Influence of *cis* and *trans* Double Bonds on the Thermal and Structural Properties of Monoacid Triglycerides

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In order to determine the importance of *cis* or *trans* unsaturations from a technological point of view, the study of the structural and thermal properties of monoacid triglycerides: tristearin (SSS), triolein (OOO) and trielaidin (EEE) has been undertaken. X-ray powder diffraction and differential scanning calorimetry are useful tools to elucidate the physicochemical properties of such compounds. In this work, polymorphism, kinetics of polymorphism and intersolubility have been investigated. From a structural point of view, we have shown that, according to the polymorphic form, the conformational properties of EEE are similar to those of the corresponding saturated molecule SSS or to those of the *cis* unsaturated analogue OOO. The study of the intersolubility behavior of these three compounds has shown a different affinity of the *cis* and *trans* unsaturated molecules vs the completely saturated one. By the same method, we have observed that *trans* unsaturated hydrocarbon chains cocrystallize with both *cis*-unsaturated (OOO) and totally saturated hydrocarbon chains (SSS); the *trans* double bond of EEE can adapt to the two kinds of lattices. The study of the kinetics of polymorphism has shown that 5% of OOO or EEE accelerate the $\beta' \rightarrow \beta$ transition of SSS, while the reason for the two phenomena is quite different. The adaptation of EEE to *cis*-unsaturated and to saturated hydrocarbon chains shown in the structural and intersolubility behavior analyses also appears in the kinetic study, after adjunction of 5% of OOO into EEE. All the results confirm that, from structural and thermal points of view, EEE has an intermediate behavior between SSS and OOO.

KEYWORDS: **Intersolubility, kinetics, phase diagrams, phase transitions, polymorphism, structural properties, thermal behavior, trielaidin, triolein, tristearin.**

The thermal properties of natural fats, polymorphism and intersolubility, are essentially due to triglycerides which are their principal constituents. The complexity of the thermal behavior of fats is due to the great variety of triglycerides which may differ by the length of the hydrocarbon chains, by their unsaturation degree and by their position on the glycerol residue. In crude fats, only *cis* type unsaturated fatty acids (oleic, linoleic, linolenic, etc.) are found; *trans* double bonds exist in nature, but are produced mainly by hydrogenation. The presence of *trans* fatty acids in the refined fractions modify their technological properties (1–4)—polymorphism, kinetics of polymorphism and intersolubility. From a nutritional point of view, the *trans* isomers may induce modifications of biochemical processes (5–8). In order to clarify the role played by *cis* and *trans* double bonds, we have undertaken the study of structural and thermal properties (polymorphism and intersolubility) of three monoacid triglycerides having the same number of carbon atoms (C18), but differing by the presence and the type of unsaturation (*cis* vs *trans*), i.e., tristearin (SSS), triolein (OOO) and trielaidin (EEE).

Triglycerides present different crystalline forms still called polymorphs. Three main forms (α, β' and β) are generally accepted in order to describe polymorphism (9–14); an additional low melting sub-α form is sometimes found (15–16). It is known that each form can be detected by X-ray powder diffraction measurements—the short spacings, consisting in the small distances between the hydrocarbon chains and defining the polymorphic form (sub-α, α, β' or β), and the long spacings corresponding to the great distances representative of the longitudinal packing noted two or three according to the carbon chains number by layer (α-2, β-3, etc.). Except for the sub-$\alpha \leftrightarrow \alpha$ transformation, the transitions that occur between the different polymorphic forms are irreversible and classically depicted as follows: sub-$\alpha \leftrightarrow \alpha \rightarrow \beta' \rightarrow \beta$. From a technological point of view, the slackening of the $\beta' \rightarrow \beta$ transition is often of the most interest; the β polymorphic form may give some problems consisting, for example, in the growth of hard and brittle crystals with a grainy structure.

Another important property of glyceride mixtures is the possibility of forming solid solutions (complete solubility) or mixtures of mixed crystals limited solubility in the solid phase by intersolubility (17–18). The construction [by differential scanning calorimetry (DSC) and X-ray powder diffraction (XRD) techniques] of phase diagrams gives a graphic representation of the cocrystallization phenomena involved during the mixing of triglycerides. In general, the binary systems described in the literature (19–23) do not take into account the relation existing between intersolubility and polymorphism in the mixtures of fats. Due to this relation, our phase diagrams (16,18,24,25) are not real equilibrium systems—they consist of a succession of the thermal behavior of unstabilized polymorphic forms. They are nevertheless interesting from a technological point of view because they are helpful for the understanding of the dynamic phenomena which govern the thermal properties of natural fats.

MATERIALS AND METHODS

The purity of the compounds (Sigma Chemical Co., St. Louis, MO) which was verified by gas liquid chromatography (GLC) was about 99%. The chromatographic analyses were performed on a Carlo Herba HRGC Mega 5160 apparatus (Carlo Erba, Milano, Italy). A FFAP CB Machery Nagel column was used for the analyses of the methyl ester ratio and a CP SIL 5 CB Chrompack was used for the triglyceride carbon number analy-

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ses. The experimental conditions have been established by G. Lognay (private communication).

Differential scanning calorimetry (DSC) measurements were carried out on a Setaram DSC 111 apparatus (Setaram, Lyson, France) using a liquid nitrogen device; samples of about 10 mg were used. After tempering the samples for 10 min 20°C above the melting point the temperature was dropped quickly to −40°C at the rate of 25°C/min, and the melting curves were recorded at the rate of 5°C/min. This particular thermal conditioning was chosen in order to obtain, after a rapid cooling, the most unstable polymorphic forms (sub-α or α); heating at the rate of 5°C/min is a compromise between the time measurement and the ability to detect the most polymorphic forms (sub-α, α, β' and β). Note that due to the complexity of the recorded thermograms (succession of numerous endo- and exotherms), all the melting and transition points are read at the maximum of both endo- or exothermic peaks.

For the X-ray powder diffraction measurements (XRD), a Philips PW 1050 diffractometer ($K\alpha_{cu}$ = 1.54178 Å; 2θ precision: 0.05°) equipped with a temperature control system (Philips PM 2522 A digital VAΩ meter and Pt probe; Philips, Eindhoven, The Netherlands) was used. The heating (>20°C) was performed with a TTK Anton Paar system (Anton Paar, Graz, Austria) and the cooling (<20°C) with a Huber HS 60 cryostat (Huber, Milano, Italy). The aluminum sample holder contained about 100 mg of material. A gaseous nitrogen flow prevented the condensation of water during measurements at low temperatures. The thermal conditioning was the same as in the case of DSC measurements; due to the fact that X-ray powder identification takes time (detector scan speed: 1° 2θ/min), each polymorphic form identification was performed after melting, rapid cooling and heating the samples at a constant rate to the temperature of measurement (one thermal treatment by X-ray powder spectrum).

RESULTS AND DISCUSSIONS

Polymorphism. XRD and DSC measurements data show that SSS, EEE and OOO crystallize, after melting and rapid cooling (see Experimental section), under the sub-α-2 and/or α-2 polymorphic forms. During controlled speed heating (5°C/min), SSS and EEE are transformed into the β'-2 form and they melt under the β-2 polymorphic form. In these conditions, the α-2 and β'-2 forms of OOO are not easily detected due to their instability and to the rapid transformation to β-2 polymorphic form.

The short spacing values associated to the α and β forms of SSS, EEE and OOO are summarized in Table 1. We observed that, in the α and β polymorphic forms, the short spacings of SSS and EEE are very similar. Under the same conditions, OOO crystallizes into a mixture of sub-α-2 and α-2 polymorphic forms, and although the characteristic lines corresponding to the β form of OOO are more numerous, the more intense ones are quite similar to those observed for SSS and EEE.

The long spacing values are characteristic of a double length arrangement (Table 2). The shorter values observed for OOO in the α plus sub-α polymorphic forms, compared to SSS and EEE, are probably due to the presence of the *cis* double bond which imposes a special packing to the acyl chain. This difference in value, not observed in the β polymorphic form, seems to indicate that SSS and EEE are more tilted in this form than OOO. The long spacing values vs polymorphic form evolution (Fig. 1) seem to show that SSS and EEE present a similar structural behavior during the phase transition (same slope). This slope may provide some information on the stability of the α crystalline lattice—the $\alpha \rightarrow \beta$ transition could require more energy for SSS and EEE than for OOO. DSC curves indicate that EEE and SSS present important endo- and exothermic peaks preceding transition to the β-2 form; this phenomenon is not observed for OOO, where all these endo- and exotherms are really diffuse (Fig. 2). In the same way, EEE and OOO, for which the long spacings are very close in β, present a greater melting enthalpy (obtained after melting, cooling in α or sub-α and heating), probably corresponding to a greater compactness of the lattice in this form (Table 3).

TABLE 1

Short Spacing Values (Å) Observed for sub-α,α and β Forms of SSS, EEE and OOO (Precision in 2θ Values: 0.05°)

Compound	α Form	β Form
SSS	4.2	3.7-3.9-4.6-5.3
EEE	4.2	3.7-3.9-4.6-5.3
OOO	4.3-4.0 (α + sub-α)	3.7-3.9-4.0-4.6-5.3

TABLE 2

Long Spacing Mean Values (Å) Observed for sub-α,α and β Forms of SSS, EEE and OOO (Precision in 2θ Values: 0.05°)

Compound	α Form	β Form
SSS	54	47
EEE	53	45
OOO	47 (α + sub-α)	45

Intersolubility. As noted above, the intersolubility behavior of the triglycerides can be observed by DSC and XRD. In fact, the existence of a complete (solid solution) or a limited (mixture of mixed crystals) solubility can be detected essentially by the long spacing values—the first and the third order lines are split into two parts when a mixture of mixed crystals is present.

Phase diagram of the binary mixture [SSS-EEE] (Fig. 3). Tristearin (SSS) and trielaidin (EEE) crystallize under the α-2 polymorphic form after melting and rapidly cooling. During the heating at controlled speed (5°C/min), they are transformed into the β'-2 form and melt under the β-2 form. The binary phase diagram seems to correspond to the superposition of three monotectic systems with a partial intersolubility in each polymorphic form. The first monotectic line (around 20°C) corresponds to an α-2 $\rightarrow \beta'$-2 transformation, the second to a β'-2 $\rightarrow$ β-2 transition and the third to the melting of [EEE-SSS]MC in the β-2 polymorphic form. We may attribute a solubility for EEE in SSS under

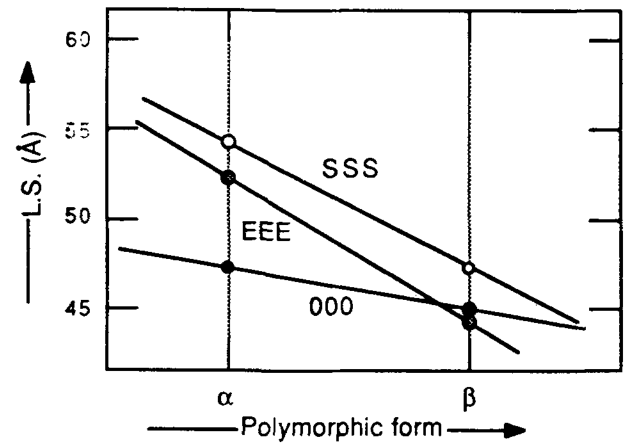

FIG. 1. Long spacing evolution according to the polymorphic form for SSS, EEE and OOO.

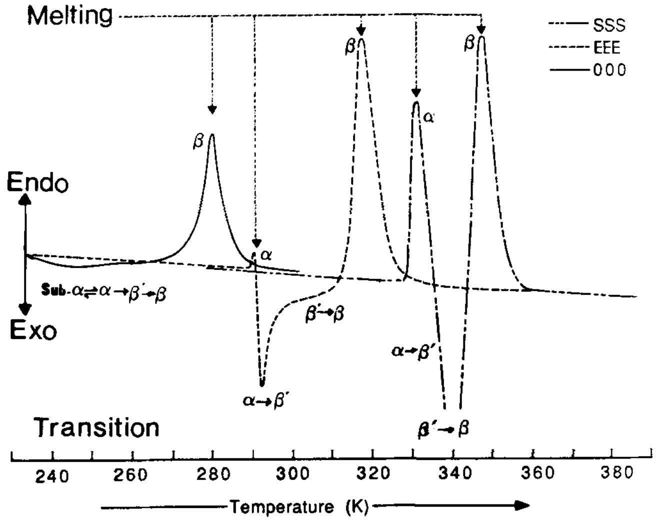

FIG. 2. DSC curves obtained for SSS, EEE and OOO after melting, rapid cooling (25°C/min) and heating at constant rate (5°C/min).

the α-2 form of about 15% and under the β'-2 and β-2 forms of about 35%. Note the presence of the β' phase on all the spreading of the binary diagram.

Phase diagram of the binary mixture [SSS-OOO] (Fig. 4). After melting and rapid cooling, triolein (OOO) crystallizes under a mixture of sub-α-2 and α-2 polymorphic forms and transforms rapidly into β' and β forms during heating at controlled speed (5°C/min). Although being of monotectic type under the β polymorphic form, this binary phase diagram is quite different from [SSS-EEE] mixture. OOO is included in the crystal lattice of SSS in weaker proportions (less than 2% in β). Until 20% of OOO, [SSS-OOO]MC has a behavior similar to the pure substance SSS; the liquid phase constituted by OOO (melting point; 4°C) doesn't seem to influence the transitions and meltings of [SSS-OOO]MC. After 20% of OOO, the succession of the different transitions (α→β' and β'→β) are not detectable in DSC, and the increasing proportion of the destabilizing liquid phase formed by OOO could be the reason. Although they are observed in X-ray diffraction, the different transitions preceding the monotectic melting are not observed in DSC (reason for the horizontal dotted lines). Note that, in this phase diagram, the β' polymorphic form is only detectable in a limited proportion of the system.

Phase diagram of the binary mixture [EEE-OOO] (Fig. 5). Except for the greater solubility of OOO in EEE in the β form (about 20%) and the separation of OOO from the solid solution constituted by EEE and OOO near 0°C, this monotectic type phase diagram is quite similar to the one describing the binary mixture of SSS and OOO. A solid solution of EEE and OOO appears at low temperatures for the sub-α, α and β forms. A recrystallization corresponding to the separation of OOO from the solid solution in the β form occurs near 0°C; in this part of diagram [EEE-OOO]MC β-2 and OOO β-2 coexist. Note that the β'form is detectable only for a small fraction of OOO in EEE. Like the SSS-OOO system, the horizontal dotted lines correspond to phase transitions that were not detected in DSC but were observed in XRD.

TABLE 3

Enthalpy Values (kcal.mol^{-1}) Calculated for the Melting of the β Form of SSS, EEE and OOO, After Quenching and Heating at Constant Rate (Precision: 1 kcal.mol^{-1})

Compound	ΔH_β (kcal.mol^{-1})
SSS	15
EEE	32
OOO	26

Schematic view of the three binary diagrams (Fig. 6). In this schematic view, we see that EEE is quite soluble in SSS under the β form, about 35%. A very small miscibility of OOO in SSS is observed in this crystalline form, less than 2%, although the solubility of OOO into EEE is about 15%. This allows us to observe the interesting behavior of EEE as compared to SSS and OOO; after adaptation of the torsion angles of the methylene groups on both sides of the *trans* double bond, EEE can fit structures of totally saturated and *cis* unsaturated monoacid triglycerides. We can also say that an all-saturated lattice excludes *cis* double bonds, that an all-saturated lattice accepts *trans* double bonds and that an all *trans* double bond lattice accepts *cis* double bonds to a smaller extent. From a kinetic point of view, we can establish the destabilizing effect of OOO on EEE and SSS on the β' polymorphic form; the SSS-EEE system is the only one to present β' polymorphic form in all the variations of the weight compositions.

Kinetics of the β'→β transition. As seen before, the study of the kinetics of the β'→β transition is interesting from a technological point of view. It is known (26) that thermal conditioning is an important factor influencing the β' stability of triglycerides—α-induced β' form is more instable than the β' form directly obtained from the melt. In this case, there is a competi-

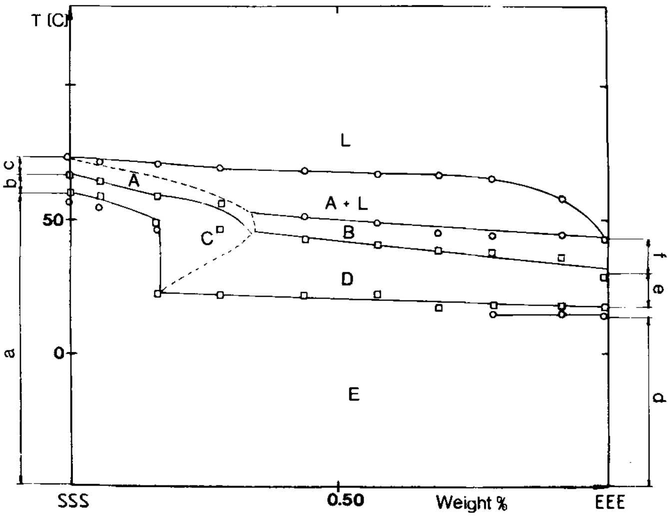

FIG. 3. (SSS/EEE) binary phase diagram constructed after melting, quenching (25°C/min) and heating at constant rate (5°C/min). (O, melting; □ transition). MC, mixed crystal; A, [SSS-EEE] MC β-2; B, [SSS-EEE] MC β-2 + [EEE-SSS] MC β-2; C, [SSS-EEE] MC β'-2; D, [SSS-EEE] MC β'-2 + [EEE-SSS] MC β'-2; E, [SSS-EEE] MC α-2 + [EEE-SSS] MC α-2; a, [SSS] α-2; b, [SSS] β'-2; c, [SSS] β-2; d, [EEE] α-2; e, [EEE] β'-2; and f, [EEE] β-2.

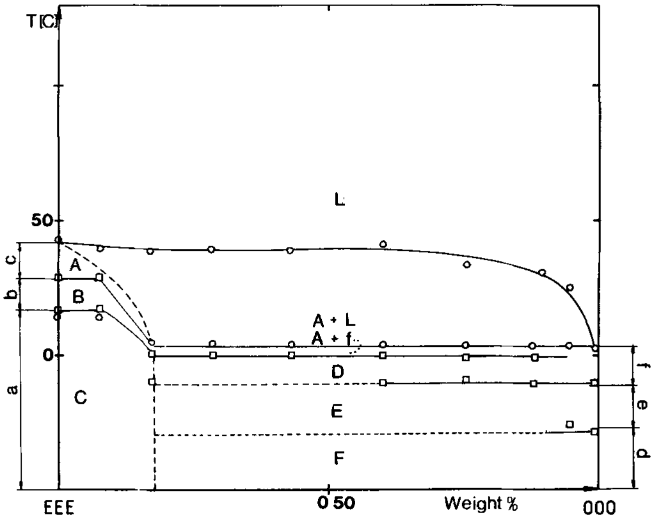

FIG. 5. [EEE/OOO] binary phase diagram constructed after melting, quenching (25°C/min) and heating at constant rate (5°C/min). (O, melting; □ transition). MC, mixed crystal; SS, solid solution; A, [EEE-OOO] MC β-2; B, [EEE-OOO] MC β'-2; C, [EEE-OOO] MC α-2; D, [EEE-OOO] SS β-2; E, [EEE-OOO] SS α-2; F, [EEE-OOO] SS sub-α-2/α-2; a, [EEE] α-2; b, [EEE] β'-2; c, [EEE] β-2; d, [OOO] α-2/sub-α-2; e, [OOO] β'-2; and f, [OOO] β-2.

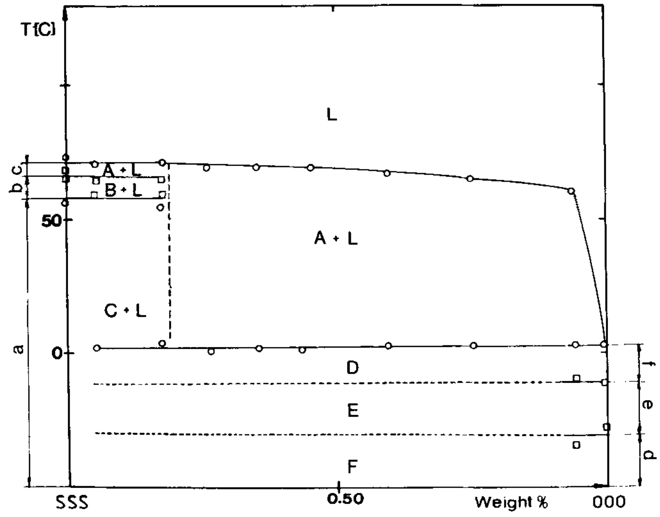

FIG. 4. [SSS/OOO] binary phase diagram constructed after melting, quenching (25°C/min) and heating at constant rate (5°C/min). (O, melting; □, transition). MC, mixed crystal; A, [SSS-OOO] MC β-2; B, [SSS-OOO] MC β'-2; C, [SSS-OOO] MC α-2; D, [SSS-OOO] MC α-2 + [OOO] β-2; E, [SSS-OOO] MC α-2 + [OOO] α-2; F, [SSS-OOO] MC sub-α-2/α-2 + [OOO] sub-α-2/α-2; a, [SSS] α-2; b, [SSS] β'-2; c, [SSS] β-2; d, [OOO] α-2/sub-α-2; e, [OOO] β'-2; and f, [OOO] β-2.

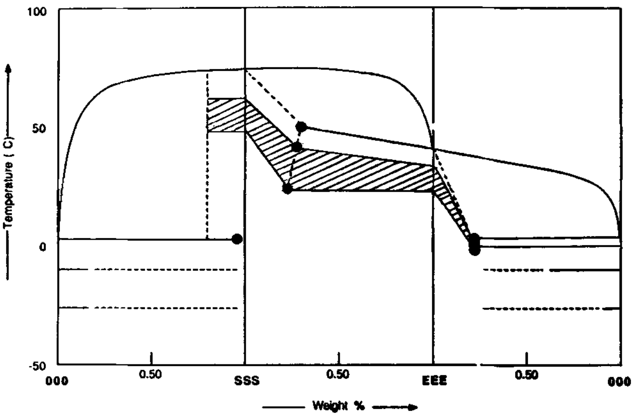

FIG. 6. Schematic view of the three binary studied diagrams. ●, maximum intersolubility; and ▨, β' polymorphic form.

tion between crystallization in β' or β and the $\beta' \rightarrow \beta$ solid state phase transition. For these reasons, our measurements have been done on substances for which the β' form is obtained after heating of the α polymorphic form.

The role played by *trans* and *cis* double bonds on the β' form stability has been studied with systems constituted of pure SSS, EEE and OOO and with mixtures in 95/5 proportion (weight %) of SSS/EEE, SSS/OOO and EEE/OOO.

The kinetic model chosen to describe the global transition process is based on the theory of Avrami (27–29). Avrami's equation ($1\text{-}x = e^{-kt^n}$), with $x = \beta$ fraction, describes the kinetics of the global transformation-nucleation, growth and coalescence of nuclei. "n" Corresponds to the mode of nucleation and growth of β nuclei and "k" to the shape of the β nuclei and to the nucleation and growth rates. Experimental "n" and "k" values were obtained by fitting the recorded kinetic curves with Avrami equation, these curves are obtained by positioning the X-ray detector at a 2θ value corresponding to a short spacing line of the β

TABLE 4

"n" Avrami Exponent of EEE, SSS, PPP, MMM and LLL

EEE		SSS		PPP		MMM		LLL	
Transition temperature (°C)	Avrami exponent "n"	Transition temperature (°C)	Avrami exponent "n"	Transition temperature (°C)	Avrami exponent "n"	Transition temperature (°C)	Avrami exponent "n"	Transition temperature (°C)	Avrami exponent "n"
12.0	1.4	55.0	4.0	44.0	1.0	31.0	0.7	11.0	1.1
13.0	1.4	56.0	3.0	45.0	1.1	32.0	1.1	12.0	1.0
14.0	0.8	57.0	3.1	46.0	1.3	33.0	1.2	13.0	1.0
15.0	0.4	58.0	2.9	47.0	0.9	—	—	14.0	1.1
—	—	59.0	2.2	48.0	0.7	—	—	—	—
1.0[a]		3.0[a]		1.0[a]		1.0[a]		1.0[a]	

[a]Mean value of "n".

form (19.2° 2θ), and by following the intensity of this line vs time at different temperatures. The "n" and "k" values allow calculation of activation energy "E_a" corresponding to the global $\beta' \rightarrow \beta$ transformation; this activation of energy is obtained following the Arrhenius theory by taking ln k′ vs the inverse of the absolute temperature ($k' = nk^{1/n}$). Nevertheless, this model doesn't allow the separation of the two fundamental processes of transformation—the nucleation and the growth of nuclei. For these reasons, the isolation methods described by Delmon (30) have been used and allow the determination of an activation energy corresponding to the β'/β reactional interface progression "E_i". This experimental technique consists in interrupting the $\beta' \rightarrow \beta$ transformation by a rapid cooling, when the transition rate is maximal, and in continuing it at different temperatures; the slope of the resulting curves corresponds to the constant rate k" of the β'/β interface progression (growth of β nuclei) and provides the activation energy "E_i" after an Arrhenius treatment.

Influence of the chain's length and of the trans or cis *isomers (LLL, MMM, PPP, SSS and EEE).* The "n", "E_a" and "E_i" values calculated for different pure triglycerides (26) differing by the chain's length and the unsaturation *cis* vs *trans* are summarized in Tables 4, 5 and 6.

Global processes of transformation (Fig. 7). The "n" value on which the shape of the kinetic curves depends, is approximately one for EEE, PPP, MMM and LLL. According to Avrami (27–29) this could correspond to the apparition with a constant probability into space and time of weakly growing nuclei. Let us remember (26) that the particularly high value of "n" observed for SSS could probably be the result of the two β′ forms (here called β'_1 and β'_2) observed for this triglyceride (31–34); the $\beta'_1 \rightarrow \beta'_2$ transition, associated to the existence of these two polymorphic forms, could precede the growth of the β nuclei at these temperatures. The "E_a" values, calculated for the saturated molecules, indicate an increasing stability of the β′ polymorphic form going with the increasing number of carbon atoms constitutive of the hydrocarbon chains. From the same number of atoms (SSS↔EEE), the *trans* double bonds seem to stabilize this polymorphic form to a greater extent.

Isolation method (Fig. 8). Even more than for SSS, we observe in EEE a superior reactivity of the β'/β interface as compared to PPP, MMM and LLL. The *trans* double bond seems to destabilize the β'/β reactional interface just after the formation of the first β nuclei. In other words, EEE could generate more reactive but less numerous β nuclei than PPP, MMM and LLL, so that the global $\beta' \rightarrow \beta$ transformation could be slackened.

TABLE 5

Global Activation Energy: "E_a" Calculated of EEE, SSS, PPP, MMM and LLL

Compound	Ea (kcal.mol^{-1})[a]
EEE	95
SSS	82
PPP	70
MMM	46
LLL	28

[a]Estimated standard deviation: ± 5 kcal.mol^{-1}.

TABLE 6

Interfacial Activation energy: "E_i" Calculated for EEE, SSS, PPP, MMM and LLL

Compound	Main temperature (°C)	Ei (kcal.mol^{-1})[a]
EEE	14.0	47
SSS	58.0	55
PPP	47.0	64
MMM	32.0	67
LLL	14.0	66

[a]Estimated standard deviation: ± 3 kcal.mol^{-1}.

Influence of the mixture of triglycerides. The introduction of impurities (fatty acids, mono-, di- or other triglycerides) greatly modifies the thermal properties of pure molecules. In order to express rules that could help to control the β′ stability of natural fats or complex mixtures of triglycerides, we have chosen to describe the influence of the introduction of other triglycerides on the $\beta' \rightarrow \beta$ transformation of pure molecules.

Comparative study of SSS, SSS 95%/EEE 5% and SSS 95%/000 5% (Figs. 9 and 10). Table 7 summarizes the values of "n", "E_a" and "E_i" calculated for pure SSS and for SSS/EEE and SSS/OOO binary systems in 95/5 weight proportion. The "n" value is situated between one and two for the two mixtures. The particular behavior of SSS (n = 3) disappears with the incorporation of 5% of EEE or OOO. A systematic study of global and interfacial activation energies al-

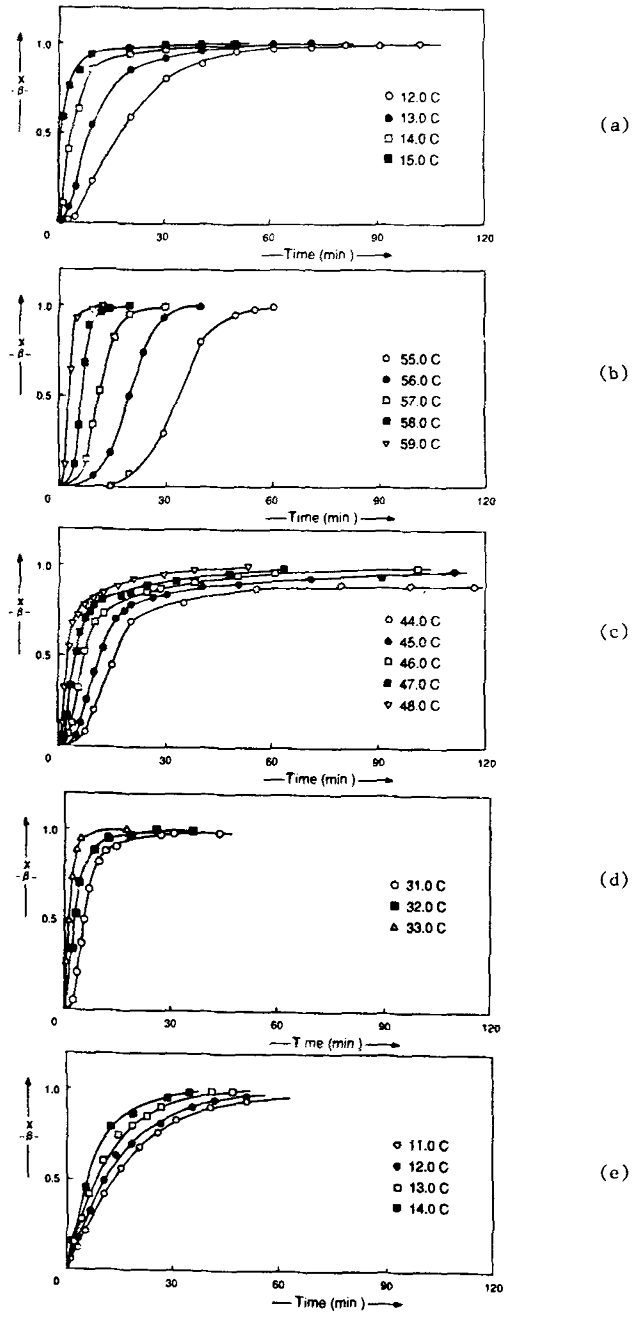

FIG. 7. Kinetics of the global processus of $\beta' \rightarrow \beta$ transition recorded for EEE, SSS, PPP, MMM and LLL.

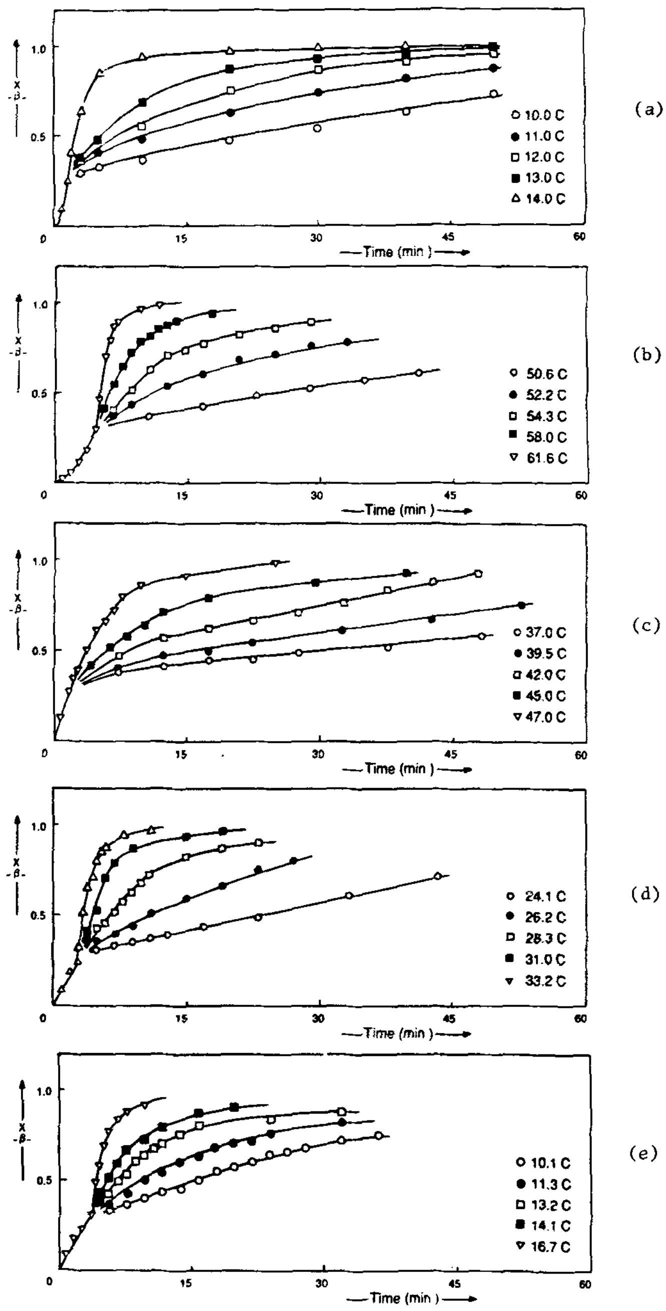

FIG. 8. Isolating method performed for EEE, SSS, PPP, MMM and LLL.

lows us to see that EEE and OOO, for an accurate composition of 5% into SSS, have the same destabilizing effect on the global transformation and on the β'/β interface progression; this phenomenon is even more pronounced for OOO. In fact, due to the very low intersolubility of SSS and OOO (less than 2%), the mixture in 95/5 proportion contains about 3% of pure OOO liquid, which acts as a solvent, accelerating the $\beta' \rightarrow \beta$ transition. EEE is only present as in impurity into the mixed crystal which destabilizes the β' form.

Special behaviors of pure OOO and of EEE 95%/OOO 5% mixture (Fig. 11). The same type of thermal treatment has been applied to pure OOO and to EEE/OOO 95/5 binary mixture; a special behavior appears for those two samples. For OOO, a biphasic behavior is detected at low temperatures, and it disappears when the temperature is increased. This phenomenon could be related to the existence of more than one β' polymorphic form for OOO as, described by Hagemann et al. (31). Considering that at least two β' polymorphic forms (β'_1 and β'_2) could be stable under these conditions, a competition between $\beta'_1 \rightarrow \beta'_2$ and $\beta'_{1 \text{ or } 2} \rightarrow \beta$ trans-

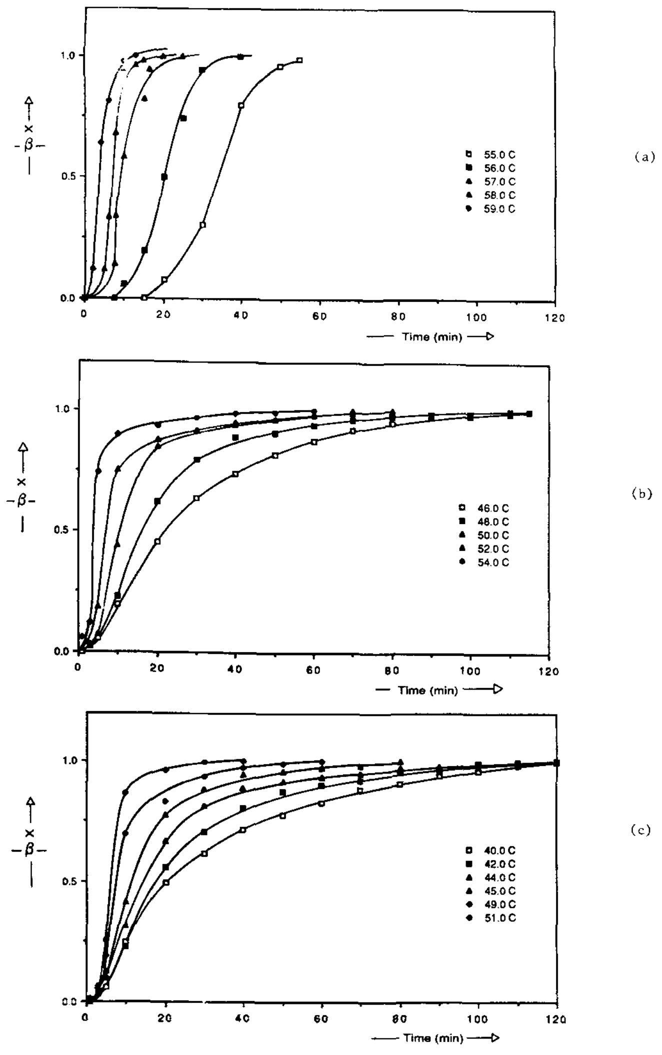

FIG. 9. Kinetics of the global processus of $\beta' \rightarrow \beta$ transition recorded for a) SSS, b) SSS/EEE (95/5) and c) SSS/OOO (95/5).

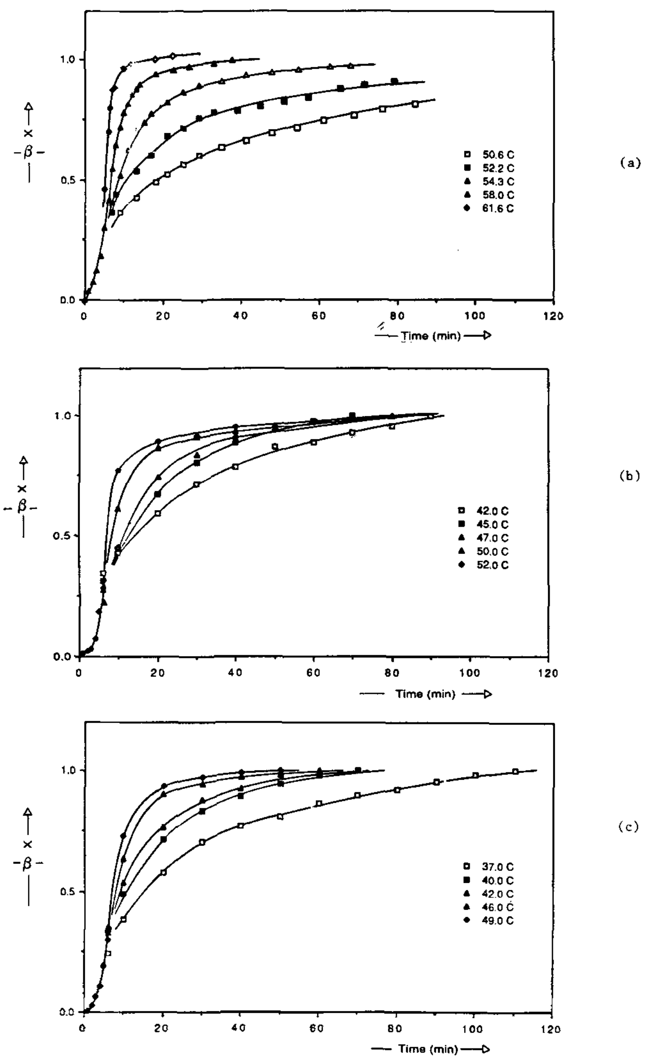

FIG. 10. Isolating method performed for a) SSS, b) SSS/EEE (95/5) and c) SSS/OOO (95/5).

TABLE 7

"n", "E"$_a$ and "E"$_i$ Values for SSS and the Mixtures SSS/EEE (95/5) and SSS/OOO (95/5)

Compound	"n"	"E"$_a$ (kcal.mol^{-1})	"E"$_i$ (kcal.mol.$^{-1}$)
SSS	3.0	82	55
SSS 95%—EEE 5%	1.4	27	20
SSS 95%—OOO 5%	1.6	20	12

The estimated standard deviation is 5 kcal.mol^{-1} for the "E"$_a$ values and 3 kcal.mol^{-1} for the "E"$_i$ values.

formations could occur; β'_1 could transform more rapidly into β than β'_2 nuclei, and the first phenomenon could be favored at higher temperatures.

In the global transformation analysis of EEE/OOO 95/5 system, the period of nuclei formation follows a normal kinetics according to the temperature. This phenomenon is not observed for the period of nuclei growth (β fraction = 30%), which shows a clear overlapping of different curves without any obvious logic. In those proportions, the solubility of OOO in EEE is total. As we have seen before, EEE can fit to saturated and *cis*-unsaturated monoacid triglycerides; it is obvious that what is observed for OOO can be transmitted to the mixed crystal, essentially constituted by EEE. A simple $\beta'_1 \rightarrow \beta$ transformation could begin which could be followed by a tendency of the

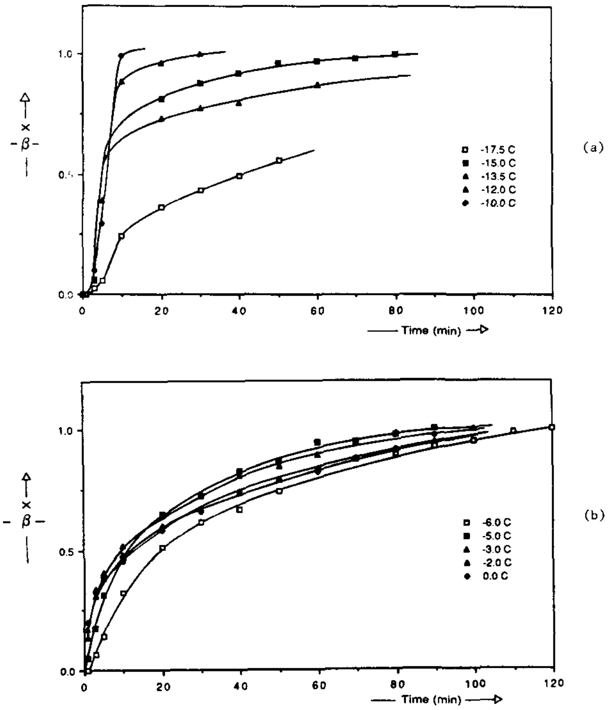

FIG. 11. Kinetics of the global processus of $\beta' \rightarrow \beta$ transition recorded for a) OOO and b) EEE/OOO (95/5).

mixed crystal to be transformed into a β'_2 polymorphic form.

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