4.

TABLE 7
Recrystallization of G1 at T_{cryst} After Heating to T_{max}[a]

	T_{max} (°C)											
	35.0			36.0			37.0			38.0		
T_{cryst} (°C)	CSP (min)	CEP (min)	CR (min^{-1})	CSP (min)	CEP (min)	CR (min^{-1})	CSP (min)	CEP (min)	CR (min^{-1})	CSP (min)	CEP (min)	CR (min^{-1})
17.0	2.0	52.5 β(V)	2.00	3.0	49.0 β(V)[b]	2.17	3.0	46.5 β(V)[b]	2.30	15.0	101.0 β(V)[b]	1.16
19.0	4.5	61.0 β(V)	1.80	13.5	55.5 β(V)	2.38	22.0	49.5 β(V)[b]	3.64	20.5	51.0 β(V)[b]	3.28
21.0	2.5	27.0 β(V)	4.08	14.0	35.5 β(V)	4.65	41.0	62.0 β(V)[b]	4.76	37.5	57.0 β(V)[b]	5.13
23.0	7.0	41.5 β(V)	2.90	35.0	72.0 β(V)	2.70	52.0	97.5 β(V)	2.20	61.0	87.5 β(V)[b]	3.77
25.0	15.0	81.5 β	1.50	36.5	83.0 β	2.15	65.0	108.0 β(V)	2.33	90.0	<120 β(V)[b]	<3.3
26.0	26.0	96.0 β	1.43	70.0	>120 β	<2.0	—	—		—	—	
27.0	60.0	>120 β(VI)	<1.7	—	—		—	—		—	—	
28.0	—	—		—	—		—	—		—	—	

[a]The phases after recrystallization were determined from their standard X-ray powder diffraction patterns and melting ranges (Table 6).
[b]Besides β, metastable phases (α and/or β′) were observed during the experiment. For abbreviations see Tables 2 and 5.

most T_{max}–T_{cryst} experiments with G1 was induced mainly by other high-melting seed crystals. This is emphasized by the fact that the concentrations of $C_{18:1}$ and $C_{18:2}$ in G1 were much lower than those in B1.

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