

Phase Behavior and Extended Phase Scheme of Static Cocoa Butter Investigated with Real-Time X-Ray Powder Diffraction

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ABSTRACT: A complete isothermal phase-transition scheme of cocoa butter under static conditions is presented, based on time-resolved X-ray powder diffraction experiments. In contrast to what is known from literature, not only β V, but also β VI can be obtained directly through transformation from β' . Another remarkable result is that β' exists as a phase range rather than as two separate phases. Within this β' phase range no isothermal phase transitions have been observed. More detailed information concerning the observed cocoa butter polymorphs was obtained by determination of melting ranges, using time-resolved X-ray powder diffraction. Also standard X-ray powder diffraction patterns of the γ , the α , and the two β phases and parts of the β' phase range have been recorded. The observed phase behavior of cocoa butter has been explained based on the concept of individual crystallite phase behavior of cocoa butter

Paper no. J8719 in *JAOCs* 76, 669–676 (June 1999).

KEYWORDS: Cocoa butter, isothermal crystallization, phase transitions, polymorphism, X-ray powder diffraction.

Polymorphism, the occurrence of various solid phases (Table 1), of cocoa butter has a large impact on the product quality of chocolate and confectioneries. Obviously, intimate knowledge of the (isothermal) phase behavior of cocoa butter is of utmost importance to optimize production processes and to maintain product quality. An enormous amount of research has already been performed in the field of melting and crystallization of cocoa butter, its constituents, and related compounds (1–6). Typically, the work in this field is based on differential scanning calorimetry (DSC) experiments, often supplemented by X-ray powder diffraction (XRD). Recently Loisel *et al.* (7) used this combination to examine nonisothermal phase behavior of cocoa butter. The subcell of fat crystals (8–10) gives rise to a diffraction pattern between 3 and 5 Å that is unique for each different solid phase (1). Nevertheless, ambiguities and contradictions in the description of the polymorphism of cocoa butter still exist in literature (11).

Like DSC, time-resolved X-ray diffraction (tr-XRD) (12)

is a suitable technique to investigate solid–solid and liquid–solid–liquid phase transitions, but it has the advantage over DSC of giving unambiguous phase information. In previous work tr-XRD has been used to investigate the primary crystallization behavior of cocoa butter (13), the melting behavior of β -cocoa butter as function of the cocoa butter composition (14), and the occurrence of a memory effect (15).

Results obtained so far have led to the current study on the isothermal phase behavior of static cocoa butter. As a main result of this study, a cocoa butter phase scheme covering all isothermal phase transitions in the temperature range from -20 to 40°C and a time range of 10 d can be presented. A standard XRD pattern has been recorded for each identifiable solid phase in this scheme. This enables determinations of differences, if any, between the various β' and β subphases. In addition, the melting ranges of the various solid phases have been established.

In the memory-effect studies, it was proposed that cocoa butter might be considered to consist of a conglomerate of individual crystallites with individual fat composition and phase behavior (15). This model is sustained by the analysis of the results presented in this paper and can explain the observed phase behavior of cocoa butter.

MATERIALS AND METHODS

Samples and sample preparation. Experiments were performed with cocoa butter originating from Cameroon. This butter has been chosen from the set of 12 cocoa butters used in previous work (14,15) since its composition (Table 2) is close to the average of the set. Samples were prepared by pressing cocoa butter into the sample holder, resulting in a sample size of $10 \times 15 \times 1 \text{ mm}^3$ (~150 mg) with a flat surface. Before isothermal crystallization, samples were heated to 60°C for 60 s and then cooled linearly in 120 s to a preset solidification temperature (T_p).

Standard X-ray powder diffraction. For each solid cocoa butter phase encountered in the experiments (γ , α , and various appearances of β' and β), full XRD patterns were recorded. After preparation, samples were kept isothermally until the polymorphic phases of interest were fully developed. Subsequently, XRD patterns were recorded from 0.5 – 90° 2θ

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TABLE 1
Cocoa Butter Solid Phases

Phase		Melting points (°C)				Triacylglycerol (TAG) equivalent phase	Short spacings (Å)	
Wille & Lutton (1)	Vaeck (6)	Reference						
		1	4	5	20 ^a			
I	}	17.3		2 ^b	-5+5	β' ₃	4.19	3.7
II		23.3		16 ^b	17-22		α	4.24
III		25.5				β' ₂₋₂	4.25	3.86
IV	}	27.5	25.6	25 ^b	20-27	β' ₁₋₂	4.35	4.15
V		33.8	30.8				β' ₂₋₃	4.58
VI		36.3	32.3	32	29-34	β ₁₋₃	4.59	

^aMelting ranges.^bDisappearance of polymorph by melting or phase transition.

(CuKα) with a standard Philips PD1050 powder diffractometer (Philips Analytical, Almolo, The Netherlands) with Bragg-Brentano geometry, equipped with an Anton Paar Low Temperature camera, having a sample size of 1 × 10 × 15 mm³. The thermal history before the measurements is listed in Table 3. The isothermal phase diagram (see Fig. 5) indicates at which points in the phase transition scheme these measurements started. The relevant experimental settings are listed in Table 4.

Time-resolved XRD. The changes of the polymorphic state were investigated using the tr-XRD equipment as used in the earlier studies, with the same instrumental setting (13). The use of CuKα radiation and a diffraction range from 14.6–29.6° 2θ resulted in an observed d-range of 3.0–6.1 Å. Samples were kept at T_p up to a maximum of 10 d. T_p was chosen at 20.0, -15.0, and 10.0°C and from -5.0 to +30°C in steps of 1.0°C. From the moment samples were cooled to T_p the isothermal crystallization period was divided in equal-spaced intervals of I_t seconds, each. At the start of each interval, an X-ray pattern was recorded with an exposure time of E_t seconds. I_t and E_t were chosen short (*ca.* 10 measurements per minute) for fast phase transitions or long (*ca.* six measurements per hour) for slow phase transitions. In this way each phase transition was monitored with at least eight diffraction patterns from start to finish.

The X-ray patterns of these experiments were analyzed using the dynamic difference function (DDF) that expresses

TABLE 3
Thermal History for Complete Diffractograms and Melting Ranges

T_p (°C)	Time before measurement	Phase	MSP (°C) ^a	MP (°C)	MEP (°C) ^b
25.0	4 d ^c	β	29.0	30.5	33.7
20.0	11 d	β			
15.0	11 d	β	28.0	29.4	32.5
25.0	24 h	β'			
22.5	3 h	β'			
20.0	2 h	β'	24.2	25.3	29.0
17.5	2 h	β'			
15.0	2 h	β'	22.2	24.0	28.7
12.5	3 h	β'			
10.0	24 h	β'	21.5	22.9	27.2
7.5	24 h	β'			
5.0	91 h	β'	19.6	21.8	26.7
5.0	15 m	α			
0.0	45 m	α	17	19	22.5
-10.0	15 m	γ	-8.0		5

^aMelting start point.^bMelting end point.^cSample reprepared in order to obtain flat surface and to remove remaining β'.

the squared difference between various patterns as function of time (13). DDF ($j, 1$) expresses the relative difference between pattern j and the first pattern; DDF (j, m) expresses the relative difference between pattern j and the final pattern m . DDF values are scaled from 0–100%.

Determination of melting range. The melting behavior for β and β' states in the solid cocoa butter was monitored by record-

TABLE 2
Cocoa Butter Composition^a

Fatty acid	Percentage		
C _{14:0}	0.00	Iodine value	36.6
C _{16:0}	22.80	% Free acids	0.78
C _{17:0}	0.15	% Monoglycerides	0.1
C _{18:0}	31.03	% Diglycerides	1.2
C _{20:0}	0.91		
C _{16:1}	0.23		
C _{18:1}	31.21		
C _{18:2}	2.69		
C _{18:3}	0.06		

^aThe complete TAG composition of this cocoa butter is listed in (14) Tables 1, 5, 6, 7, and 8. For abbreviation see Table 1.**TABLE 4**
Settings for Full X-Ray Diffraction Patterns

Radiation:	Ni filtered CuKα	
Wavelength:	1.5418 Å	
Voltage:	40 kV	
Current:	30 mA	
	First 2θ range	Second 2θ range
2θ range:	0.5–5.0°	5.0–90.0°
Step 2θ:	0.02°	0.02°
Time per step:	2 s	1 s
Divergence slit:	1/30°	1/6°
Receiving slit:	0.1 mm	0.1 mm
Anti scatter slit:	1/2°	1/2°

ing diffraction patterns every 15 s, while samples were heated from T_p to 40.0°C at a heating rate of 0.5°C/min. For the γ and α melting behavior a heating rate of 2.0°C/min was utilized, in order to obtain accurate data, while other phase transitions besides melting were excluded as much as possible.

The melting start point (MSP), the point of maximum melting (MP), and the melting end point (MEP) characterize the melting trajectory. MSP, MP, and MEP were calculated using the DDF ($j,1$), DDF ($j,j-1$), and DDF (j,m) functions (14). β' solids formed at four selected temperatures were analyzed in order to compare the melting behavior in more detail. Since the calculated curves, especially DDF ($j,1$), depend strongly on the starting situation, such as the solid fat content, the DDF ($j,1$), DDF ($j,j-1$), and DDF (j,m) for each of these were recalculated, using 20°C as the starting situation.

RESULTS

Standard XRD patterns. In the recorded patterns no diffraction lines outside the subcell-range (3–6 Å) were observed, except for a few lines at longer spacings for the β phases. The relevant part of the XRD patterns is presented in Figures 1–3. For α , β' , and γ the interesting part of the standard XRD pattern is from 2.5–6.0 Å (Fig. 1 and 2). For the two β phases this is from 2.5–17.6 Å (Fig. 3). No interpretable long spacings were observed.

While only one γ phase and one α phase could be distinguished with the recorded XRD patterns, the variation in β' -phases is remarkable. As can be seen in Figure 2, in almost the whole T_p range different β' XRD patterns have been recorded. They have small, but significant, differences in number of peaks, peak shape, position, and intensity. Note that the diffraction pattern of γ , according to the standard definition a special case of β' (13), is very similar to the pattern of β' that arises at $T_p < 10^\circ\text{C}$.

Two β phases were observed with diffraction patterns that correspond with Wille and Lutton's phases V and VI (1).

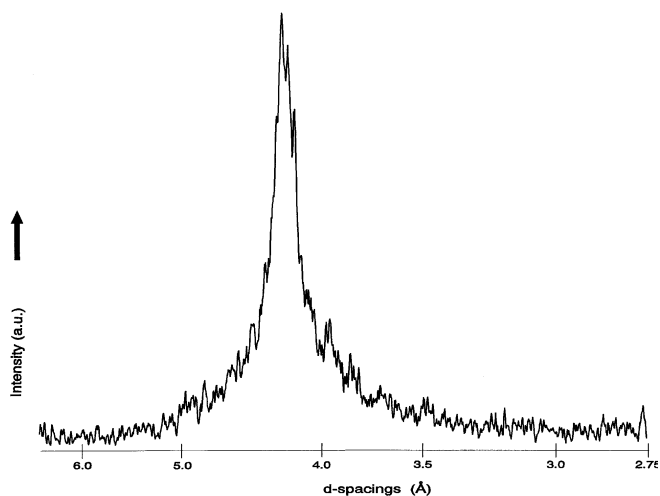


FIG. 1. X-ray powder diffraction pattern of α cocoa butter, recorded after 45 min. at $T_p = 0^\circ\text{C}$.

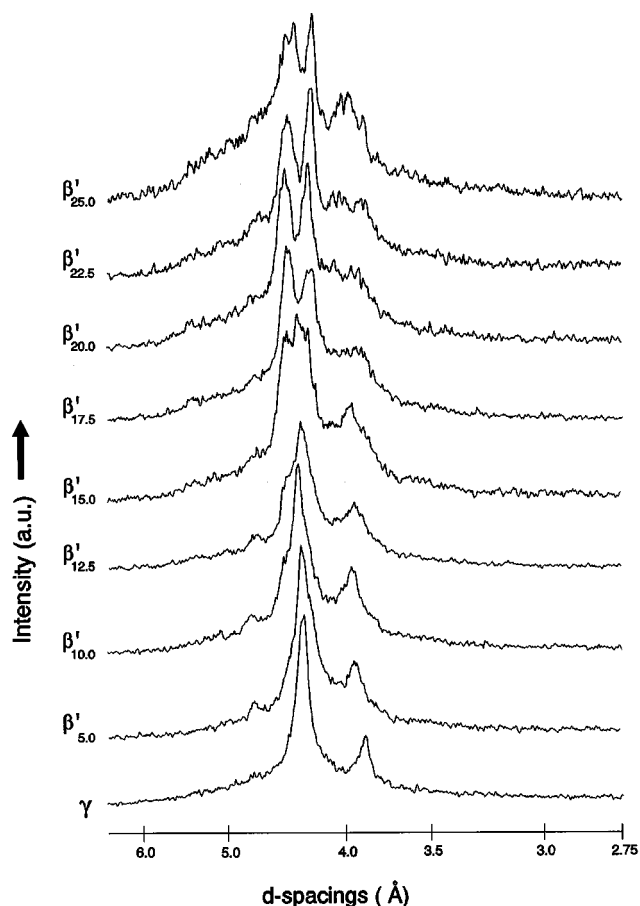


FIG. 2. X-ray powder diffraction patterns of γ and β' cocoa butter formed at different T_p .

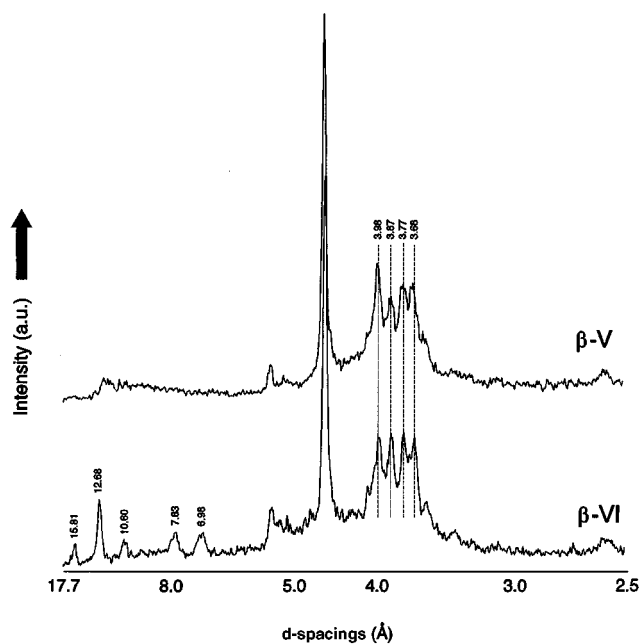


FIG. 3. X-ray powder diffraction patterns of β -V and β -VI cocoa butter: β -V, recorded after 11 d at $T_p = 15^\circ\text{C}$; β -VI, recorded after 4 d at $T_p = 25^\circ\text{C}$. Both samples have been prepared in order to avoid surface roughness.

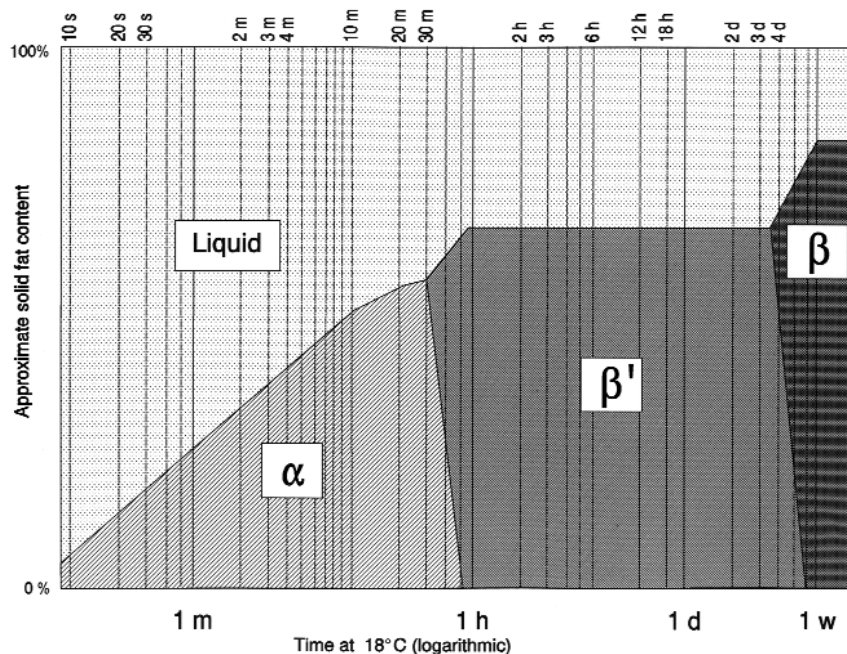


FIG. 4. Qualitative isothermal phase transition of static cocoa butter at 18°C. The fraction of the various solid phases estimated qualitatively based on increased diffraction intensity.

Only small differences can be pointed out in the subcell range. In the group of peaks between 3.6 and 4.0 Å, β V has slightly more intensity on the 4 Å side, whereas β VI has more intensity on the 3.6 Å side. The differences at longer spacings are clearer, since several peaks (e.g., at 12.68 and 6.98 Å, see Fig. 3) from the diffraction pattern of β VI are absent in the pattern of β V.

In Figure 4, it can be seen that caution is needed in choosing the correct period for recording XRD patterns. Phase transitions take quite some time and for a correct XRD pattern, one needs to ensure that only one solid phase is present during the entire recording time.

Isothermal solidification and phase transitions as function of T_p . The results are extensively listed in Table 5 and presented as

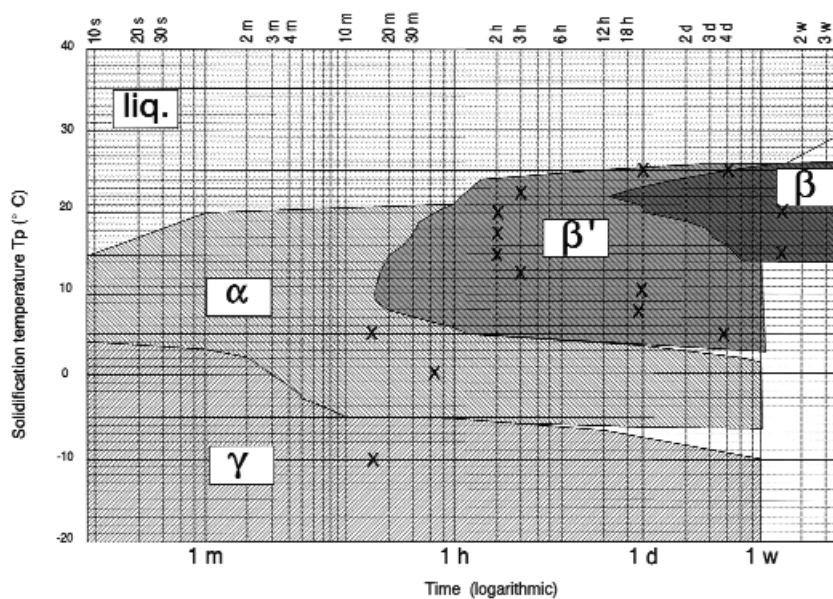


FIG. 5. Isothermal phase transition scheme of static cocoa butter. Solid phase present after isothermal crystallization time at T_p . When at a certain position two or more solid phases are present, only the most stable phase is indicated. Symbols \times indicate from which time at a certain temperature a standard X-ray powder diffraction pattern has been recorded, in order to be sure to measure only one phase. In the blank areas, the phase has not been established, either by experiment or by interpolation.

a phase transition scheme in Figure 5. Changes in the polymorphic state that might have taken place over 10 d after the start of the isothermal stay have not been taken into account. Terms like stable and unstable should be read with this 10-d period in mind.

As shown by Van Malssen *et al.* (13), the initial cocoa butter phase obtained in the solidification process depends heavily on T_p . At $T_p \leq 20^\circ\text{C}$ solidification occurred in a few minutes or even in a few seconds at lower T_p , resulting in either γ or α . At $20 < T_p \leq 27^\circ\text{C}$ solidification slowed down to hours and days, resulting in the β' phase. At $T_p \geq 28^\circ\text{C}$ no sign of solidification was observed.

At $T_p \leq -10^\circ\text{C}$, γ is a stable phase. At $T_p > 10^\circ\text{C}$ γ transformed within a few minutes at least partly into α , which subsequently stayed stable under these conditions. It is remarkable that 50–75% of γ transformed rather quickly into α (in 10 min at most), while it can take one or more days before the

transition is completed, especially at lower T_p . Coincidentally at the same T_p where γ is not the initial phase, that is at $T_p \geq 5^\circ\text{C}$, α is no longer stable but transforms into β' . At $T_p = 5^\circ\text{C}$ the diffraction pattern typical for β' can be observed after approximately 75 min. The β' phase develops slowly and takes up to 6 h before transformation is complete. At higher T_p the development of β' started earlier and completed faster: for example, at $T_p = 10^\circ\text{C}$ the transition from α to β' started after approximately 15 min, and it was completed within 3 h. At higher T_p the transition became faster, but only at $T_p \geq 15^\circ\text{C}$, the β' formation was completed within 1 h. When no significant amount of α was formed initially ($T_p > 20^\circ\text{C}$), it took much more time to initiate β' formation. At $T_p = 21^\circ\text{C}$ it took 60 min before some β' was present and at $T_p = 26^\circ\text{C}$ the first sign of crystallization was observed only after 60 h.

At low T_p ($T_p < 10^\circ\text{C}$) the β' polymorph did not transform

TABLE 5
Solidification in Minutes (m), Hours (h) or Days (d) as Function of Preset Temperatures T_p ($^\circ\text{C}$)^a

T_p	Experiment time	γ	α	β'	β	d
≥ 27	240 h			>10 d	>10 d	
26	240 h			60 h	120 h	8 d
25	168 h			8 h	24 h	4 d
24	192 h			1.5 h	6.0 h	38 h
23	192 h			1.5 h	4.5 h	22 h
22	96 h			1.5 h	3.0 h	13 h
21	168 h		0 m	30 m ^b	60 m	90 m
20	168 h		0 m	20 m	50 m	65 m
19	72 h		0 m	25 m	30 m	40 m
18	144 h		0 m	20 m	30 m	55 m
17	168 h		0 m	25 m	30 m	55 m
16	144 h		0 m	20 m	25 m	50 m
15	96 h		0 m	20 m	20 m	50 m
14	240 h		0 m	20 m	25 m	55 m
13	5 h		0 m	20 m	18 m	80 m
12	5 h		0 m	20 m	18 m	95 m
11	5 h		0 m	20 m	18 m	126 m
10	120 h		0 m	10 m	15 m	3 h
9	1 h		0 m	10 m	15 m	>60 m ^c
8	24 h		0 m	10 m	20 m	4 h
7	24 h		0 m	8 m	30 m	5 h
6	24 h		0 m	8 m	60 m	10 h
5	166 h		0 m	8 m	75 m	6 h
4	1 h	0 m	3 m ^b	0 m	8 m	
3	1 h	0 m	3 m	3 m	5 m	
2	1 h	0 m	3 m	3 m	5 m	
1	1 h	0 m	3 m	3 m	5 m	
0	96 h	0 m	3 m	3 m	10 m	
-1	1 h	0 m	2 m	5 m	10 m	
-2	1 h	0 m	2 m	5 m	20 m	
-3	1 h	0 m	2 m	5 m	>1 h ^c	
-4	1 h	0 m	2 m	5 m	>1 h ^c	
-5	24 h	0 m	2 m	10 m		
-10	120 h	0 m	2 m			
-15	27 h	0 m	2 m			
-20	24 h	0 m	2 m			

^aFor each phase has been indicated in what period, relative to the moment T_p has been reached, it is formed. The first time denotes start of the formation, the second the completion. ">" in the starting column means that the experiment showed no sign of any crystallization.

^bOnly weak diffraction observed; small amount of this phase developed.

^cThis time corresponds with the duration of the experiment.

^dTransition almost completed. Very slow continuation until time within parentheses.

into another phase. At higher T_p ($T_p \geq 14^\circ\text{C}$) β' transformed to the β phase only; during this study no isothermal phase transition from one β' to another β' was observed. The transformation from β' to β is a slow starting process. At $T_p = 14^\circ\text{C}$ the first signs of β were observed after 5 d and after 10 d still a significant amount of β' was present. At higher T_p the development of β started earlier, the earliest at $T_p = 22^\circ\text{C}$, when the first sign of the β phase was observed after 13 h. At this temperature, β formation was also the quickest; the phase transition was almost completed within 26 h from the start of the experiment. At $T_p > 22^\circ\text{C}$ the phase transition from β' to β started later: at $T_p = 26^\circ\text{C}$ the first sign of β was seen only after 8 d. Figure 5 qualitatively illustrates how the fractions of the various polymorphs vary as function of time when $T_p = 18^\circ\text{C}$, liquid cocoa butter transforms to α and, via the β' phase, finally into β .

After 10 d at $T_p = 27.0^\circ\text{C}$ the sample is a cloudy fluid, without any significant X-ray diffraction. At $T_p \geq 28.0^\circ\text{C}$ no solidification has been observed during the first 10 d; the fluid remains clear.

Melting ranges of cocoa butter phases. Various melting ranges could be observed. They are listed in Table 3. The melting characteristics for γ had to be estimated, since this melting, or disappearing, is accompanied by a simultaneous increase of the amount of α . For the other phases, the melting characteristics could be calculated straight on.

A single melting range has been observed for α , while each investigated β' showed a different melting range. This can be seen in Figure 6, in which the disappearance of the diffracted intensity as a function of temperature is illustrated for four different parts of the β' phase. Finally, the two investigated forms of β showed melting ranges differing by approximately 1°C .

DISCUSSION

The present investigation of the isothermal behavior of static cocoa butter confirms the conclusion of our earlier work (13) that γ , α , and β' phases can crystallize directly from the melt and that β' formation *via* transformation from α is much quicker than directly from the melt, as can be concluded from Figure 4. However, two β' -phases, V and VI, are obtained *via* a phase transformation from the β' phase only. Therefore, the overall phase-transition scheme as presented by Van Malssen *et al.* (15) should be adapted. The renewed scheme is presented in Figure 7. Besides the isothermal phase transitions, it includes melting, solidification, and phase transitions under non-isothermal conditions as known from literature and additional experiments.

The standard XRD measurements revealed single patterns for γ and α , two patterns for β , while a range of patterns for β' has been found. These varieties are indicated in Figure 7. Unlike Wille and Lutton (1) and Chapman *et al.* (4) no reliable long spacings were observed. This was probably caused by the use of the specific XRD equipment, that is not optimal to record long spacings in the chosen experimental conditions.

Least stable phases γ and α . The γ phase of cocoa butter is

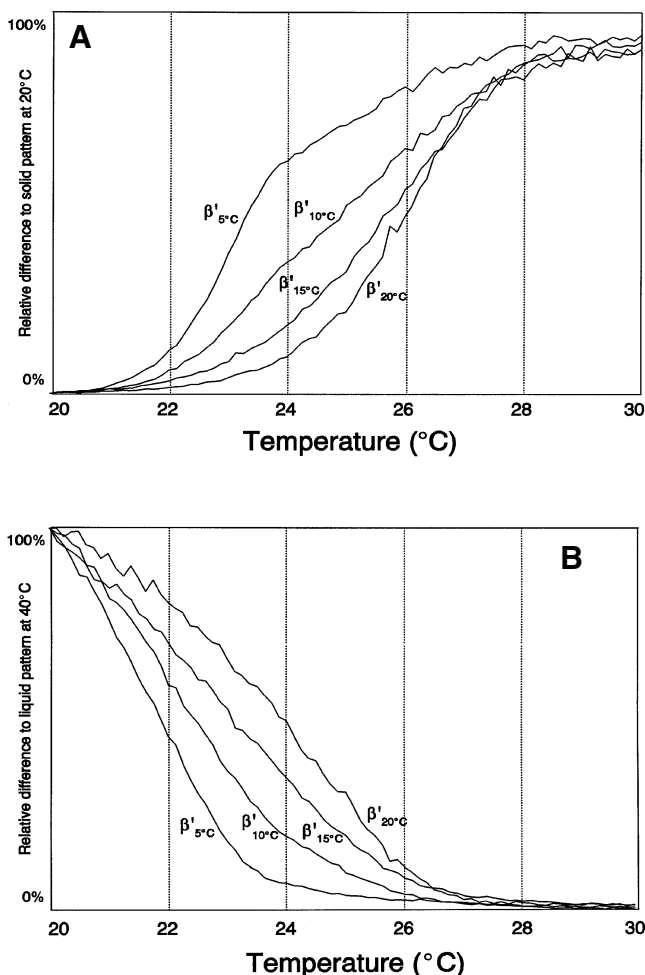


FIG. 6. Differences in melting behavior of β' s formed at $T_p = 5, 10, 15,$ and 20°C . (A) differences of diffraction pattern relative to solid at 20°C ($\text{DDF}(j,1)$) presenting details of the start of the melting ranges; (B) differences of diffraction pattern relative to liquid at 40°C ($\text{DDF}(j,m)$) presenting details of the end of the melting range.

by far the least stable of all encountered solid phases. Only at $T_p \leq -10^\circ\text{C}$, does it stay unchanged for at least 10 days. At higher T_p , it transforms within a short time into α . This observation, combined with the quick development of α at $T_p \leq 10^\circ\text{C}$, makes it difficult to determine the exact melting range of γ . It could not be established experimentally whether the α formation is preceded by a liquid intermediate phase. Nevertheless, the melting or disappearing range of γ could be established to be approximately -8 to $+5^\circ\text{C}$.

These results provide an explanation for the discrepancy between the γ melting point of roughly 0°C obtained in this work, our preliminary work (13), and reported by Riener (5), and a melting point of approximately 17°C , as reported in most other literature (16). The latter value corresponds with the first observed peak in a DSC measurement if started at 0°C . The assignment to the γ phase is then based on the XRD pattern of the phase formed at 5 – 10°C . However, tr-XRD experiments show that there is no doubt that the γ phase observed at $T_p = 0^\circ\text{C}$ and the β' phase observed at $T_p = 5^\circ\text{C}$ are different phases, in spite of having remarkably similar diffraction patterns. Tr-XRD

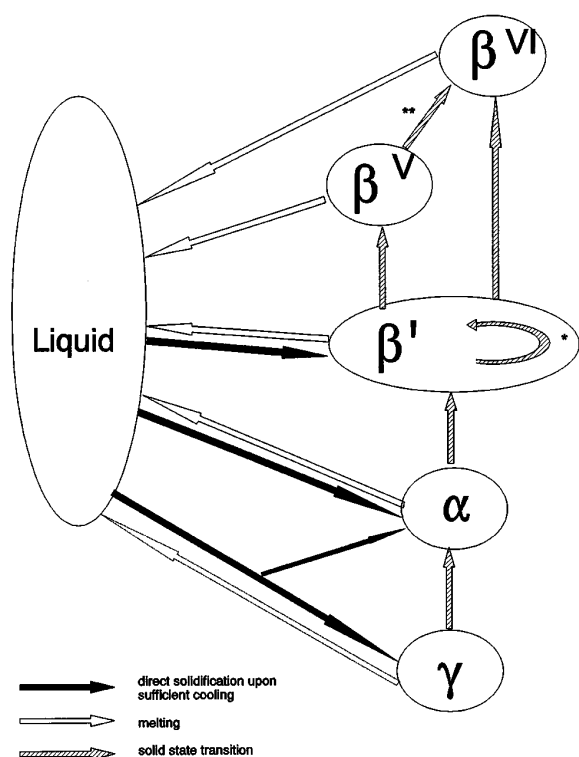


FIG. 7. Cocoa butter phase transition scheme. Both isothermal and non-isothermal phase transitions. *This non-isothermal transition has been reported in literature (1) and has been observed in our experiments (van Langevelde, A.J., and K.F. van Malssen, unpublished data). ** This transition has been reported in the literature (1).

shows that γ always transforms into α and α into β' . Thus, solid cocoa butter at 7°C , having the same XRD-pattern as solid cocoa butter formed at -5°C , will not transform into α . Only with time-resolved observations of the diffraction patterns did it become certain that γ and β' are both unique phases.

The α phase is formed easily, either *via* a transformation from the unstable γ or directly from the melt. The ease of this formation was emphasized in the previous study (13) by the observation that some α is formed before the start of γ formation even when the liquid cocoa butter is cooled with a rate of $360^\circ\text{C}/\text{min}$. The α phase is much more stable than γ , but not stable enough to prevent its transformation into β' within an hour or less, at temperatures above 6°C .

Metastable β' phase range. There are various reasons to consider β' cocoa butter to exist as a phase range rather than as separate (sub)phases: (i) Seven different and apparently continuously varying β' XRD-patterns have been observed in this study. (ii) Melting ranges investigated at four points from the β' range show different melting characteristics. (iii) Using DSC, Schlichter-Aronhime *et al.* (11) found more observed DSC-melting peaks for β' phases than the two corresponding with Wille and Lutton's I to VI cocoa butter scheme. (iv) There is a wide variety in β' melting points in literature [Table 1, Manning and Dimick (16)]. (v) Various authors, for example, Wille and Lutton (1) distinguished six melting points for cocoa butter solid phases, even though the α melting point was incorrectly assigned to the γ phase, of which the melting point was left out.

When we look at the XRD patterns in detail, a smooth shift of peaks can be observed. This implies that the differences are gradual and apparently continuous, making it impossible to single out separate phases. One might be tempted to explain this variety by assuming the existence of two basic patterns, which in various combinations would result in the remaining five patterns. However, no pair of patterns could give this result, neither could such a pair be derived from the observed patterns. An explanation in terms of an anisotropic expanding of the subcell as function of temperature is also unlikely to be correct. This would not agree with the variation in observed melting ranges and with the earlier results (13), that upon melting diffraction patterns only change in intensity and not in peak width and peak position. In contrast, it is more likely that β' exists as a phase range than as a set of individual phases. A phase range resulting in a wide variety of β' appearances could very well explain the variety of melting and diffraction characteristics of β' , and the six melting points (exclusive the γ melting point) reported in literature. It also throws new light on the everlasting discussion about the various β' phases.

The physical basis of a β' phase range depends eventually on cocoa butter being a mixture of TAG, and solid cocoa butter existing as a conglomerate of crystallites with individual TAG composition. When the distribution of crystallites over the various possible TAG compositions is considered, different cooling rates or crystallization temperatures would influence this distribution. This results in a different distribution of individual melting and diffraction characteristics and thus a different overall melting behavior and diffraction pattern. Since the distribution of TAG over the individual crystallites can vary continuously, the resulting characteristics will also.

Therefore, due to the nature of cocoa butter, it is more likely that β' exists as a phase range than as a set of individual phases, independent from the question of whether different β' chain packings are possible.

Stable β phases. The β phase is formed *via* a phase transformation from β' . Direct β -crystallization occurs only when the liquid is not memory-free and β -crystallization is induced by the memory effect (15). When liquid cocoa butter is memory-free, it will not crystallize directly into β , at least not within 10 d. In the current work, two types of the β phase have been observed. The diffraction patterns correspond to Wille and Lutton's phases V and VI (1). It is remarkable that not only β -V but also β -VI can be formed directly from β' . Both results are in contrast with the remarks of Schlichter-Aronhime and Garti (17) who noted that β -V can be formed directly from the melt and that β -VI can be formed only from the transformation of β -V.

The observation of two different β phases may seem to conflict with earlier results (13), where only β -VI has been found, despite four different preparation methods (taken from a 12-yr-old stock, crystallized at 25°C from liquid *via* β' to β , recrystallized at 25°C *via* a strong memory effect and recrystallized at 25°C *via* a long-term memory effect). At 25°C β was already formed as the result of a phase transition from β' and, according to literature (17), form VI would only result from β -V to β -VI phase transition. Therefore, no β' to β phase

transition at lower temperatures was investigated. However, the β -V is only formed as the result of a phase transition from β' at temperatures below 25°C.

It is appropriate to notice that the complete β formation as the result of a memory effect (15), within one-half hour, is much faster than the fastest β formation from β' . At 22°C, the latter starts after 13 h and is completed after 26 h.

Individual phase behavior. It is possible to explain the observed phase behavior. It is known from previous work (12–15) that: (i) the average crystallite size does not change during melting; (ii) the average lateral chain packing does not change during melting; (iii) the melting ranges of β cocoa butter are a function of the composition of the cocoa butter; (iv) the strength of the β memory effect is a function of the composition of the cocoa butter.

In this study, it was found that: (i) at temperatures of approximately –5°C only part of the γ phase transforms quickly into α , while another part transforms very slowly from γ to α ; (ii) β' exists as a phase range.

In the memory-effect study (15) it has been proposed that solid cocoa butter should be considered a conglomerate of individual crystallites, each having a sharp melting point that depends on the individual TAG-composition (see also (18,19)). More precisely, each individual crystallite is expected to have an individual melting range, while the total melting trajectory of the cocoa butter phase is the integral representation of all these individual melting ranges. Such a consideration explains (i) the long melting trajectories for each of the solid states; (ii) why the solid-state phase-transition times under static conditions exceed to such an extent the corresponding transition times under dynamic conditions as known from manufacturing practice. Under static conditions, each crystallite has to reach the transition state individually and attain the more stable conformation using structure information from directly neighboring crystallites only. In dynamic systems crystallites in a less stable phase will meet crystallites that are already in the more stable phase regularly, thus coming into contact with the latter's structure information more often; (iii) the memory effect: during the quasi-liquid stage, when the cocoa butter is above the melting point but below 39°C, a few β crystallites, with high melting points, remain randomly distributed in the liquid. They provide structural information necessary for a quick β re-formation when the liquid is cooled below the melting point; (iv) depending upon individual composition, only a part of the crystallites will transform quickly from γ into α at temperatures just below zero.

It is clear that research on cocoa butter phase behavior is far from finished. The work is continuing in order to present a more detailed assessment of the β' phase range and the individual crystallite concept.

ACKNOWLEDGMENT

These investigations are supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Technology Foundation (STW). The authors thank the members of the User Committee for fruitful discussion and structural interest.

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[Received November 20, 1997; accepted February 28, 1999].