

Polymorphism Behavior in Fully Hydrogenated Mono Acid Triglycerides

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ABSTRACT AND SUMMARY

The radical expansion behavior of saturated, mono-acid triglycerides has been studied, using X-ray diffractometry. The isothermal transition of metastable β' -polymorph into the stable β -form is diffusion controlled and appears to follow two distinct rate relationships. The rate of the $\beta' \rightarrow \beta$ transition is also effected by the nature of the precursor polymorph. In common with long chain polymers, quenched, annealed samples of melted tristearin (SSS) reach the stable β -polymorphic state faster than isothermally crystallized samples of melt annealed at the same temperature. Somewhat speculative mechanisms for these processes are discussed in this paper.

INTRODUCTION

Early in work on hydrogenation catalyst development, the unusual expansion behavior of fully hydrogenated soybean oil (FHSBO) became apparent. Samples cleared of catalyst, via sedimentation, then solidified slowly in warm (40-50 C) ovens, climbed out of their containers; other samples sometimes appeared to migrate toward the cooler side of the container and form tilted masses in apparent defiance of gravity.

Consultation with the literature of saturated, mono-acid triglycerides led to Hvolby's recent work (1) with its excellent discussion of expansion behavior; to Craig's careful dilatometric experiments (2); and to the reviews of Lutton (3) and Larsson (4). It was clear that a material such as FHSBO (Iodine value <1.0) would lend itself to simple X-ray diffraction studies of phase and polymorphism behavior. Lutton has pointed out and emphasized the importance of these properties. They are exhibited by most long-chain fatty substances whose bulk behavior and poly-phase properties are related to the basic lipid forms and their relative stabilities.

A series of simple experiments were performed and the results indicate some unusual properties for this material (FHSBO). We use Larsson's criteria (5) in referring to the polymorphs of tristearin (the principal fat—ca. 85%—in FHSBO), and following Hoerr and Paulicka (6) have made our phase determinations by regular wide-angle, X-ray diffraction techniques.

Starting with both α -SSS and β' -SSS, we found that the phase transition, $\beta' \rightarrow \beta$, follows two different rate laws and that transitions to the β -form are restricted, to some real degree, according to the precursor crystalline form. Unlike Hvolby (1), we did not find that all solidified, expanded fats were in the β -form. We did find that tempering or annealing of α -SSS resulted in transition to β -SSS if the temperature was above a threshold value (~ 45 C). Just as all expanded samples were not β -SSS, the solid, unexpanded β -polymorph could be made by a process of quenching the melt, followed by annealing above the threshold temperature, but below the β' -melting point [$mp(\beta')$]. It was found that the transition to β -SSS was faster if the starting material was a quenched sample of melted SSS, than if the process were carried out, isothermally, at a temperature above the melting point of the α -polymorph. In other

words, the process $\alpha \rightarrow \beta' \rightarrow \beta$ at ~ 55 C, started with a quenched melt (-20 C) is more rapid than the process $\beta' \rightarrow \beta$ carried out at ~ 55 C starting with melted SSS.

EXPERIMENTAL PROCEDURES

Materials

The FHSBO used in these experiments were made by exhaustively hydrogenating commercial soybean oil purchased locally from the Loos and Dillworth Company of Bristol, PA. Its properties were

Iodine Value (IV)	131
Free Fatty Acid (FFA)	0.08%
Saponification Value (SV)	194

The hydrogenations were done by procedures described elsewhere (7) using Girdler G-53 catalyst. Finished fats with $IV < 0.5$ were usually obtained by these techniques.

All tempering and annealing experiments were carried out in laboratory ovens with temperature controls capable of at least ± 2 C regulation. Samples were poured, in thin sections ($\sim 2-4$ mm), into flat bottomed dishes. The sections thus made, whatever the post-hardening treatment, were used directly for X-ray examination.

Instruments

A Philips Electronics Mark II x-ray diffractometer using monochromated Cu-radiation ($\lambda = 1.5405\text{\AA}$) was used for phase analysis. The instrument settings were generally 35-40 kV with filament currents of 15-20 mA. For certain comparisons, beam intensity readings were set using a hard standard form of each polymorph.

RESULTS AND DISCUSSION

The Basic Forms

The basic forms of tristearin were made and characterized by x-ray diffraction. The three spectra shown in Figure 1 conform to Larsson's criteria (5) and are qualitatively identical to the spectra of Hoerr and Paulicka (6).

We were unable to prepare α -SSS at room temperature. Invariably, melted FHSBO in thin sections, solidified at room temperature (~ 25 C), gave β' -SSS x-ray diffraction spectra. Following Hoerr and Paulicka (6), we prepared α -SSS by a rapid quenching process (-22 C) starting with melt at ~ 85 C. This basically unstable polymorph converts to β' and β -polymorphs if warmed 10-15 degrees above room temperature. Conversion to the β -polymorph has been accomplished by annealing α -SSS at 37 C, and complete transformation, $\alpha \rightarrow \beta' \rightarrow \beta$, has been observed when the β' -polymorph found at 37 C was annealed for ~ 700 hr at 45 C. If α -SSS was the starting form, annealing for 1000 hr at 52 ± 2 C yielded an unexpanded β -SSS, whose x-ray diffraction spectrum was indistinguishable from that for reagent grade β -tristearin purchased from a laboratory supply house. This is somewhat at variance with Hvolby (1) who writes that "... the nonexpanded fats ended up with the β' -form." It is not clear that Hvolby did experiments similar to these, but in this laboratory, α -SSS annealed for 500-1000 hr at temperatures above 45 C invariably yielded an unexpanded β -SSS.

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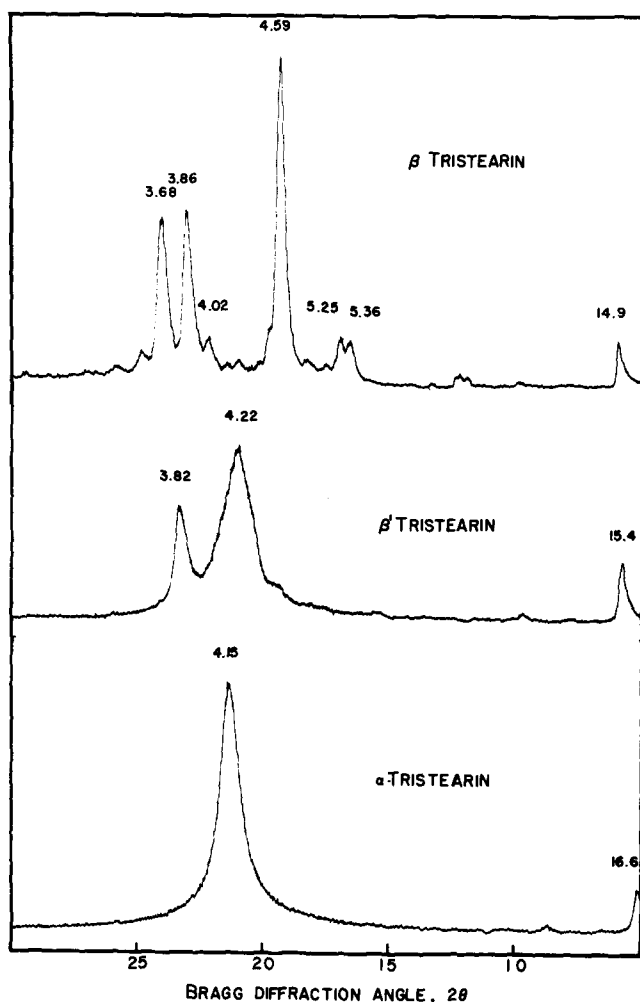


FIG. 1. X-ray diffraction spectra of the basic polymorphs of tristearin. The α -SSS was made by quenching melt at -22°C . The β' -SSS resulted from 1 hr of annealing at 52°C . The β -SSS was made by annealing α -SSS for more than 1000 hr at 52°C .

The α -SSS prepared in this laboratory also exhibited a reasonably strong line at ~ 16.6 Å. This minor line shifts toward smaller values as α -SSS is annealed. This line is present in both the β' -form and the β -form, but in β' -SSS, the exact position of this line is different, depending on the manner in which the β' -SSS was prepared.

The unstable (preferably *meta*-stable) β' -SSS can be made by fast room temperature crystallization of melted FHSBO; by short term annealing of α -SSS; or by isothermal crystallization from melted FHSBO at temperatures near $\text{mp}(\beta')$. The higher the temperature of the crystallization from melted FHSBO, the better is the "qualitative perfection" of the β' -polymorph, as indicated by X-ray diffraction line-width (8). The β' -SSS shown in Figure 1 is the result of 1 hr of annealing of α -SSS at 52°C (the examples used in Figure 1 are, in fact, samples that started from the same source of α -SSS but were annealed for different periods).

We found β' -SSS prepared by isothermal crystallization was more highly ordered than that made by annealing α -SSS, a quenched material. Figure 2 shows the X-ray diffraction spectra of two β' -SSS samples made by isothermal crystallization at two different temperatures: 37°C and 52°C . Both samples were allowed to remain at their respective temperatures for 123 hr. Both were expanded fats in the sense of Hvolby's work (1), but the degree of apparent expansion was greater in the 52°C material. The higher temperature sample is demonstrably more ordered in structure, having an X-ray line width of $1.48^\circ 2\theta$ compared to $1.87^\circ 2\theta$ for the 37°C material.

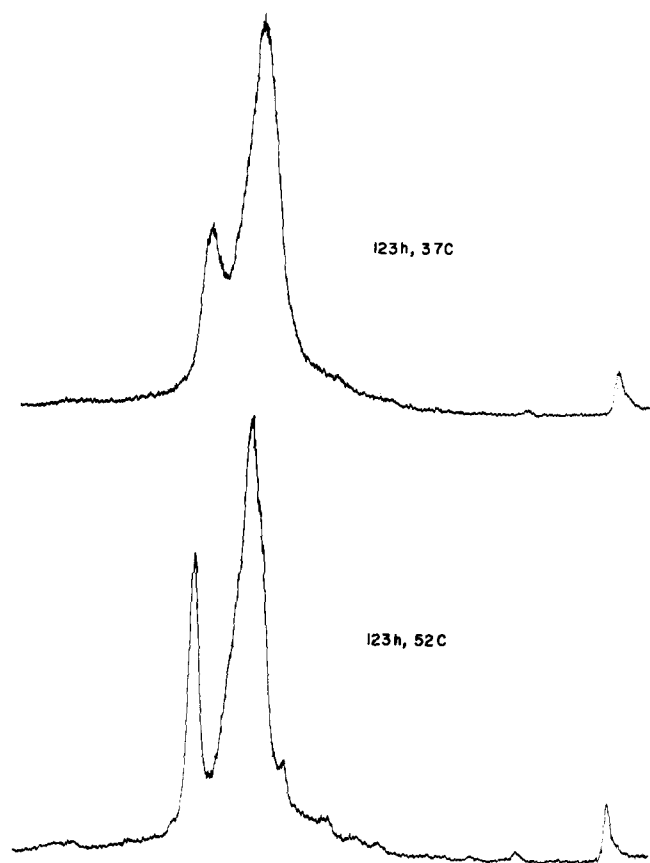


FIG. 2. X-ray diffraction spectra of β' -SSS prepared by isothermal crystallization at 37°C and 52°C .

TABLE I

	This work		Hoerr & Paulicka (6)	
	D(hkl), Å	CrA	D(hkl), Å	CrA
α -SSS	92	9.9	87	6.6
β' -SSS	59	4.5	400	33
β -SSS	300	42.6	240	20

The stable polymorph, β -SSS, can be made by annealing the α - or β' -form at temperatures above $\sim 45^\circ\text{C}$. The example in Figure 1 was made by annealing α -SSS for more than 1000 hr at $52 \pm 2^\circ\text{C}$. The X-ray diffraction lines are very slightly displaced from those on the standard pattern (Joint Comm. Pwd. Diff. Stds, #8-591), but the identification is obvious, and in accordance with Larsson's criteria.

Crystalline Order and "Qualitative Perfections"

For a given, broadened X-ray spectral line, it is possible, always, to make a determination of the average crystallite size perpendicular to that line's orientation (8). The technique owed to Scherrer is approximate because there is contained in it a form constant that is set arbitrarily. We can, however, use the technique with confidence to compare sizes of crystallites in samples of the same species.

The Scherrer equation for crystallite dimension perpendicular to a given hkl -direction is

$$D(hkl) = K\lambda/B \cos \theta \quad (1)$$

where

- D(hkl) \equiv dimension perpendicular to the hkl axis.
- K \equiv constant related to crystal shape.
- λ \equiv wavelength of analyzing radiation.
- B \equiv line width of the hkl diffraction line.
- 2θ \equiv Bragg angle of hkl -line.

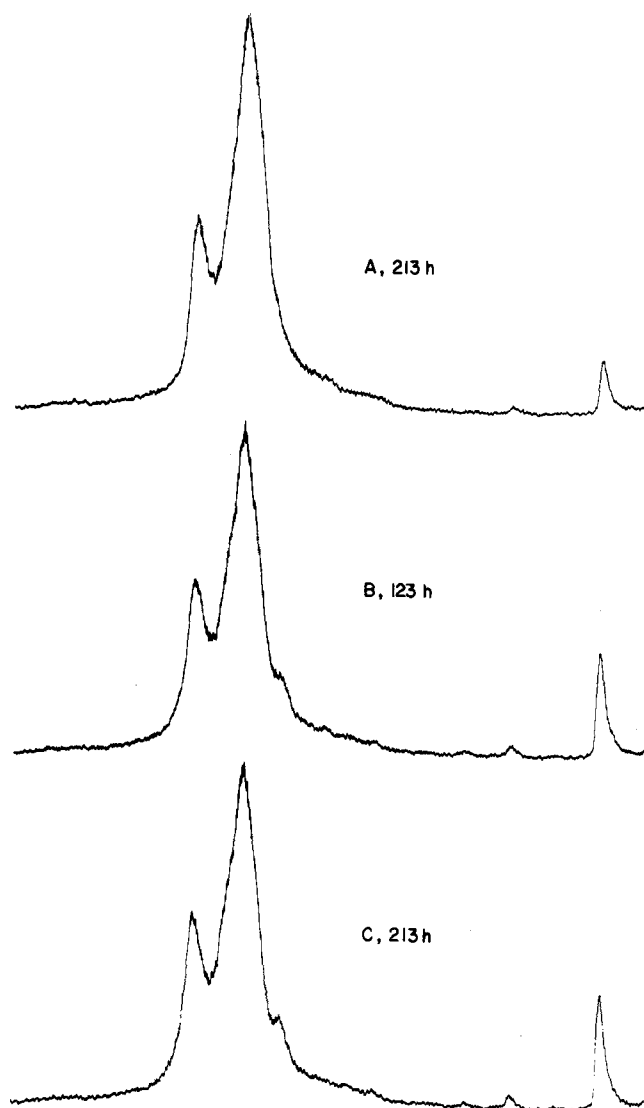


FIG. 3. Processes at 37 C produced these X-ray diffraction spectra. A, SSS crystallized and annealed for 213 hr; B, quenched SSS (α -form) annealed 123 hr, C, quenched SSS annealed 213 hr.

Of perhaps greater importance in interpreting the results of tempering and annealing experiments is a term that may be labeled "qualitative perfection" (9,10). This is a rather primitive measurement, mathematically, but is related to the distribution of crystallite sizes. For a given diffraction line of intensity $I(hkl)$, and half-intensity width $W(hkl)$, the qualitative perfection is correlated by $CrA \equiv I(hkl)/W(hkl)$. Warren and Averbach (11) and Bienenstock (12) have shown that analysis of the X-ray intensity spectrum can be used to derive a numerical distribution of crystallite sizes. It will be enough, here, to cite a simpler, but I think convincing empirical argument [for these comparison, X-ray beam intensities are pre-set so that $I(hkl)$ in each case is referenced to a standard value, I^0].

If two lines for the same hkl -spacing have differing $I(hkl)$ -values, but the same widths, $W(hkl)$, then we infer from Scherrer's equation that the average crystallite sizes are the same. The difference in intensities for the lines means, simply, a different number of first-order diffractors. Assuming the crystallite sizes are distributed, then the distributions to be derived are different, a fortiori, and the primitive quantity $I(hkl)/W(hkl)$ is proportional to that distribution. Differences, therefore, in CrA -values between two lines are related to differences in the distribution of crystallite sizes.

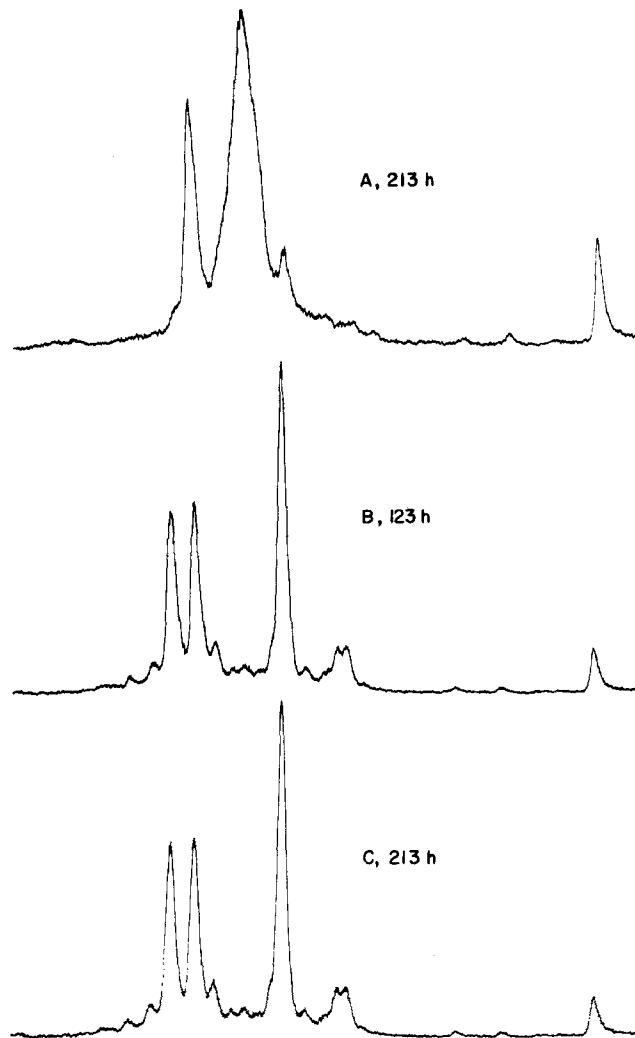


FIG. 4. Processes at 52 C produced these X-ray diffraction spectra. A, SSS crystallized and annealed 213 hr; B, quenched SSS (α -form) annealed 123 hr; C, quenched SSS annealed 213 hr.

As a point of departure, we compared $D(hkl)$ -values, as calculated via the Scherrer equation, for the major X-ray lines shown in Figure 1. We compared these to the values of Hoerr and Paulicka, extracted from the figures in their paper (6). These values are summarized in Table I.

The basic polymorphs have quite similar values for CrA , except for the β' -form. Hoerr and Paulicka's β' -SSS is quite "orderly" compared to the example seen in Figure 1, while the α - and β -forms made here surpass theirs in "qualitative perfection."

In the case of the two β' -SSS examples seen in Figure 2, the crystallite sizes are widely different, the example made at 52 C having 62A crystallites while the 37 C material has 48A crystallites. The values for "qualitative perfection" are quite different, too, that for the higher temperature example being 13.1 compared to 10.3 for the lower temperature β' -SSS.

Annealing: The Role of Temperature

In the limited experiments done, it is obvious that the temperature of annealing plays a dominant role in polymorphism behavior. The sharp transition temperatures (mp 's) appeared to play a minor role. The α -form of SSS will transform slowly to the β' -form at 37 C which is 17.5 C below its melting point, while at 52 C, just below $mp(\alpha)$, the α -polymorph converts rapidly to the β' -form, then undergoes transition to the stable β -polymorph [without

TABLE II

Crystallite Sizes and CrA-Values for Different β' -SSS Examples		
Mode of preparation	D(hkl), A	CrA
Quenched-annealed α -SSS		
25 C, 24 hr	55	5.4
52 C, 1 hr	59	4.5
37 C, 123 hr	52	8.0
37 C, 213 hr	51	8.0
Isothermal crystallization and annealing		
37 C, 123 hr	48	10.3
37 C, 213 hr	51	10.1
52 C, 123 hr	62	13.1
52 C, 213 hr	60	9.7

expansion (1,3)]. Below ~ 40 C, the α -SSS does not appear to undergo the $\alpha \rightarrow \beta' \rightarrow \beta$ transition but retains β' character. Figure 3 shows the X-ray diffraction spectra of SSS subjected to both isothermal crystallization (A) and quenching, followed by annealing at 37 C (B and C).

The spectra are quite similar, with differences only in the intensity of the long period diffraction maxima. In both the quenched/annealed samples, the forward side of the main X-ray diffraction maximum shows the presence (more pronounced in the 213 hr sample) of some β -SSS signal.

More interesting than this behavior are the differences seen between samples crystallized and quenched/annealed at 52 C. The resultant X-ray spectra are shown in Figure 4. Examples of quenched α -SSS and melted SSS were placed in a 52 C oven and annealed for 123 hr and 213 hr, as was done for 37 C samples. The isothermally crystallized sample (A) after 213 hr, retained the β' structure, albeit now showing some β -SSS signal on the forward side of the principal diffraction maximum. The two quenched/annealed samples (B and C) underwent the transition $\alpha \rightarrow \beta' \rightarrow \beta$ in the same annealing period at this higher temperature.

An example of β' -SSS made by isothermal crystallization at 37 C and annealed for 213 hr was placed in the 52 C oven and annealed for ~ 200 hr. The result, when this material was analyzed, was a rather poor β -SSS X-ray diffraction spectrum. When compared to spectra of α -SSS undergoing transition-time studies (see following discussion) the spectrum was representative of an α -SSS annealed for ~ 32 hr at 52 C. The only measurable difference between β' -SSS made by isothermal crystallization and β' -SSS made by annealing α -SSS for 1 hr is in the CrA-values, but they behave quite dissimilarly when annealed.

It is clear from these experiments that the crystalline precursor state plays a signal role in determining the time needed to reach equilibrium forms. A highly structured β' -SSS transforms to β -SSS much more slowly than does α -SSS. Below some still undefined threshold temperature (~ 40 -45 C), the phase transformation stops at the β' -polymorph, whether started with the quenched polymorph (α) or done by isothermal crystallization. The essential stability of the β -polymorph is indicated by the data summarized in Table II, where crystallite sizes and CrA-values for β' -SSS made in different ways is shown.

The Transition Process

Theories of diffusion in discrete media (13-16) lead to exponential solutions for the Diffusion Coefficient. The transition from one polymorph to another is surely an atom-jump process of the type treated by Pearlstein (14) with the jump-probability given by a Boltzmann factor

$$P(\beta'/\alpha) = \exp(-E/t) \quad (II)$$

where $P(\beta'/\alpha)$ is the probability of a particle jumping from a stable α -lattice location to a β' -lattice location, E is the difference in energy of the two lattice positions, k is Boltzmann's constant, and T is the absolute temperature. This leads to an exponential jump frequency and finally to a diffusion coefficient, D , of exponential form

$$D = D_0 \exp(-\psi/kt) \quad (III)$$

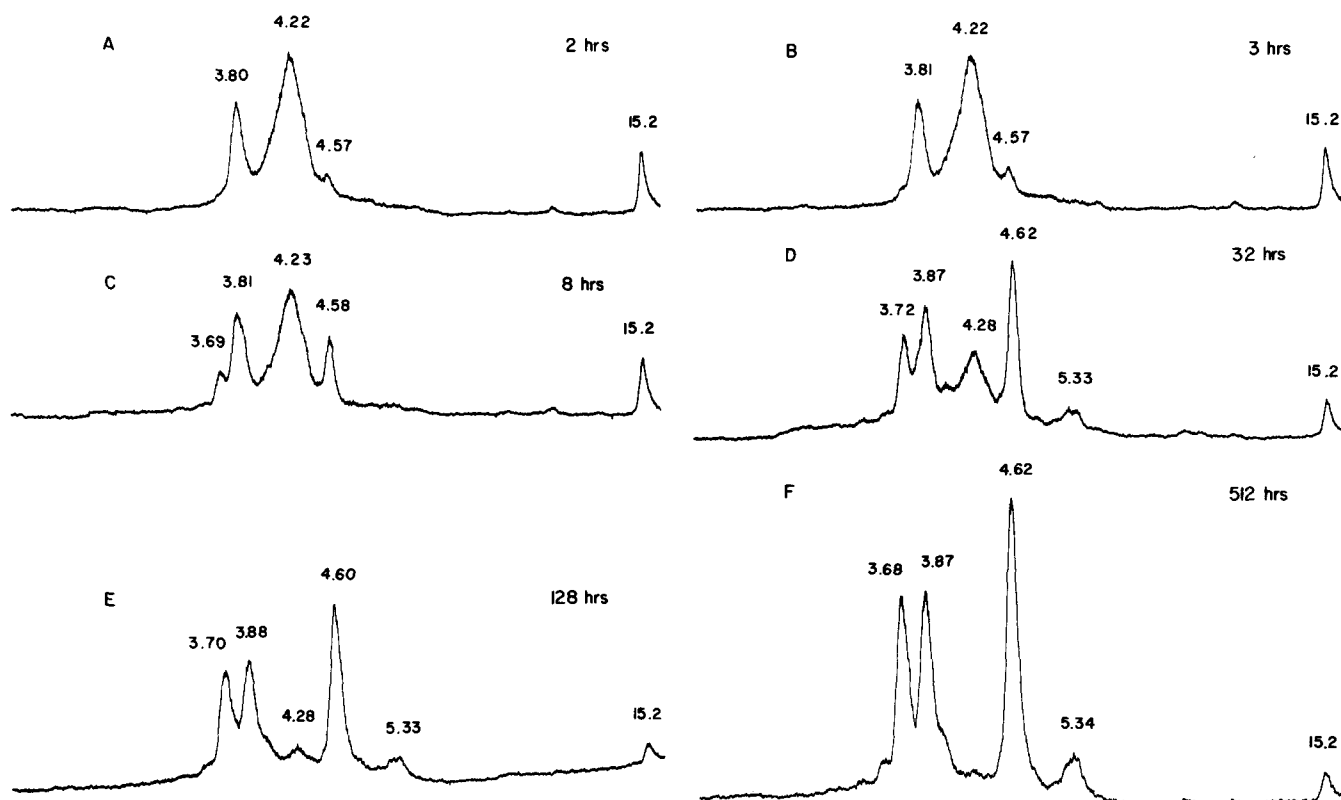


FIG. 5. X-ray diffraction spectra of quenched, annealed tristearin at 52 ± 2 C. The time are indicated on each spectrum.

where D_0 is a constant and ψ includes E and a generating function for thermal production of both kind of sites (α and β').

In this laboratory, we chose to investigate the transition $\alpha \rightarrow \beta' \rightarrow \beta$ as an isothermal phenomenon, assuming a relationship of the form

$$C(\alpha)/C(\beta) = -m \ln t + C_0 \quad (IV)$$

where $C(\alpha)$ and $C(\beta')$ are concentrations of α -SSS and β' -SSS, t is the time of annealing, and C_0 is a constant.

A series of annealing experiments were done, starting with the α -form. For convenience, after 3 hr of annealing, the samples were analyzed in increments based on 2^x hr, with x taking values 3, 5, 7, and 9.

The values of $C(\alpha)$ and $C(\beta')$ are difficult to assess, but the ratio $C(\alpha)/C(\beta')$ should be directly proportional to the ratio of their x-ray diffraction intensities. In practice, the transition $\alpha \rightarrow \beta'$ was exceptionally rapid and what was tabulated was $C(\beta')/C(\beta)$, using the 4.22 A-line intensity for $C(\beta')$ and the emerging 4.59 A-line intensity as $C(\beta)$. Figure 5 indicates the progress of the $\beta' \rightarrow \beta$ transition as function of time with the annealing temperature = 52 C. In Figure 6, the values of $C(\beta')/C(\beta)$ are plotted as a function of log time.

The results are striking. The plot of $C(\beta')/C(\beta)$ is remarkably linear, but there appear two separate, definite rate constant, suggesting that the diffusion of particles from (in this case) β' -sites to β -sites is controlled by two different mechanisms.

The exceptionally rapid $\alpha \rightarrow \beta'$ transition may well be, as Larsson suggests (17) a collapse of vertical chained α into the herringbone structured β' . The transition takes place very rapidly if fully developed α -SSS is gently warmed.

The slower transition $\beta' \rightarrow \beta$ is clearly diffusion controlled, and if we accept Muller's findings (18,19) for hydrocarbon chain packing, the fast $\alpha \rightarrow \beta'$ transition can be seen as a simple, almost unhindered ordering (collapse) into alternately parallel rows (3). Muller's hypothesis also indicates that the $\beta' \rightarrow \beta$ transition is slow, because it involves a complete reordering of every other row in the β' -structure (17), and as we have observed, the more ordered the β' -phase, the slower is the $\beta' \rightarrow \beta$ change.

The initial rate in the $\beta' \rightarrow \beta$ transition is probably a simple, thermally activated process, while the slower, later part of the transition depends on the rate of generation (cf. Eq. II) of β -sites, and is, in effect, a concentration dependent process; that is, generation of β -sites in a partially developed β -SSS is more difficult than in a β' -SSS.

We do not proffer an explanation for the fact that β' -SSS formed from melt undergoes transition to the β -form much more slowly than β' -SSS made by annealing α -SSS. We suggest, however, that it is closely related to the size of the crystalline domains in the samples, and to the qualitative perfection. The more perfect (the higher the CrA-value, the larger the crystallites) the β' -SSS, the more slowly the transition to β -SSS takes place.

This suggests that the smaller the crystalline domains, the more likely is fast transition to the final stable form. This appears to fit the situation, at least intuitively. If we assume that grain boundaries provide a "working space" for small scale expansion or relief of lattice strain, then a high density of grain boundaries (small crystal domains) will permit easier relief of thermally induced strain, and a faster rate of phase transition may occur. The forces that bind amorphous domains and regions made up of very small crystallites are weaker van der Waals type. These make small contributions to the elastic moduli of the bulk sample, and grain boundaries provide a region for relief of strain without large volume changes (20).

If the lamellar structures Larsson has found in liquid fats (4) are quite stable, then perhaps slow "voluntary" crystal-

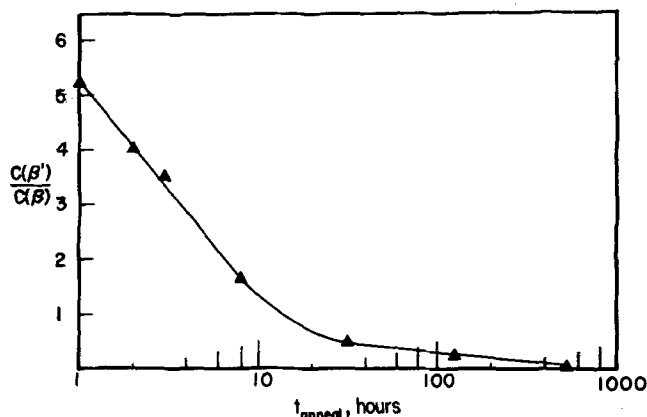


FIG. 6. Semilog plot of $C(\beta')/C(\beta)$ as a function of annealing time at 52 ± 2 C. Two distinct rate constants are indicated.

lization (1) results in a mock-geological folding and bending of stable layers caught in a temperature gradient. This "layer building" may serve to explain the radical expansion behavior of these materials.

Larsson has adumbrated the use of polymer concepts to treat the crystallization of fats (4). He used Hosemann's paracrystal concept (21,22) to estimate the size of the lamellar regions in liquid trimyristin. Hermans and Weidinger had, much earlier, compared commercial paraffin to polyethylene (23). They found considerable order in the liquid and a structure similar to the α -polymorph of fats for the quenched material.

In polymers the morphology naturally assumed is that in which the chains are extended and segregated so that like chain lengths crystallize together (24,25). In saturated fats there are no differing chain lengths, but the similarity with respect to alignment remains. Quenched, annealed samples of high polymers are found to reach their equilibrium density (or specific volume) in shorter times than isothermally crystallized samples (17,26). In this study the same has been found for tristearin. The same equilibrium forms are approached no matter what the mechanism, but the process is faster if started with the α -polymorph made by low temperature crystallization. Peterlin (17) indicates that for polymers this is due to changes which parallel the long spacing (in a high polymer, admittedly, the short spacings cannot be very effective in controlling properties) of the polymer; it is not too much a leap in reasoning to assume that it is the small differences in long spacing that are responsible for the radical expansion behavior (1) of saturated, mono-acid triglycerides. As Larsson has pointed out, it is end group alignments and their differences that explain alternation of transition temperatures in even- and odd-numbered members of this class of compounds (27). It is known, too, that the tilt structures in triglycerides are responsible for differences in polymorph stability (3,6,17) and phase behavior. In quenched samples of SSS, the long period spacing changes relatively little (cf. Fig. 3), while there are different equilibrium long spacings for all three polymorphs as seen in Figures 1 through 4. Regions of lamellar, melted SSS in different temperature environments could conceivably solidify quickly in such a way that neighboring regions of different long period spacing would be highly strained at the interface. Mechanical relief of these strains could serve to explain the radical expansion behavior seen in voluntary-cooled samples of FHSBO.

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