

Real-Time X-Ray Powder Diffraction Investigations on Cocoa Butter. I. Temperature-Dependent Crystallization Behavior

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ABSTRACT: The crystallization behavior of cocoa butter has been investigated by means of real-time X-ray powder diffraction. Two procedures have been followed: cooling from 60°C at a constant rate until maximum solidification has taken place; and cooling from 60°C in 2 min to a constant solidification temperature. It appears that all polymorphic forms of cocoa butter, with the exception of the β form, can be formed from liquid. The solidification temperature appears to be the most important crystallization parameter.

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KEY WORDS: Cocoa butter, crystallization, phase transitions, polymorphism, X-ray powder diffraction.

Crystallization of a complex fat mixture, such as cocoa butter, depends on a range of parameters, such as cooling rate, solidification temperature, degree and nature of seeding (presence of crystallization nuclei), mechanical treatment (stirring, crunching) and composition of the cocoa butter. To date, crystallization has been investigated mainly by means of differential scanning calorimetry (1–3), or with the diffraction pattern vs. temperature camera, constructed by Abrahamsson after the original design of Stenhagen (4–7). X-ray powder diffraction is an appropriate tool to study cocoa butter for the following reasons: (i) the powder pattern itself can be used to identify polymorphic phases unambiguously; all polymorphs have a characteristic pattern in the range of 3.0–6.0 Å. (ii) Successive powder patterns, e.g., as a function of temperature or time, may reveal details of the crystallization, melting and phase transition processes. (iii) The total diffracted intensity is related to the amount of crystalline material in the sample.

Apart from the crystallization temperature, the cooling rate has also been recognized as important for the crystallization of the polymorphic forms of cocoa butter, e.g., by Schlichter Aronhime *et al.* (8). Unfortunately, however, in many rele-

vant papers, the cooling rates are specified only in a qualitative way, e.g., as being slow, quick or rapid, which makes it difficult to compare the often conflicting experimental results.

In our laboratory, a real-time X-ray powder diffractometer has been constructed (9,10), which is particularly suited to carry out temperature-dependent crystallization experiments. In this paper, experiments with this equipment to investigate the static, or motionless, crystallization behavior of cocoa butter as a function of crystallization temperature and cooling rate are described.

MATERIALS AND METHODS

Samples and sample preparation. Two West-African cocoa butters, from Ivory Coast (harvested November 1980) and from Equatorial Guinea (harvested February 1981), were obtained from Cacao de Zaan (Koog aan de Zaan, The Netherlands). The characteristics of these samples, which are listed in Table 1, have been established at the laboratory of Cacao

TABLE 1
Characteristics of the Cocoa Butter Samples^a

	Fatty acid content (%)			TAG content(%)	
	EG	IC		EG	IC
16:0	21.72	22.40	POS	34.3	36.6
18:0	31.17	31.84	SOS	22.6	23.9
20:0	0.91	1.11	POP	13.0	14.0
18:1	31.54	30.73	SOO	6.7	5.3
18:2	3.01	2.46	POO	5.1	4.0
others	0.83	0.46	PLS	3.5	3.0
			SLS	2.3	2.0
IV ^b	37.0	34.7	SOA	1.4	1.7
Free			PLP	1.3	1.2
acids(%)	1.20	1.45	POA	1.0	1.3
MG ^c (%)	0.1	0.1	SOL	0.6	0.5
DG ^d (%)	1.5	1.3	Others	7.6	5.7

^aEG = cocoa butter from Equatorial Guinea; IC = cocoa butter from Ivory Coast. Samples have been characterized at the laboratory of Cacao De Zaan, The Netherlands. The triacylglycerol (TAG) composition is calculated from the total fatty acid composition and the fatty acid at the 2-position, as described by Coleman (Ref. 11). ^bIodine value. ^cMonoglycerides. ^dDiglycerides.

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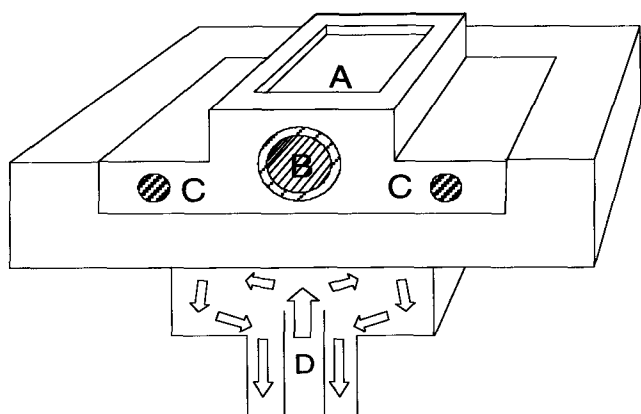


FIG. 1. Sample holder. (A) Space for sample, (B) position of Pt-100 temperature sensor, (C) heating connections, (D) coolant flow.

De Zaan. The triacylglycerol (TAG) composition is calculated from the total fatty acid composition and the fatty acid composition at the 2-position, as described by Coleman (11). Samples were prepared by pressing cocoa butter into the sample holder (Fig. 1), resulting in a sample size of $10 \times 15 \times 1$ mm with a flat surface. We ascertained, by preparing samples in various ways, that the diffraction characteristics are independent of the method of filling the sample holder.

Real-time X-ray powder diffractometer. All measurements were performed with the real-time X-ray powder diffractometer (9), whose instrumental settings are listed in Table 2. A diffraction range of $15^\circ 2\theta$, resulting in measured d-spacings from 3.0 to 6.1 Å, is recorded simultaneously. The recording time can be set from 0.02 s. The sample is placed in a vacuum, temperature-controlled camera. The temperature in the sample holder (Fig. 1) is controlled via a Pt-100 element, which measures the temperature just below the sample, while the temperature is regulated by a combination of heating from the side and cooling from the bottom. By computer control, the temperature is regulated within 0.1°C from preset values. Recording of diffraction patterns does not interfere with temperature control.

Cocoa butter nomenclature. Different nomenclatures are used to name the solid phases of cocoa butter. Commonly,

they are identified by means of characteristic X-ray diffraction peaks. The specific packing of the fatty acid hydrocarbon chains leads to strong and characteristic short spacings in the diffraction pattern from which a crystallographic subcell can be derived. The subcell concept has been reviewed by Larsson (12) and dealt with in detail by Abrahamsson (13) and De Jong (14). In the classification of TAG polymorphs, three subcell types are used: the hexagonal subcell H ; the orthorhombic subcell O_\perp , and the triclinic subcell T_\parallel .

The nomenclature of TAG polymorphs is based upon the work of Lutton (15). Polymorphs are divided into three groups: α , β' and β . Their characteristics are listed in Table 3. For pure TAG, which have several polymorphs with the same subcell, but different chain-length multiplicity, the latter is used for further classification. It is referred to by a number, e.g., β -2 or β -3. If all polymorphs are still not described uniquely, an index number is used, denoting the forms in order of decreasing melting point, e.g., β'_1 -2, β'_2 -2 and β'_3 -2.

In principle, the TAG-polymorph nomenclature, as described in Table 3, can be used to describe the polymorphic forms of cocoa butter. However, an alternative system, more "cocoa-butter-specific" and used by many authors, has been introduced by Wille and Lutton (16). The phases are numbered I (lowest-melting form) to VI (highest-melting form). Vaeck (17) uses γ for the lowest-melting form, but he assumes that only four real polymorphic forms exist. The characteristics of the cocoa butter phases, as reported in the literature, are summarized in Table 4. In some papers, γ is referred to as sub- α because its melting point is below that of α . In our study, the nomenclature of Vaeck will be used, supplemented with Wille and Lutton's I-VI system wherever it is necessary for a proper discussion.

Analysis of real-time diffraction data. Each powder diffraction pattern, recorded in the interval 3.0–6.1 Å, consists of channel intensity values $I(j,i)$, with j denoting the pattern number and i ($= 1$ –1024) the channel number. A set of m diffraction patterns with identical d-spacing ranges but successively recorded, thus being a function of time and/or temperature, is referred to as a dynamic diffraction measurement. The difference between two diffraction patterns can be attributed to either noise or systematic change. Obviously, the latter contains the relevant information to be extracted. The difference $\Delta(j,k)$ between two patterns, j and k , is defined as the overall squared difference of the corresponding channel intensities in the two patterns,

TABLE 2
Instrumental Parameters

Radiation	Monochromated Cu K α
Wavelength	1.5418 Å
Voltage	40 kV
Current	20 mA
2θ Range	14.6 – 29.6°
Corresponding d-spacings	3.0–6.1 Å
Divergence α	0.35°
Sample angle Ψ	8.5°
Detector angle ϕ	22.1°
Sample distance X	63 mm
Detector distance R	101 mm
2θ -Calibration	Potassium iodide (25.208° , 21.765°)
Sample size	$1 \times 10 \times 15$ mm

TABLE 3
Nomenclature of Triacylglycerol Polymorphs

Polymorph name	Strongest X-ray short spacings(Å)	Associated subcell	Cross-sectional chain area (Å ²)
α	4.15	Hexagonal H	20
β'	3.8, 4.2 or 3.71, 3.97, 4.27	Orthorhombic O_\perp	18.5
β	4.6	Triclinic T_\parallel	18.5

TABLE 4
Cocoa Butter Solid Phases

Phase	Melting points (°C)				TAG Symbol	Short spacings (Å)		Type ^b
	Reference							
	16	5	7	10 ^a				
I	17.3		2 ^c	−5−+5	β ₃	4.19	3.7	γ
II	23.3		16 ^c	17–22	α	4.24		α
III	25.5				β ₂ ′-2	4.25	3.86	β′
			25 ^c	20–27				
IV	27.5	25.6			β ₁ ′-2	4.35	4.15	
V	33.8	30.8			β ₂ ′-3	4.58		β
			32	29–34				
VI	36.3	32.3			β ₁ ′-3	4.59		

^aMelting ranges. ^bReference 17. ^cDisappearance of polymorph by melting or phase transition.

$$\Delta(j,k) = \sum_{i=p}^q [I(j,i) - I(k,i)]^2 \quad [1]$$

In practice, only a relevant channel subset p – q , in which the systematic changes occur, has to be considered, thus ignoring the remaining channels that involve mostly noise.

From the initial analyses, it turned out that the use of squared intensity differences, as in Equation 1, leads to a better recognition of systematic differences between patterns than do the normal intensity differences $I(j,i) - I(k,i)$. Moreover, this approach overcomes the problem that simultaneously occurring intensity increases and decreases in different parts of the pattern may cancel out in a final summation.

Maxima of systematic change in a dynamic diffraction measurement can be located easily by analyzing consecutive $\Delta(j,k)$ values as function of j . Such series will be referred to as dynamic difference functions (DDF). Each DDF is a function of both j and a particular choice of k .

Various $\text{DDF}(j,k)$ turn out to be useful. Besides $\text{DDF}(j,j-1)$ which expresses the difference between two subsequent patterns, $\text{DDF}(j,1)$ and $\text{DDF}(j,m)$ are also commonly used in the analyses, being difference functions with respect to the first and last pattern, respectively. Because the changes between patterns are on a relative scale, for each particular choice of k , DDF is normalized so that the largest observed $\Delta(j,k)$ in the series is scaled to 100 (on the scale 0–100).

Determination of solidification temperature (range). Systematic analysis of DDF is expected to reveal the stage(s) during which a significant change in the powder diffraction pattern takes place. This analysis leads to the identification of the cocoa butter polymorph(s) and the corresponding observed solidification range(s). If only a single polymorph is encountered in the complete diffraction pattern series, its solidification behavior can be described unambiguously. The temperature T_m that corresponds with the maximum in $\text{DDF}(j,j-1)$ is taken as the temperature of maximum solidification. The start of the solidification at temperature T_s is defined as corresponding with the threshold level at 10% of the maximum in $\text{DDF}(j,j-1)$. Finally, the solidification is said to be finished at temperature T_e , once $\text{DDF}(j,m)$ is below 1%.

If two different polymorphs are involved, the end of the first solidification stage may overlap with the start of the second; thus the first stage is said to be ended if the $\text{DDF}(j,j-1)$ is below 10%. Obviously, the individual diffraction patterns are still indispensable for a correct interpretation of the complete measurement.

Solidification as function of cooling rate. Motionless samples were heated to 60°C for 60 s, subsequently cooled to 44°C in 60 s, and finally cooled with a constant cooling rate R_c to a final temperature T_f . R_c was chosen from 6°/s to 1°/h. Starting from 44°C, the experiments were divided into equally spaced intervals of I_t s each. At the start of each interval, an X-ray pattern was recorded with an exposure time of E_t s. Values for R_c , T_f , I_t and E_t are presented in Table 5, together with the experimental results. The polymorphic forms obtained were established from the final diffraction patterns.

Solidification as function of final temperature. Motionless samples were heated to 60°C for 60 s and cooled in 120 s to a preset solidification temperature (T_p). T_p was chosen at 0.0, 2.0, 4.0, ..., 28.0°C. At T_p below 17°C, the samples were kept isothermally for 1 h. At $T_p = 18.0, 20.0$, and 22.0°C, the samples were kept isothermally for 95 min. At $T_p = 24.0$ and 26.0°C, the samples were kept isothermally for 20 h. At $T_p = 28.0$ °C, the sample was kept isothermally for 10 d. Starting from the moment the samples were cooled to T_p , the experiments were divided into equally spaced intervals of I_t s each. At the start of each interval, an X-ray pattern was recorded with an exposure time of E_t s. Values for T_p , T_f , I_t , E_t , and the experimental results are presented in Table 6.

Melting of phase γ , α and β' . The solid sample obtained after cooling from 60 to −150°C at a cooling rate of 6°C/s was melted by heating at 2°C/min to determine the melting ranges of γ and α . Diffraction was measured constantly, with 15 s exposure time per diffraction pattern. The solid sample, obtained by solidification during 20 h at 18.0°C was heated at a rate of 1°C/min to 35.0°C to determine whether the β' -phase obtained is a single phase or a mixture of phases. X-ray diffraction was constantly recorded at an exposure time of 30 s per pattern.

β -Crystallization. A motionless sample was heated to 60°C for 60 s, cooled at a rate of 3.5°C/min to 25.0°C, and kept at this temperature for 60 h. A diffraction pattern with an exposure time of 120 s was recorded during the first 2 min of every hour.

RESULTS

Solidification as function of cooling rate. The results of these experiments are listed in Table 5. Among the final diffraction patterns, four different patterns have been observed (Fig. 2). Solidification with $R_c < 0.25$ °C/min results in β' -crystallization near 17°C. Solidification with R_c between 0.25°C/min and 1°C/min results in α -crystallization only. Solidification with $R_c \geq 2$ °C/min results in α -crystallization near 12°C, followed by (some) γ -crystallization near 3°C.

TABLE 5
Solidification as Function of Cooling Rate^a

<i>Rc</i> °C/min	<i>T_f</i> °C	<i>I_t^c</i> s	<i>E_t^c</i> s	T-range 1 ^b			T-range 2 ^b			Observed solid phase in T-range number			
				<i>T_s</i> °C	<i>T_m</i> °C	<i>T_e</i> °C	<i>T_s</i> °C	<i>T_m</i> °C	<i>T_e</i> °C	β	β′	α	γ
0.0166	0	3600	120	19	18	16		—		—	1	—	—
0.033	0	1800	60	19	18	16		—		—	1	—	—
0.10	0	600	60	19	17	13		—		—	1	—	—
0.25	−10	240	30	20	16	12		—		—	1	1	—
0.50	−10	120	30	19	15	9		—		—	—	1	—
1	−20	30	30	15	13	11		—		—	—	1	—
2	−20	15	15	15	13	11	(4	2	0)	—	—	1	(2)
4	−20	15	15	16	13	10	7	4	0	—	—	1	2
8	−20	7.5	7.5	16	13	11	6	4	0	—	—	1	2
12	−20	5	5	16	13	10	6	4	1	—	—	1	2
16	−30	5	5	17	12	10	5	3	−1	—	—	1	2
20	−30	4.3	4.3	15	10	9	5	3	0	—	—	1	2
30	−30	3	3	13	10	7	3	2	−1	—	—	1	2
360	−180	0.5	0.5	<i>d</i>			<i>d</i>			—	—	1	2

^aObserved solidification-temperature ranges of cocoa butter while cooling from 44°C to final temperature *T_f* with a cooling rate *Rc*.

^b*T_s* = start of solidification; *T_m* = maximum solidification speed; *T_e* = (almost) completed solidification.

^cEach solidification process has been divided into equally spaced intervals of *I_t* s. At the start of each interval, an X-ray pattern was recorded with an exposure time of *E_t* s.

^dTemperature ranges not determined exactly.

In the case of cooling with liquid nitrogen (*Rc* at 6°C/s, Fig. 3), the solidification period has not been indicated; due to the sample holder design (Fig. 1) and the fast cooling, it is likely that the recorded temperature is lower than the actual temperature of the sample. The cooling rate itself could be determined accurately, being constant over a large temperature range. All of the relevant diffraction patterns have been recorded during this period of constant cooling.

Solidification as function of final temperature. The results are listed in Table 6. The sample kept at 28.0°C was not solidified after 10 d, except for a thin film on top of the sample. When solidification takes place at 24.0 or 26.0°C, a very slow crystallization behavior is observed: β' develops without any indication of α-crystallites. It takes several hours before crystallization starts.

At 22.0°C, a weak initial 4.2 Å α-peak can be observed. Its intensity increases slowly in the next 60 min. Peaks then arise at 3.9 and 4.4 Å, while the peak at 4.2 Å also increases, as a result of the formation of β'. At 20.0°C, solidification starts with the formation of α-crystallites, although the intensity of the 4.2 Å α-peak barely increases in time. After 30 min, diffraction peaks develop at 3.9 and 4.4 Å, while the peak intensity at 4.2 Å also increases, as a result of β'-crystallization.

At 18.0°C, the formation of α-crystallites can be observed within 5 min, as shown in Figure 4, by the increase of the characteristic peak at 4.2 Å in the next 20 min. Then, peaks at 3.9 and 4.35 Å increase, indicating the formation of β'-crystallites. In the meantime, the amorphous diffraction decreases further. At the position of the 4.2 Å β'-peak, no increase of intensity can be observed. This can be explained by the trans-

TABLE 6
Solidification as Function of Preset Temperatures *T_p*

T _p °C	I _t ^b s	E _t ^b s	Time range 1 ^a			Time range 2 ^a			Observed solid phase in range number			
			t _s	t _m	t _e	t _s	t _m	t _e	β	β'	α	γ
28	3600	40		—			—		—	—	—	—
26	3600	40	4 h	9 h	16 h		—		—	1	—	—
24	3600	40	4 h	5 h	5 h		—		—	1	—	—
22	300	30	0 min	5 min	70 min	70 min	75 min	>95 min	—	2	1 ^c	—
20	300	30	0 min	5 min	5 min	30 min	40 min	65 min	—	2	1 ^c	—
18	300	30	0 min	5 min	20 min	20 min	30 min	65 min	—	2	1 ^c	—

^aAll time ranges listed relate to the start of the isothermal period, with *t_s* denoting the start of a solidifying phase, *t_m* the moment of its maximum solidification speed, and *t_e* its (almost) complete solidification.

^bAs in Table 5.

^cPhase first present, later disappeared.

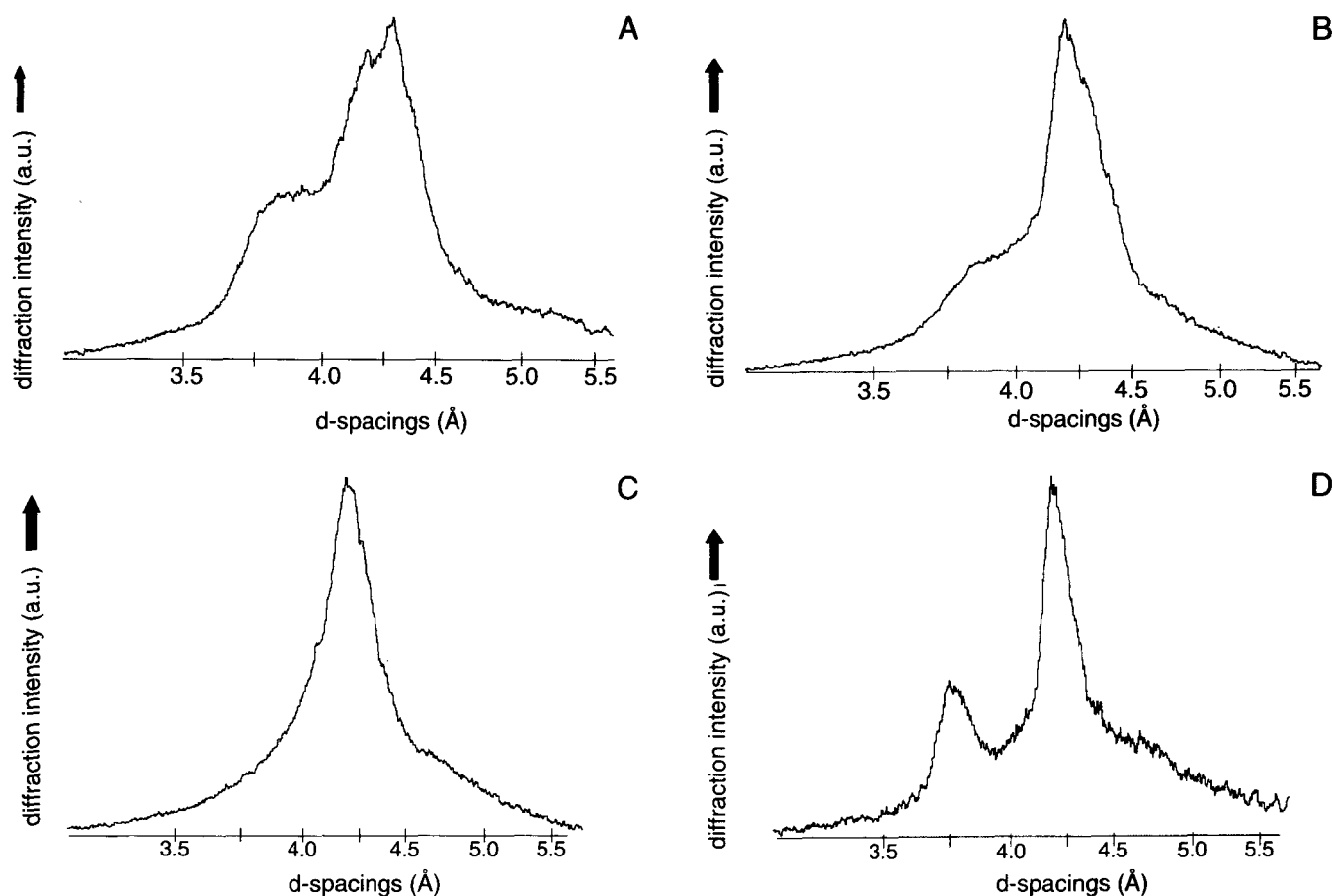


FIG. 2. X-ray diffraction patterns obtained after cooling liquid cocoa butter from 60°C with a constant cooling rate R_c until maximum solidification was obtained. (A) The diffraction pattern of β' obtained with R_c at 2.0°C/h; (B) the diffraction pattern of a mixture of α and β' , obtained with R_c at 0.25°C/min; (C) the diffraction pattern of pure α obtained with R_c at 1.0°C/min; (D) the diffraction pattern of γ obtained with R_c at 20.0°C/min. Part of the 4.2 Å peak results from α -crystallites.

formation of α -crystallites into β' -crystallites, which results in a decrease of the 4.2 Å α -peak intensity that equals the increase of the 4.2 Å β' -peak intensity.

Samples kept at 6.0–16.0°C showed a clear α -diffraction peak from the moment the isothermal period started. The initial intensity of this peak was temperature-dependent: highest at 6.0°C and lowest at 16.0°C. In all cases, the intensity of the α -peak increased until it disappeared in favor of β' -diffraction during the rest of the 60 min in which the isothermal stage was monitored. The transition rate was also temperature-dependent: highest at 16.0°C and lowest at 6.0°C. Samples kept at 0.0, 2.0, and 4.0°C showed immediately typical γ -diffraction patterns, which changed to α -diffraction patterns within 1 h. At 0.0°C, not all γ -diffraction disappeared, while at 4.0°C, traces of γ -diffraction could be observed only in the first minutes.

Melting of γ , α , and β' . Melting of the cocoa butter sample, cooled at $R_c = 6^\circ\text{C/s}$, revealed disappearance of the γ -diffraction between -5 and $+5^\circ\text{C}$. The α -diffraction disappeared between 17 and 22°C. Melting of the β' -cocoa butter, resulting from solidification at 18.0°C, made the diffraction intensity decrease simultaneously over the whole pattern, until at

27.5°C, all peaks had disappeared completely (Fig. 5). This indicates that the observed β' was a single phase.

β -Crystallization. The formation of β is illustrated in Figure 6. At first, β' -crystallization took place, starting after several hours. Then, after 35 h total time, β -characteristic diffraction peaks started to increase for the next 10 h, while the β' -peaks decreased simultaneously. After 60 h, the cocoa butter was removed from the sample holder, and the sample was reprepared with the same butter. This was done because the sample showed some texture (preferred orientation). The diffraction pattern of this reprepared sample showed a dominant presence of β , while β' had disappeared.

DISCUSSION

These results show clearly that the phase in which cocoa butter solidifies is determined mainly by the solidification temperature, provided this temperature is arrived at quickly enough to prevent the formation of higher-melting polymorphs. The results also show that the phases γ , α and β' can crystallize directly from the melt, whereas the β -phase is obtained only *via* a phase transformation from the β' -phase.

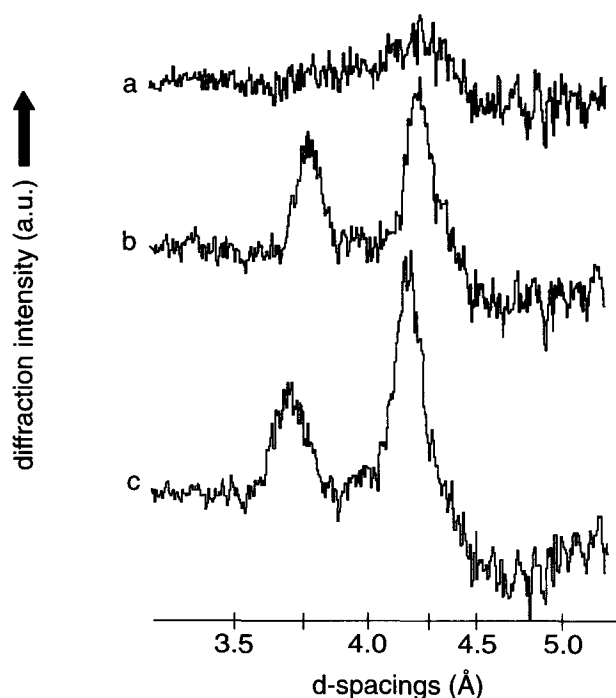


FIG. 3. Solidification during cooling with liquid N_2 at a cooling rate of 6°C/s . Three diffraction patterns, marked a, b and c, have been reproduced in the figure, recorded at temperatures around 10, -20 , and -90°C , respectively. The graphs show the difference between the recorded pattern and the diffraction pattern of liquid cocoa butter.

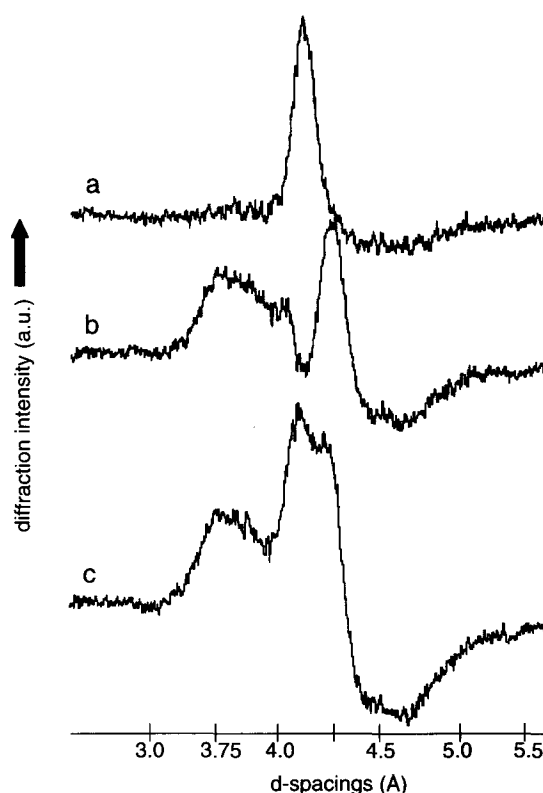


FIG. 4. X-ray diffraction patterns after solidification at a constant temperature of 18°C after cooling from 60°C in 2 min. Pattern a is recorded after 5 min at 18°C and shows clear α -diffraction; pattern c is recorded after 95 min and shows β' -diffraction; pattern b presents the difference between a and c. Patterns a and c show the difference between the recorded pattern and the diffraction pattern of liquid cocoa butter.

γ -Crystallization starts below 7°C , but it is always preceded by some α -crystallization, even at a cooling rate of 6°C/s . The γ -crystallization takes place within a second. The α -phase is formed at temperatures between 3 and 22°C , without higher-melting polymorphs, when the cooling rate is 2°C/min or larger. The solidification rate depends on the temperature, but solidification is always completed within 20–25 min. At temperatures above 20°C , substantial parts of the sample stay fluid. The β' -phase is formed directly from the melt at 24 and 26°C , regardless of the cooling rate. This result contrasts with that of Hernqvist and Larsson (18), who reported that β' can be formed only *via* α . It takes several hours to start and complete β' -solidification. No independent phase III or IV could be observed in the formation of this phase β' , nor in the melting. β' can be obtained *via* transformation of α -crystallites much faster than directly from the melt. β -Formation is observed only as a transformation of β' -crystallites.

Freezing polymorphic state of cocoa butter. Analysis of the experiment at a R_c of 6°C/s demonstrates the formation of α -crystallites before γ -crystallites start to grow, as shown in Figure 3. At first, a single peak at 4.2 Å develops, followed a few seconds later by a peak at 3.7 Å . The only result of further cooling is a peak shift of $\pm 0.6^\circ 2\theta$ ($\approx 0.1\text{ Å}$) to higher an-

gles, which is the result of sample shrinkage. The sample exists as a mixture of γ and α .

This experiment shows that partially liquid cocoa butter samples that are frozen will contain an amount of γ -crystallites, which is related to the fluid part before freezing, while a small α -fraction is also present. This is true even on extreme cooling, such as with liquid nitrogen as coolant. Great care should be taken in interpreting of results obtained from the analysis of such samples, for example, from the common manufacturing practice of dropping samples from production into liquid nitrogen or dry ice to freeze the polymorphic state of the sample for an off-line analysis. It is remarked that the γ -phase melts around 0°C , a common starting point for DSC measurements.

These experiments are not sufficient to gain a complete understanding of the solidification and phase transition processes of cocoa butter. Additional experiments are necessary to establish not only the solidification times but also rates of transitions. Experiments concerning the melting of solid cocoa butter and the claimed memory of cocoa butter under certain conditions are also necessary. These experiments will be described in following papers.

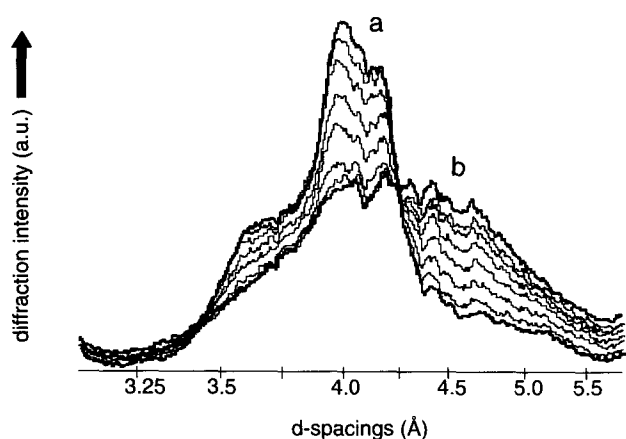


FIG. 5. Melting at 1°C/min of β' cocoa butter obtained by solidification at 18°C. Diffraction patterns change gradually and unequivocally from 18.0°C (pattern a) via 20.5, 22.5, 24.0, 25.0, 26.0 and 27.0°C to 27.5°C (pattern b).

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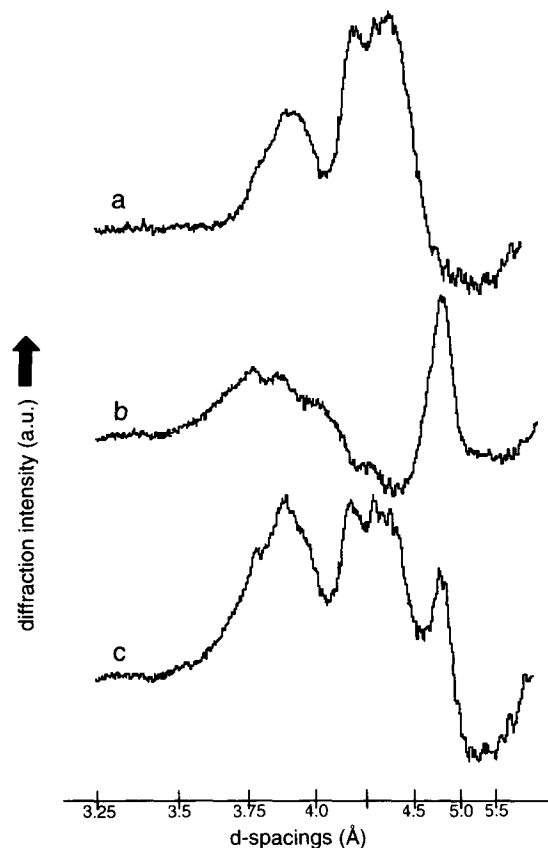


FIG. 6. X-ray diffraction patterns of solid cocoa butter during transformation from β' to β . Pattern a, showing β' -diffraction, was recorded after 30 h isothermal stay at 25°C; pattern c, showing a mixture of β' and β , was recorded after 60 h isothermal stay at 25°C; pattern b presents the difference between patterns a and c and shows β -diffraction. Patterns a and c show the difference between the recorded pattern and the diffraction pattern of liquid cocoa butter.

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