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In situ crystallization and transformation kinetics of polymorphic forms of saturated-unsaturated-unsaturated triacylglycerols: 1-palmitoyl-2,3-dioleoyl glycerol, 1-stearoyl-2,3-dioleoyl glycerol, and 1-palmitoyl-2-oleoyl-3-linoleoyl glycerol

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ABSTRACT

We examined the influence of dynamic thermal treatment (variation of cooling/heating rates) on the polymorphic crystallization and transformation pathways of 1-palmitoyl-2,3-dioleoyl glycerol (POO), 1-stearoyl-2,3-dioleoyl glycerol (SOO), and 1-palmitoyl-2-oleoyl-3-linoleoyl glycerol (POL), which are major saturated-unsaturated-unsaturated (SUU) triacylglycerols (TAGs) of vegetable oils and animal fats (e.g., palm oil, olive oil, and Iberian ham fat). Using mainly a combination of differential scanning calorimetry (DSC) and synchrotron radiation X-ray diffraction (SR-XRD), we analyzed the polymorphic behavior of TAGs when high (15 °C min^{-1}), intermediate (2 °C min^{-1}), and low (0.5 °C min^{-1}) cooling and heating rates were applied. Multiple polymorphic forms were detected in POO, SOO, and POL (sub-α, α, β'_2, and β'_1). Transient disordered phases, defined as kinetic liquid crystal (KLC) phases, were determined in POO and SOO for the first time. The results demonstrated that more stable forms were directly obtained from the melt by decreasing the cooling rates, whereas less stable forms predominated at high cooling rates, as confirmed in our previous work. Regarding heating rate variation, we confirmed that the nature of the polymorphic transformations observed (solid-state, transformation through KLC phase, or melt-mediation) depended largely on the heating rate. These results were discussed considering the activation energies involved in each process and compared with previous studies on TAGs with different saturated-unsaturated structures (1,3-dioleoyl-2-palmitoylglycerol, 1,3-dipalmitoyl-2-oleoyl-glycerol, trioleoyl glycerol, and 1,2-dioleoyl-3-linoleoyl glycerol).

1. Introduction

Lipids are major nutrients and are widely employed as lipophilic materials in food, pharmaceutical, and cosmetic industries (Larsson, Quinn, Sato, & Tiberg, 2006). Triacylglycerols (TAGs) are the main components of natural and industrial fats and oils, and their polymorphism greatly influences the physical properties (e.g., morphology, rheology, texture, and melting) of lipid-based end products. In addition to the chemical nature of the fatty acid components (chain length, saturated/unsaturated, and cis or trans double bonds) and the connection of these fatty acids to the glycerol structure, the use of specific external factors (Sato, Bayés-García, Calvet, Cuevas-Diarte, & Ueno, 2013; Bayés-García, Patel et al., 2015) strongly influences the polymorphic crystallization and transformation of TAGs (e.g., the use of additives (Smith, Bhaggan, Talbot, & van Malssen, 2011), shear (Mazzanti, Li, Marangoni, & Idziak, 2011), sonication (Ueno, Ristic, Higaki, & Sato, 2003; Chen, Zhang, Sun, Wang, & Xu, 2013; Ye & Martini, 2015) and emulsification (Wassell et al., 2012)). In addition, applying dynamic temperature variations permits the monitoring and controlling of the polymorphic behavior of TAGs, with the aim of obtaining desired product characteristics. Many studies have been conducted to characterize the effects of dynamic temperature variation, since the kinetic properties of polymorphic crystallization and transformation of TAGs (Smith, Cain, & Talbot, 2005; Bayés-García, Calvet, Cuevas-Diarte, Ueno, & Sato, 2011; Bouzidi & Narine, 2012; Bayés-García, Calvet, Cuevas-Diarte, Ueno, & Sato, 2013a, 2013b; Baker, Bouzidi, Garti, & Narine, 2014a, 2014b) and more complex lipid samples (Lopez, Lesieur, Bourgaux, & Ollivon, 2005; Tippets & Martini, 2009; Ronholt, Kirkensgaard, Pedersen, Moretensen, & Knudsen, 2012; Bayés-García, Calvet et al., 2015) are significantly influenced by cooling and heating rates. Recently, we reported on the effect of cooling rate on the polymorphic crystallization of unsaturated-saturated-unsaturated 1,3-dioleoyl-2-palmitoyl glycerol (OPO) (Bayés-García et al., 2011) and the effects of varying both cooling and heating rates on the polymorphic crystallization and transformation pathways of saturated-unsaturated-

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Table 1
Long and short spacing values of the POO, POL and SOO polymorphs.

	Long spacing/nm	Short spacing/nm
POO		
Sub-α	5.8 2.9	0.42 0.38
α	5.7 2.8	0.41
KLC	6.0	–
β'_2	6.7 3.2	0.43 0.41
β'_1	6.7 3.2	0.47 0.46 0.45 0.43 0.41 0.40 0.39
POL		
Sub-α	5.7 2.8	0.42 0.38
α	5.6 2.7	0.41
β'_2	6.3 3.1	0.42 0.38
β'_1	6.4 3.1	0.47 0.46 0.45 0.44 0.42 0.41 0.40 0.39
SOO		
Sub-α	6.2 3.0	0.42 0.38
α	6.0 2.9	0.41
KLC	6.7	–
β'_2	7.1 3.4	0.43 0.41
β'_1	6.9 3.3	0.47 0.45 0.43 0.42 0.41 0.40 0.39

saturated 1,3-dipalmitoyl-2-oleoyl (POP) (Bayés-García et al., 2013a), triunsaturated trioleoyl glycerol (OOO), and 1,2-dioleoyl-3-linoleoyl glycerol (OOL) (Bayés-García et al., 2013b). For that study, differential scanning calorimetry (DSC) and synchrotron radiation X-ray diffraction (SR-XRD) with small-angle (SAXD) and wide-angle (WAXD) simultaneous measurements were used. These techniques enabled in situ monitoring of the occurrence of complex polymorphic transformation even when high rates (15 °C/min) were applied.

In the present study, we used SR-XRD and DSC to dynamically follow the polymorphic crystallization and transformation kinetics of 1-palmitoyl-2,3-dioleoyl glycerol (POO), 1-stearoyl-2,3-dioleoyl glycerol (SOO), and 1-palmitoyl-2-oleoyl-3-linoleoyl glycerol (POL), which are major saturated-unsaturated-unsaturated (SUU) TAGs of lipid products (e.g., palm oil, olive oil, and Iberian ham fat).

Some previous research focused on the polymorphic characteristics of these TAGs. Miura and Konishi (2001) studied the crystallization of POO and some POO:POP mixtures, as they play important roles in the formation of granular crystals in margarine. In addition, Zhang, Ueno, Miura, and Sato (2007) determined the eutectic binary phase behavior of POP:POO in metastable and stable conditions, due to its practical importance in dry fractionation of palm oil. In these previous studies, only two polymorphic forms (α and β') of POO were observed. Later, Zhang, Ueno, Sato, Adlof, and List (2009) reported on the immiscible phase behavior of SOS:SOO binary mixtures, determining the presence of three SOO polymorphs (α, β'_2, and β'_1). Recently, Baker et al. (2014b) examined the effect of cooling rate on the polymorphism, thermal properties, and microstructure in symmetric and asymmetric TAGs containing stearic and oleic fatty acids (OSO and SOO). They observed that cooling rates have more limited effect on the phase behavior of asymmetric TAGs than on that of symmetric TAGs.

In the present work, we applied different thermal treatments to TAG samples (changing cooling/heating rates from 0.5 °C min^{-1} to 15 °C min^{-1}) to characterize a higher number of polymorphs (sub-α, α, β'_2, and β'_1). To the best of our knowledge, this is the first time that POL polymorphism has been reported. Considering the results of the present study as well as those of our previous work, we can compare the influence of kinetic factors (e.g., cooling/heating rates) on the polymorphic behavior observed in TAGs with different saturated-unsaturated structures (OPO, POP, OOO, OOL, POO, SOO, and POL).

2. Experimental

Samples of POO, SOO, and POL were purchased from Tsukishima Foods Industry (Tokyo, Japan) and used without further purification (purity > 99%). It should be noted that the samples were not enantiopure, as they consisted of the racemic mixture of corresponding enantiomers (R and S).

DSC experiments were conducted at atmospheric pressure using both a Perkin-Elmer DSC-7 and a Perkin-Elmer DSC Diamond. The DSC thermograms obtained by the two calorimeters were comparable. Samples (9.0 to 9.4 mg) were weighed into 50 μl aluminum pans, and covers were sealed into place. Both instruments were calibrated with reference to the enthalpy and the melting points of indium (melting temperature 156.6 °C; ΔH 28.45 J g^{-1}) and decane (melting temperature −29.7 °C; ΔH 202.1 J g^{-1}) standards. An empty pan was used as a reference. Dry

Table 2
DSC data of crystallization and transformation of POO polymorphs obtained by cooling rates of (A) 15 °C min^{-1}, (B) 2 °C min^{-1}, and (C) 0.5 °C min^{-1} and different heating rates. The letters, *c* and *m*, in parentheses noting polymorph forms mean crystallization and melting.

A	Cooling (15 °C min^{-1})		Heating (15 °C min^{-1})				
	α (*c*)	α → sub-α	sub-α → α	α (*m*)	β'_2 (*c*)	$\beta'_2 \rightarrow \beta'_1$	β'_1 (m)
T_{onset} (°C)	−20.4 ± 0.4	−62.9 ± 0.5	−65.8 ± 0.5	−44.0 ± 2.1	−16.3 ± 0.4	−6.6 ± 0.6	12.5 ± 0.5
ΔH (J/g)	−44 ± 1	−5 ± 1	9 ± <1	4 ± 1	−29 ± 1	−17 ± 2	111 ± 3
			(0.5 °C min^{-1})				
			sub-α ⇒ β'_1	β'_1 (*m*)			
T_{onset} (°C)			3.5 ± 2.3 (T_{end})	12.4 ± 0.3			
ΔH (J/g)			–	106 ± 21			

B	Cooling (2 °C min^{-1})		Heating (2 °C min^{-1})	
	α (*c*)	α → sub-α	sub-α ⇒ β'_1	β'_1 (*m*)
T_{onset} (°C)	−11.3 ± 1.6	–	−0.8 ± 3.7 (T_{end})	13.5 ± 0.9
ΔH (J/g)	−78 ± 2	–	–	109 ± 8

C	Cooling (0.5 °C min^{-1})	Heating (15 °C min^{-1})	
	$\beta'_2 + \beta'_1$ (*c*)	β'_2 (*m*)	β'_1 (*m*)
T_{onset} (°C)	7.3 ± 1.3	−4.5 ± 4	14.4 ± 1.5
ΔH (J/g)	−103 ± 4	1 ± <1	108 ± 5