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Conformational influences of the polymorphic forms on the C=O and C–H stretching modes of five saturated monoacid triglycerides studied by Raman spectroscopy at various temperatures

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Abstract

A study of the vibrational behavior of five saturated monoacid triacylglycerides is performed by Raman spectroscopy at various temperatures in two separate spectral ranges: 1780–1700 and 3100–2650 cm^{-1}. The samples are studied in polycrystalline phase at room temperature, in isotropic liquid phase, and in polycrystalline phase after cooling from the isotropic liquid phase. The C=O stretching mode of these triglycerides changes significantly according to the temperature: we observe three components, or an unresolved doublet, or a resolved doublet. The $I(2845)/I(2880)$ ratios (in the C–H stretching spectral region) of the different saturated monoacid triglycerides vary also according to the temperature. The study of these two indicators (the C=O stretching mode and the $I(2845)/I(2880)$ ratio) has permitted us to determine the polymorphic forms of the studied triglycerides.

Keywords: Triacylglycerides; Raman spectroscopy; Low-density lipoproteins; C=O and C–H stretching modes; Polymorphic forms

1. Introduction

Lipids, the scientific name for fats, form an important class of biological molecule found universally in all higher living organisms. Triglycerides characterize one of the most important classes of lipids. They are the main constituents of fats present in foods, pharmaceuticals, and cosmetics. Triglycerides are esters of trihydroxy alcohol glycerol. They show complicated polymorphism depending on the fatty acid compositions (saturated or unsaturated acids, short or chain acids and so on) [1,2].

In the case of triglycerides, three main polymorphic states (α, β′, and β), which have different melting points, have been determined [3–5]. X-ray diffraction analyses show that these three forms are characterized by three different subcells in polycrystalline phase: hexagonal for the α form, orthorhombic for the β′ form and triclinic for the β form [1,6,7]. Two different space arrangements of triglycerides in crystals exist: the tuning fork form and the chair form. The disposition and the orientation of the molecules in polycrystalline phase differ according to the polymorphic state. In Figs. 1 and 2, we introduce these differences when the interlocking between two molecules is performed on a length equal to a double or triple alkyl chain length of the studied triglyceride. Thus, the α and β′ forms are characterized by a tuning fork, but with a different chain orientation: vertical for the α form and titled for the β′ form; whereas for the β form the molecules of triglycerides are in stacked chair form with a titled chain orientation. In Table 1, we summarize the different characteristics of triglyceride polymorphs obtained by X-ray diffraction analyses. In order to complete our description, we introduce the cross-sectional structures of triglycerides in Fig. 3.

In a previous work [8], we have presented the systematic Raman studies of five different saturated monoacid triacylglycerides in the 3100–500 cm^{-1} spectral range at room tempera-

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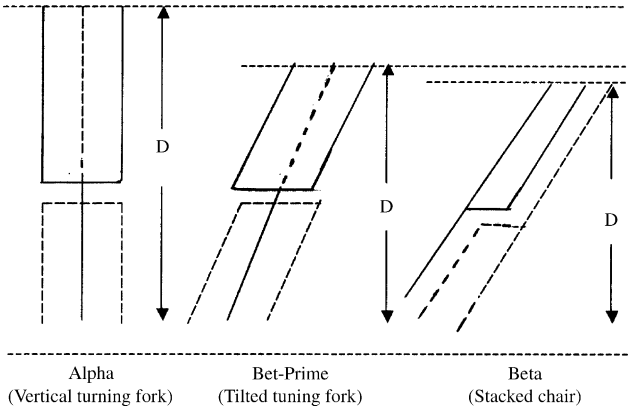

Fig. 1. Double chain length structures of triglycerides for the α, β′ and β forms.

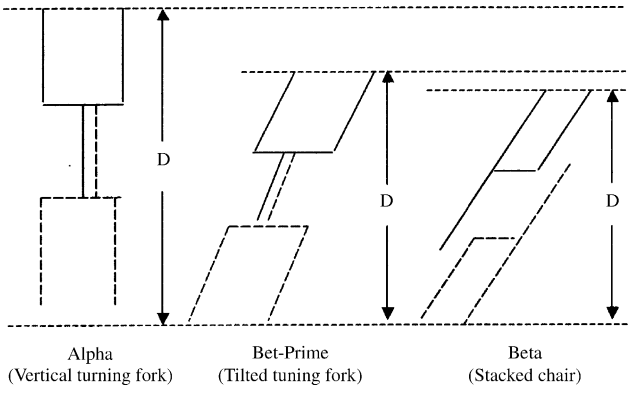

Fig. 2. Triple chain length structures of triglycerides for the α, β′ and β forms.

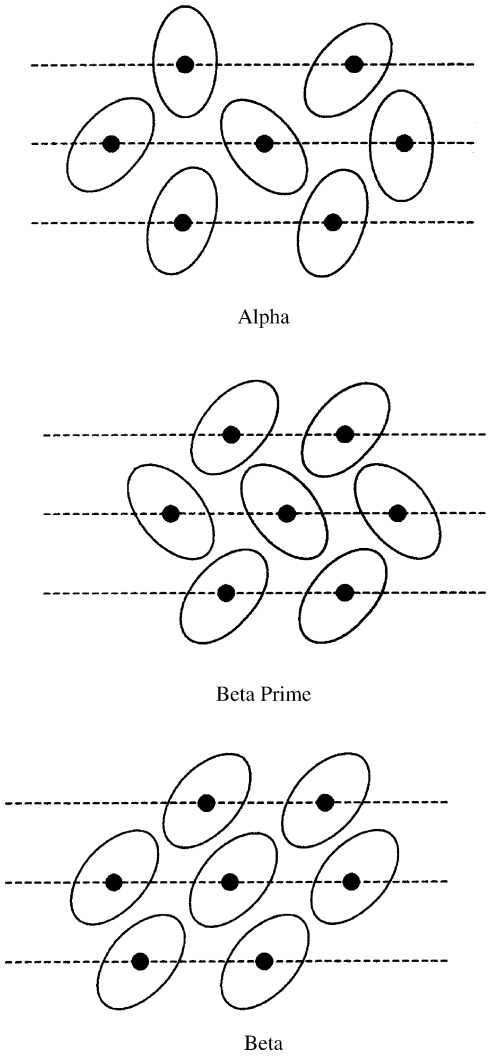

Fig. 3. Cross-sectional structures of triglycerides. The molecules are randomly ordered in the α form, in-between in the β′ form and are highly ordered in the β form.

ture: triacetin ($n = 2$), triundecanin ($n = 11$), trilaurin ($n = 12$), trimyristin ($n = 14$) and tripalmitin ($n = 16$). Our results demonstrated that in view of their C=O vibrational behaviors, the tripalmitin, the trimyristin and the trilaurin at room temperature were in the same type of polymorphic form, whereas the triundecanin presented another polymorphic form. By comparing Simpson's results with our measurements of the $I(2845)/I(2880)$ ratios of intensity (in the C–H stretching spectral region), the vibrational behavior of the alkyl chain seemed to show that, at room temperature, the tripalmitin and the trilaurin were in the β'_2 form, the trimyristin was in the β'_1 form, whereas the triundecanin was in the α form [6]. However, we have concluded that only a Raman temperature study should confirm these hypotheses.

In order to confirm that the three carbonyl groups O–C=O and the three alkyl chains can be chosen as two privileged witnesses of the triglyceride polymorphic forms, we introduce, in this paper, the Raman study of five different saturated monoacid triglycerides at various temperatures: tripelargonin

Table 1
X-ray diffraction analyses for triglycerides

X-ray diffraction	α form	β′ form	β form
Subcell	Hexagonal (H)	Orthorhombic ($O_\perp$)	Triclinic ($T_\parallel$)
Disposition	Tuning fork	Tuning fork	Chair form
Orientation	Vertical chain	Titled chain	Titled stacked chair
Angles	Acyl groups are oriented at 90° to the plane of the glyceryl group	Acyl groups are titled about 68–70° from the plane of the glyceryl group	Acyl groups are titled about 59° from the plane of the glyceryl group
Arrangements	Longest long spacing Randomly ordered Most loosely packed	Intermediate long spacing In-between More closely packed	Shortest long spacing Highly ordered Most closely packed

Table 2
Melting points of the studied saturated monoacid triglycerides

Polycrystalline phase (≥99% of purity)	Polymorphic form (°C)		
	α form	β′ form	β form
Tripalmitin ($n = 16$) [1]	46	54	66
Trimyristin ($n = 14$) [1]	32	45	57
Trilaurin ($n = 12$) [1]	15	34	46
Triundecanin ($n = 11$) [1]	4	28	31
Tripelargonin ($n = 9$) [1]	−30	7	10

Isotropic liquid phase	Melting point (°C)
Tripalmitin ($n = 16$)	72
Trimyristin ($n = 14$)	68
Trilaurin ($n = 12$)	62
Triundecanin ($n = 11$)	35

The measurements of the isotropic liquid melting points are performed during our own Raman experiments.

($n = 9$), triundecanin ($n = 11$), trilaurin ($n = 12$), trimyristin ($n = 14$) and tripalmitin ($n = 16$). Assuming that the C=O double bonds and the C–H stretching modes play a major role in identifying the polymorphic forms, we concentrated on two separated spectral ranges: 1780–1700 and 3100–2650 cm^{-1}. In this paper, we introduce the detailed studies of these two spectral ranges characterizing the vibrational behavior of these five saturated monoacid triglycerides.

2. Presentation of material

Raman spectroscopy measurements were performed in a backscattering microconfiguration using the 514.5 nm line from an Ar-ion laser focused on the surface on a spot of 1 μm in diameter and with a power density of ≈20 kW/cm^2. The scattered light was analyzed with a Jobin Yvon T64000 spectrometer, equipped with a liquid nitrogen cooled CCD detector. The spectrometer provided a wave number resolution better than 3 cm^{-1}. The Raman spectra were recorded in parallel polarization where the incident and the scattered light are parallel.

The five different triacylglycerides were supplied by ALDRICH-SIGMA-FLUKA with a degree of purity higher than 99%. In Table 2, we present the polymorphic temperatures and the melting point in isotropic liquid phase of these triglycerides [1]. At room temperature, the tripalmitin, trimyristin and trilaurin are in the powder form, whereas the tripelargonin is in isotropic liquid phase, and the triundecanin is crystallized. We have simply taken the samples as received from the supplier and run in the spectrometer.

3. Results and discussion

The Raman spectra of various saturated monoacid triglycerides in the 1780–1700 cm^{-1} spectral range are shown in polycrystalline phase at room temperature in Fig. 4, in polycrystalline phase after cooling from the isotropic liquid phase in Fig. 5, and in isotropic liquid phase in Fig. 6. The frequency values of the C=O stretching mode are presented in Table 3. The frequency values are obtained by Lorentzian

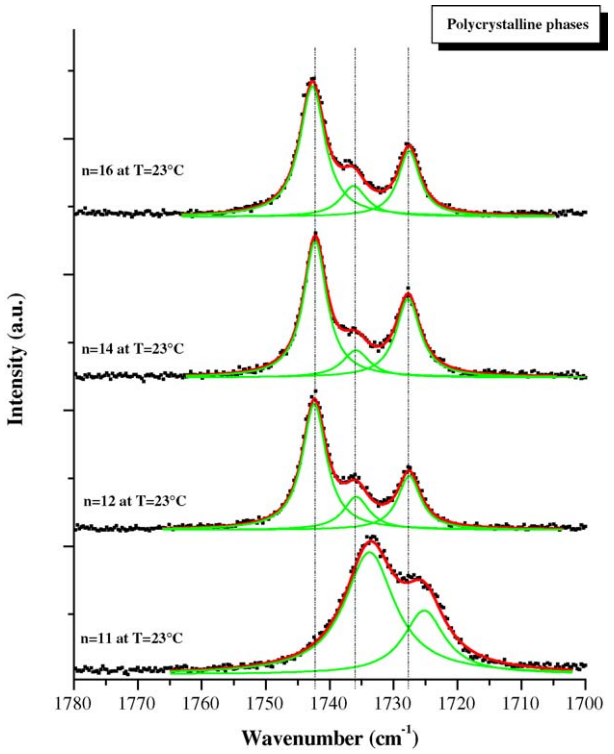

Fig. 4. Raman spectra of the C=O stretching mode for the tripalmitin ($n = 16$), trimyristin ($n = 14$), trilaurin ($n = 12$), triundecanin ($n = 11$) in polycrystalline phase at room temperature. The solid lines represent the components fitted by Lorentzian functions.

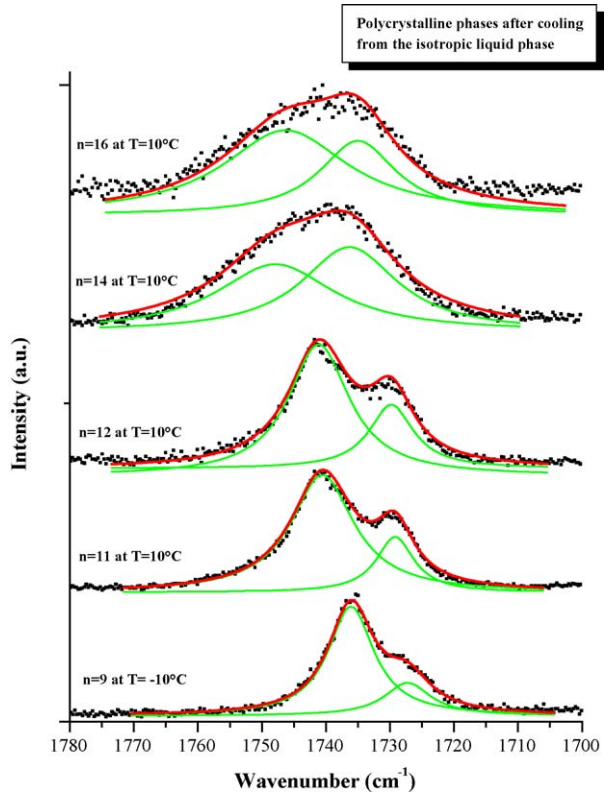

Fig. 5. Raman spectra of the C=O stretching mode for the tripalmitin ($n = 16$), trimyristin ($n = 14$), trilaurin ($n = 12$), triundecanin ($n = 11$) and tripelargonin ($n = 9$) in polycrystalline phase after cooling from the isotropic liquid phase. The solid lines represent the components fitted by Lorentzian functions.

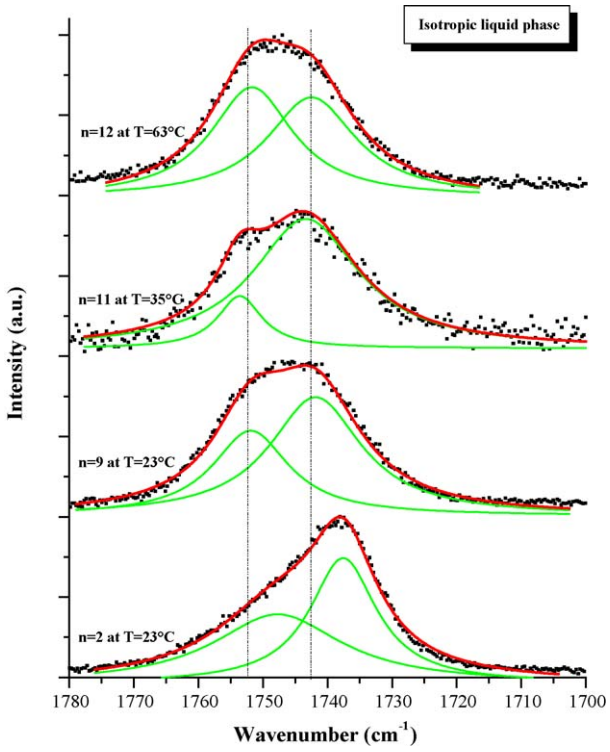

Fig. 6. Raman spectra of the C=O stretching mode for the trilaurin ($n = 12$), triundecanin ($n = 11$), tripelargonin ($n = 9$) and triacetin ($n = 2$) in isotropic liquid phase. The solid lines represent the components fitted by Lorentzian functions.

Table 3
The frequency values of the C=O stretching mode for the studied triglycerides when the samples are in polycrystalline phase at room temperature, in isotropic liquid phase, in polycrystalline phase after cooling from the isotropic liquid phase

Polycrystalline phase, $T = 23$ °C	The C=O stretching mode		
	ν_1	ν_2	ν_3
Tripalmitin ($n = 16$)	1728	1736*	1743
Trimyristin ($n = 14$)	1728	1736*	1742
Trilaurin ($n = 12$)	1728	1736*	1742
Triundecanin ($n = 11$)	1725*	1734	–
	ν_1		ν_2
Isotropic liquid phase			
Tripalmitin ($n = 16$), $T = 75$ °C	1743*		1753*
Trimyristin ($n = 14$), $T = 70$ °C	1743*		1752*
Trilaurin ($n = 12$), $T = 63$ °C	1743*		1752*
Triundecanin ($n = 11$), $T = 35$ °C	1743*		1753*
Tripelargonin ($n = 9$), $T = 23$ °C	1742*		1752*
Triacetin ($n = 2$), $T = 23$ °C	1738		1747*
Polycrystalline phase after cooling from the liquid phase			
Tripalmitin ($n = 16$), $T = 10$ °C	1735*		1747*
Trimyristin ($n = 14$), $T = 10$ °C	1736*		1748*
Trilaurin ($n = 12$), $T = 10$ °C	1729*		1741*
Triundecanin ($n = 11$), $T = 10$ °C	1729*		1741*
Tripelargonin ($n = 9$), $T = -10$ °C	1727*		1736*

In the case where the C=O stretching mode cannot be pointed, we have kept the fitted frequency value. These fitted frequency values are labeled *.

functions fit with a possible error of ± 0.5 cm^{-1} and are labeled with an asterisk (*).

At first, we concentrate on Figs. 4 and 5. We can observe that in the cases of $n = 12$, 14, 16 at room temperature, the C=O stretching mode possesses three components; whereas in the polycrystalline phase after cooling from the isotropic liquid phase, the C=O stretching mode of $n = 9$, 11, 12, 14, 16 is split into only two components. In a previous work [8], we have indicated that the observed splitting of the C=O stretching mode into two or three components revealed the existence of two or three geometries of C=O in the "knot" group O–C=O. So, it would seem that for $n = 12$, 14, 16 the arrangement of the molecules in the crystalline cell at $T = 23$ °C is different than at $T = 10$ °C after cooling the sample from the isotropic liquid phase. Therefore, the vibrational behaviors of the trilaurin, trimyristin and tripalmitin in the C=O spectral range lead us to conclude that their polymorphic forms change during the two Raman experiments ($T = 23$ and 10 °C after cooling). Moreover, we can note that for some saturated monoacid triglycerides the phase transitions are monotropic: we do not observe the same phases on heating as on cooling.

If we observe the C=O stretching mode for $n = 9$, 11, 12, 14, 16 in Fig. 5, we note that for $n = 14$, 16 the observed doublet is unresolved whereas for $n = 9$, 11, 12 it is resolved. This slight difference expresses through the frequency values of the C=O stretching mode: for $n = 11$, 12 the two components correspond to 1729 and 1741 cm^{-1} frequency values whereas for $n = 14$, 16 one measures 1736 and 1748 cm^{-1}. However, it must not be forgotten that the triglyceride molecule possesses three O–C=O carbonyl groups. Therefore, in polycrystalline phase, there can exist a priori three different bond angles for the three C=O double bonds, inducing three components for the C=O stretching mode. This phenomenon is observed for $n = 12$, 14, 16 at room temperature. The three components are centered to 1728, 1736 and 1742 cm^{-1}, labeled, respectively, ν_1, ν_2 and ν_3. When we observe two components for the C=O stretching mode, it means that from the three C=O double bonds, two of them have the same position in the crystalline cell with the same C=O frequency value. So, we can express the results presented in Table 3 in this way: at $T = 23$ °C, for $n = 12$, 14, 16 the three components of the C=O stretching mode correspond to ν_1, ν_2 and ν_3 whereas for $n = 11$ the two components are ν_1 and ν_2 with a lessening of 3 cm^{-1}. At $T = 10$ °C after cooling, the C=O stretching mode of triundecanin and trilaurin is split into ν_1 and ν_3 while for $n = 14$, 16 we observe the ν_2 and ν_3 components with an increase of 5 cm^{-1} for ν_3. At $T = -10$ °C, the tripelargonin possesses two components ν_1 and ν_2 for the C=O stretching mode with a lessening of 2 cm^{-1} for ν_1 and 5 cm^{-1} for ν_2 in comparison with the case of $T = 23$ °C.

In Fig. 6, the triglycerides studied are in isotropic liquid phase. We note that the behavior of the C=O stretching mode is different from the polycrystalline phase. In the polycrystalline phase, we have noticed the C=O stretching mode splitting into three or two components; in the isotropic liquid phase, we observe only two components for this mode for $n = 9$, 11, 12, 14, 16, centered near 1742 and 1752 cm^{-1} (see Table 3). Again, we find the two components ν_2 and ν_3 with an increase of 7–

10 cm^{-1}. Moreover, this frequency growth can be explained by the fact that in the first approximation, in isotropic liquid phase, the molecules should not be subjected to the conformational constraints induced by the packing in the unit cell. In contrary to $n = 9, 11, 12, 14, 16$, for $n = 2$ in isotropic liquid phase, we observe an increase of only 2–5 cm^{-1} for the two components ν_2 and ν_3. Considering mass effects, we know that the vibrational frequency is inversely proportional to the square root of the masses for a diatomic oscillator [9]. This means that for $n = 2$ the drop of the frequency values of the C=O stretching mode in comparison with $n = 9, 11, 12, 14, 16$ can be interpreted as an indirect mass effect induced by a significant fall of the alkyl chain length.

The study of the vibrational behavior of the C=O stretching mode for various saturated monoacid triglycerides at various temperatures suggests to us that the difference between the polymorphic forms is linked to the number of components for the C=O stretching mode (two or three components) and the different frequency values (ν_1, ν_2 and ν_3).

From a Raman study of the tristearin ($n = 18$) at room temperature, Simpson [6] indicates that the ratio of the intensities of the band at 2850 cm^{-1} to that at 2880 cm^{-1} does distinguish the triglyceride phases. So, we introduce the Raman spectra of our various saturated monoacid triglycerides at various temperatures in the 3100–2650 cm^{-1} spectral range in Figs. 7 and 8. The 3100–2650 cm^{-1} spectral range characterizes the various C–H stretching modes with their symmetry properties. Between these two figures, we observe a significant evolution in intensity of the CH_2 symmetric stretching mode at 2845 cm^{-1} in comparison with the CH_3 symmetric stretching mode at 2880 cm^{-1} for the three samples ($n = 12, 14, 16$) at various temperatures. As for the C=O stretching mode, the CH_2 symmetric stretching mode at 2845 cm^{-1} and the CH_3 symmetric stretching mode at 2880 cm^{-1} seem to be witness of the polymorphic form. In Table 4, we present the relative intensity corresponding to the $I(2845)/I(2880)$ ratio between the maximal intensity $I(2845)$ of the CH_2 symmetric stretching mode and the maximal intensity $I(2880)$ of the CH_3 symmetric stretching mode at $T = 23$ and 10 °C or $T = -10$ °C after cooling from the isotropic liquid phase. We note that at $T = 23$ °C the $I(2845)/I(2880)$ ratio seems to be the same between the tripalmitin and the trimyristin (0.46 and 0.42) but differs with the trilaurin (0.52). In comparison with $n = 12, 14, 16$, the triundecanin is distinguished by a higher $I(2845)/I(2880)$ ratio (0.80). At $T = 10$ °C after cooling, on the one hand, this ratio for $n = 12, 14, 16$ is subjected to a significant increase (from 0.50 in average to 0.90) on the other hand, in contrast to $T = 23$ °C, the triundecanin, trilaurin, trimyristin and tripalmitin have practically the same $I(2845)/I(2880)$ ratio. This standardization after cooling has been already observed for the C=O stretching mode. Therefore, this seems to confirm that after cooling, the triundecanin, trilaurin, trimyristin and tripalmitin

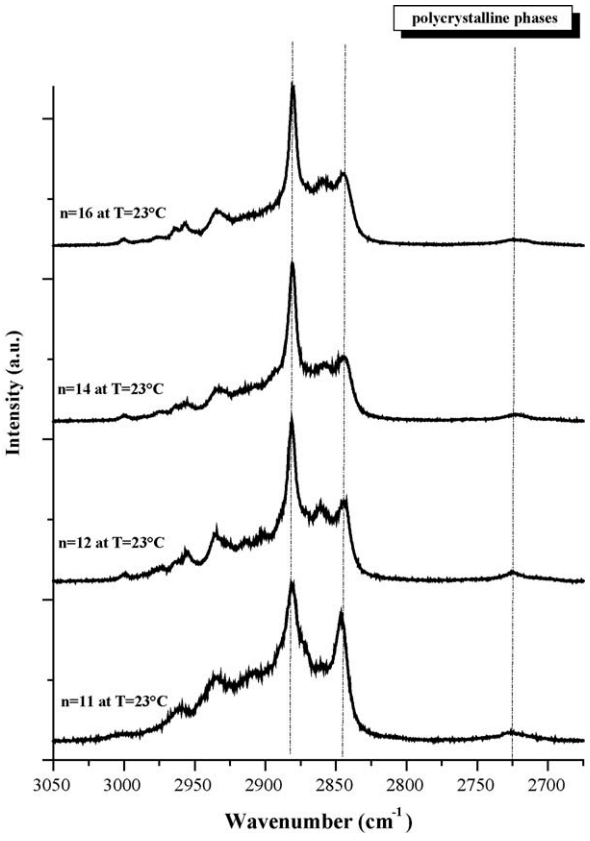

Fig. 7. Raman spectra of the C–H stretching modes for the tripalmitin ($n = 16$), trimyristin ($n = 14$), trilaurin ($n = 12$), triundecanin ($n = 11$) in polycrystalline phase at room temperature.

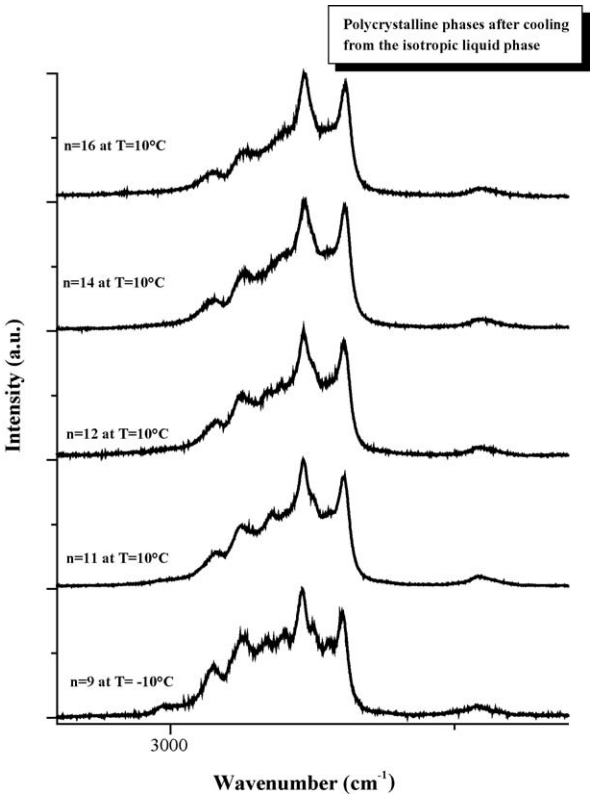

Fig. 8. Raman spectra of the C–H stretching modes for the tripalmitin ($n = 16$), trimyristin ($n = 14$), trilaurin ($n = 12$), triundecanin ($n = 11$) and tripelargonin ($n = 9$) in polycrystalline phase after cooling from the isotropic liquid phase.

Table 4
A comparison of the $I(2845)/I(2880)$ intensity ratio of the maximal intensity $I(2845)$ of the CH_2 symmetric stretching mode and the maximal intensity $I(2880)$ of the CH_3 symmetric stretching mode with Simpson's results and according to the temperature

	$I(2845)/I(2880)$
Polycrystalline, $T = 23$ °C	
Tripalmitin ($n = 16$)	0.46
Trimyristin ($n = 14$)	0.42
Trilaurin ($n = 12$)	0.52
Triundecanin ($n = 11$)	0.80
Polycrystalline after cooling from the liquid phase	
Tripalmitin ($n = 16$), $T = 10$ °C	0.90
Trimyristin ($n = 14$), $T = 10$ °C	0.93
Trilaurin ($n = 12$), $T = 10$ °C	0.91
Triundecanin ($n = 11$), $T = 10$ °C	0.87
Tripelargonin ($n = 9$), $T = -10$ °C	0.81

	β form	β'_1 form	β'_2 form	α form
Simpson [6]				
Tristearin ($n = 18$)	0.45	0.54	0.62	0.69

are in the same polymorphic form. At $T = 10$ °C, the tripelargonin possesses the same $I(2845)/I(2880)$ ratio as the triundecanin at $T = 23$ °C.

A comparison between our $I(2845)/I(2880)$ ratios with Simpson's results suggests that, at room temperature, the tripalmitin and the trimyristin are in the β form, the trilaurin is in the β'_1 form, whereas the triundecanin is in the α form. Moreover, at room temperature, we observe two components for the triundecanin C=O stretching mode, whereas for $n = 12$, 14, 16 there exist three components of the C=O stretching mode. The number of components is linked to the conformational constraints induced by the packing in the unit cell. The greater the geometric constraints, the greater the number of the components (equal to three at the most). From X-ray analyses, we know that the molecules are loosely packed in the α form, whereas they are more closely packed in the β' and β forms [7]. So, at room temperature, our results on the C=O stretching mode for $n = 11$, 12, 14, 16 coupled with our $I(2845)/I(2880)$ ratios are in agreement with Simpson's results. That is why we can conclude that, on the one hand if the C=O stretching mode of a saturated monoacid triglyceride is split into three components these molecules are packed in the β' or β forms, whereas two components for the C=O stretching mode reflect the α form in polycrystalline phase. On the other hand, the more the arrangement of the molecules in the crystalline cell is ordered, the lower the $I(2845)/I(2880)$ ratio: from Simpson's results we have an $I(2845)/I(2880)$ ratio of 0.69 in the α form, 0.54 in the β'_1 form and 0.45 in the β form.

Then, from these results, we can interpret our experimental results when the samples have been cooled from the isotropic liquid phase. In Fig. 5, we observe two components for the C=O stretching mode for $n = 9$, 11, 12, 14, 16. So, after cooling from the isotropic liquid phase, the tripelargonin, triundecanin, trilaurin, trimyristin and tripalmitin seem to be in the α form. However, only the $I(2845)/I(2880)$ ratio of the tripelargonin (0.81) corresponds to that of the triundecanin at room temperature. For $n = 11$, 12, 14, 16, the $I(2845)/I(2880)$ ratios are greater and are equal approximately to 0.90. This implies that after cooling from the isotropic liquid phase, the molecules of the triundecanin, trilaurin, trimyristin and tripalmitin are packed in the α form but they are less ordered in the crystalline cell than the tripelargonin. This can be explained by a different arrangement in the cell: for the pelargonin the interlocking between two molecules seems to be performed on a length equal to a double whereas for $n = 11$, 12, 14, 16, the triple alkyl chain length is used. The geometric constraints are less important when the unit cell is stretched.

4. Conclusion

We have presented the systematic Raman studies of five saturated monoacid triglycerides in two separated spectral ranges: the 1780–1700 and 3100–2650 cm^{-1} ranges at various temperatures. In the 1780–1700 cm^{-1} spectral range, our experimental results show that the vibrational behavior of the three carbonyl groups O–C=O depends on the temperature. The C=O stretching mode is split into two or three components with some variations of the frequency value according to the triglyceride and the temperature. In the 3100–2650 cm^{-1} spectral range, the $I(2845)/I(2880)$ ratios of the different saturated monoacid triglycerides vary significantly according to the temperature. Thus, the C=O stretching mode and the $I(2845)/I(2880)$ ratio are revealed to be two good tools to identify the polymorphic forms of these molecules. From our results, we have been able to conclude that if the C=O stretching mode of a saturated monoacid triglyceride is split into three components these molecules are packed in the β' or β forms, whereas two components for the C=O stretching mode reflect the α form in polycrystalline phase. The second important result concerns the $I(2845)/I(2880)$ ratio labeled η: the more the arrangement of the molecules in the crystalline cell is ordered, the lower the $I(2845)/I(2880)$ ratio. From a comparison between Simpson's results and our Raman results, we can note that if $\eta < 0.50$ the molecules of the studied saturated monoacid triglyceride are packed in the β form; if $0.50 < \eta < 0.70$ the molecules are packed in the β' form; and if $0.70 < \eta$ the triglyceride is in the α form. We must remark that the vibrational behavior of the carbonyl group does not permit determining the β' form or the β form. At room temperature, for $n = 12$, 14, 16 the C=O stretching mode is the same whereas the trilaurin seems to be in the β' form, and the trimyristin and tripalmitin are in the β form.

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