Electronic Supplementary Information:

Phase behaviour of model triglyceride ternary blends: triolein, tripalmitin and tristearin

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1 FTIR characterisation of pure TAGs

Figure S1 reports the ATR-FTIR characterisation of the OOO, PPP and SSS over the entire spectral range, from 3200 to 500 cm^{-1}. In the main paper, Fig.2(b), we only reported the "fingerprint region" from 1200 to 600 cm^{-1}, to highlight the differences and shifts in the peak between 717 cm^{-1} and 720 cm^{-1}, descriptive of the specific crystalline α, β' or β cage. No major changes are observable in the other spectral regions between PPP and SSS (being structurally different only by six CH_2 group). In the CH region of OOO, the stretching ν_s of the CH_2-CH_3 end group shows lower absorbance and it is shifted to higher wavenumbers, indicating a loosen and less ordered conformational order due to the unsaturation in the oleic acid chains.

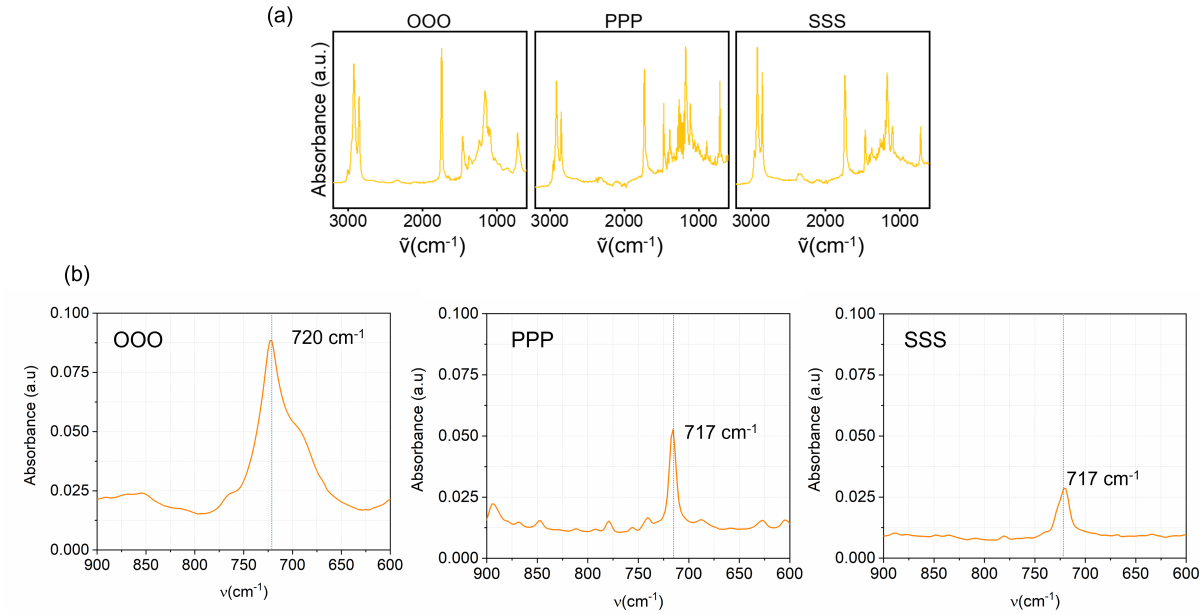

Figure 1: ATR-FTIR characterisation of the pure TAGs OOO, PPP and SSS (a) depicting the range 3200 to 500 cm^{-1} (b) displaying the position and highlighting the differences and shifts in the peaks between 720 cm^{-1} and 717 cm^{-1}

2 Binary blends melting enthalpies

DSC characterisation is an informative technique to extract not only the phase changing temperatures at melting or crystallisation, but also, by integration of the exothermic or endothermic peaks, provide additional information on the respective enthalpies involved in the phase transition and ultimately the energy involved in the process. In Fig.S2 we report the melting enthalpies ΔH_m, of the experimental binary blend (compositions reported in Tab.1 of the main paper) OOO-PPP, PPP-SSS and SSS-OOO, extracted from the DSC thermograms reported in Fig.3(a) of the main paper. Once the heat flow is normalised by the sample weight, the melting enthalpy is extracted by integrating the peak at the onset of melting. From Fig.S2, we can observe how generally the pure TAGs present higher ΔH_m. The reduction in ΔH_m when two pure TAGs are combined in a binary blend it is probably due to the disruption/alteration of the original pure polymorph crystal structure (more stable) towards less stable or mixed crystalline arrangements. As observed for the melting temperatures reported in Fig.4 of the main paper, ΔH_m for the α and β phases of OOO does not sensibly varies form the pure TAG form even at different ratios, therefore not forming any co-phase with the high melting components of the blend but just acting as a continuous demixed medium.

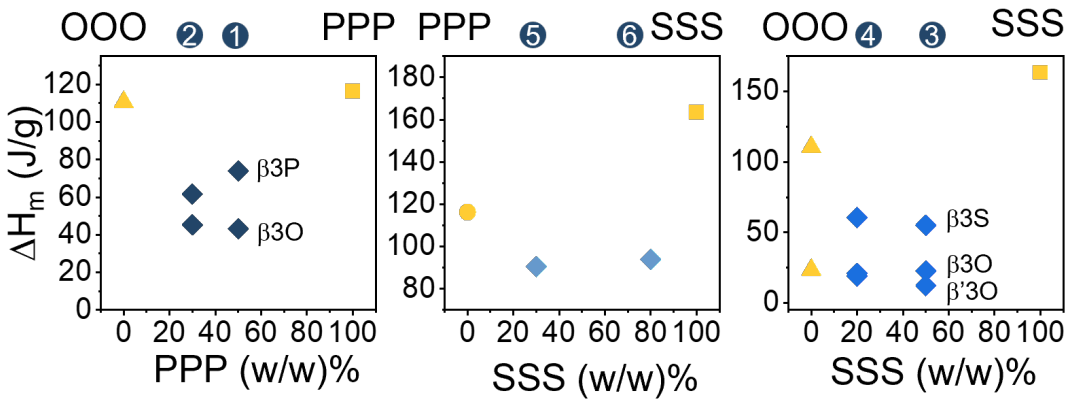

Figure 2: Experimental binary blends OOO-PPP, PPP-SSS and SSS-OOO melting enthalpies ΔH_m extracted from the DSC second heating thermograms reported in Fig.3(a) of the main paper.

3 Ternary blends composition

Table 1 reports in detail the weight fraction in OOO, PPP and SSS employed in the formation of the ternary blends reported in Fig.5 of the main paper. The blends were prepared by imposing a fixed PPP/SSS ratio of 1.5 and progressively increasing the amount of OOO, to evaluate the effect of the unsaturation on the physico-chemical of the blends.

blend	OOO	PPP	SSS
t1	0.001	0.666	0.333
t2	0.005	0.663	0.332
t3	0.01	0.66	0.33
t4	0.015	0.656	0.328
t5	0.02	0.653	0.326
t6	0.025	0.65	0.325
t7	0.03	0.646	0.323
t8	0.04	0.64	0.32
t9	0.05	0.633	0.316
t10	0.06	0.627	0.313
t11	0.07	0.62	0.31
t12	0.08	0.613	0.306
t13	0.1	0.6	0.3
t14	0.2	0.533	0.266
t15	0.3	0.466	0.233
t15(7)	0.333	0.333	0.333
t16	0.4	0.4	0.2
t17(8)	0.5	0.333	0.166
t18	0.6	0.266	0.133
t19	0.7	0.2	0.1
t20	0.8	0.133	0.066
t21	0.99	0.006	0.003

Table 1: Ternary blend compositions in w/w of OOO, PPP and SSS. t15 and t 17 in blue correspond respectively to blend 7 and blend 8, employed in structural XRD characterisation in Fig.5 of the main paper and VT-FTIR characterisation in Fig.7 of the main paper.

4 OOO-PPP-SSS ternary blend phase diagram

The first account of a compiled ternary phase diagram for OOO-PPP-SSS and in general TAGs ternary mixtures is the one reported by Kremann and Scoultz in 1912 [1]. The authors used a bottom-up approach, building the ternary phase diagram starting from binary mixtures data of the respective TAGs. The diagram, although very informative, was build acquiring the melting temperatures of the ternary blends, specifically by measuring an average melting temperature at the solid to liquid phase transition. From the XRD, DSC, VT-FTIR analysis reported in Fig.5 and Fig.7 of the main paper we can now affirm that although the blends visually appear in a liquid state above their melting temperatures, solid inclusions are still present even at 30 °C above the melting point, where solid solutions and relative phase changing are still acting. The authors, due to the poorer resolution of the characterisation technique and the unawareness of the polymorphic nature of TAGs, could not take into account and appreciate the more complex behaviour of these compounds. Still these simple experiments were able to track the eutectic found in the PPP-SSS binary blend, subsequently confirmed and more rigorously defined by Lutton et al [2]. Overall, the melting temperatures reported in this phase diagram agree with the one we found in our experiments, for the explored concentration range, and as well we identify a depression in the ternary space departing from the PPP-SSS eutectic. Nonetheless, the detailed phase characterisation we provided in our new representation of the system, reported in Fig.6 of the main paper, defines new phase boundaries, previously inaccessible, combining previous literature data and new experimental data acquired with more rigorous and updated procedures and resolutions.

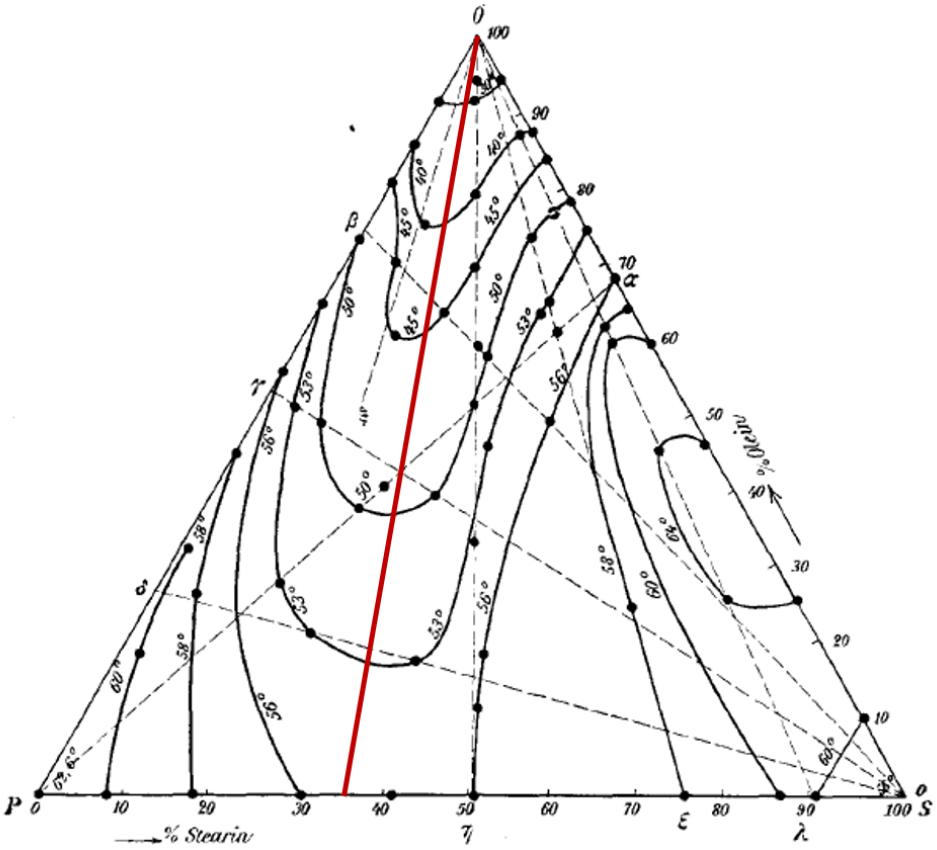

Figure 3: Ternary phase diagram from Kremann and Scoultz [1], published in 1912. The red line represents the cut explored in this paper in the OOO-PPP-SSS phase space.

5 Polarised optical microscopy of blend 8

To support the polimorphic nature of the TAGs ternary blends and to further investigate the melting behaviour, we performed polarised field optical microscopy on a case study blend, blend 8 (0.5:0.3:0.2 OOO:PPP:SSS). Polarised OM is a powerful tool to better visualise crystalline portions of materials due to the ability of crystals, as molecularly ordered materials, to double diffract light according to its polarisation, in a phenomenon defined as birefringence. Specifically a blend 8 sample was heated at 5 K/min after cooling at -40 °C (following the thermal program reported in Fig.1) up to 80 °C and imaged. The series of imaged reported in Fig. S4 shows the morphological changes of TAGs crystals and the solid to liquid transition. At -35 °C, the blend is entirely "solid", being under the crystallisation temperature of the lower melting component OOO. Progressively increasing the temperature, the dark area increase, indicating the "melting" of OOO crystals, leading dispersed PPP+SSS crystals in a continuous medium of OOO. Upon reaching the melting point of the blend, at 45 °C, more crystals approach melting, between 45 and 50 °C a solid phase changing takes place, with crystals changing shape from a semi-spherical less ordered spherulitic structures to a more ordered needle-like shape, typical of the orthorombinc and triclinic crystal cages typical of the β' and β forms respectively. The coexistence of solid and liquid fraction holds until 70 °C, where no more crystals can be observed.

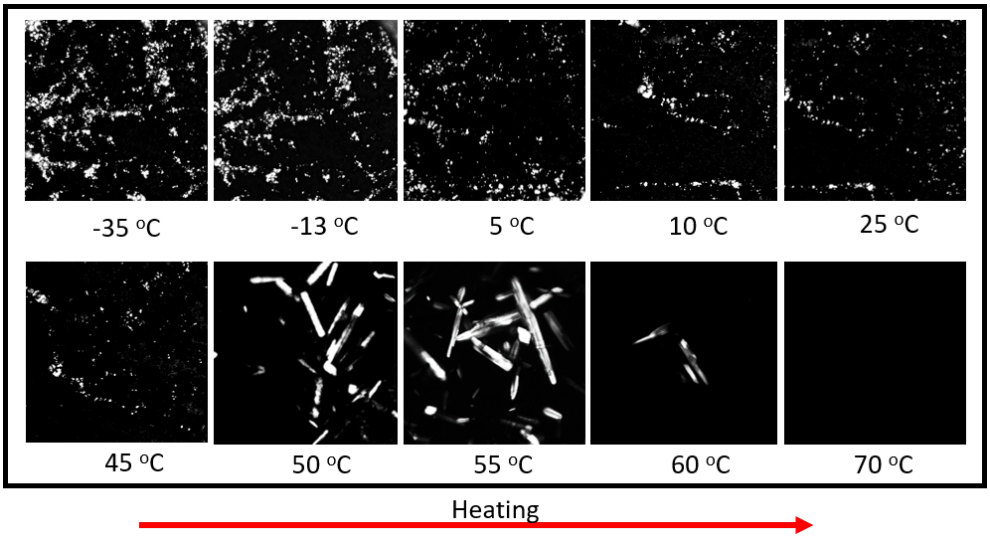

Figure 4: Polarised optical microscopy of blend 8 (0.5:0.3:0.2 OOO:PPP:SSS). The images were acquired applying a temperature ramp at 5 K/min to a sample between two coverslips and the actual sample temperature recorded by means of a temperature sensor connected to a temperature controller (PicoLog). Polymorphism of the PPP+SSS system is observed in the appearance, around 50 °C of stable orthorombic and triclinic crystals ascribed to the β' and β forms, confirming therefore the coexistence of a solid and a liquid phase even above the "melting temperature" of the blend at 45 °C.

References

1 R. Kremann, R. Schoulz, *Zur synthese der nat urlichen fette vom standpunkt der phasenlehre*, Monatshefte fur Chemie und verwandte Teile anderer Wissenschafte 33 (9) (1912) 1063–1076.

2 E. Lutton, *Phase behavior of triglyceride mixtures involving primarily tristearin, 2-oleyldistearin, and triolein*, Journal of the American Oil Chemists' Society 32 (2) (1955) 49–53.