

## Poster

## Polymorphism in triglyceride systems: in bulk and in emulsion droplets

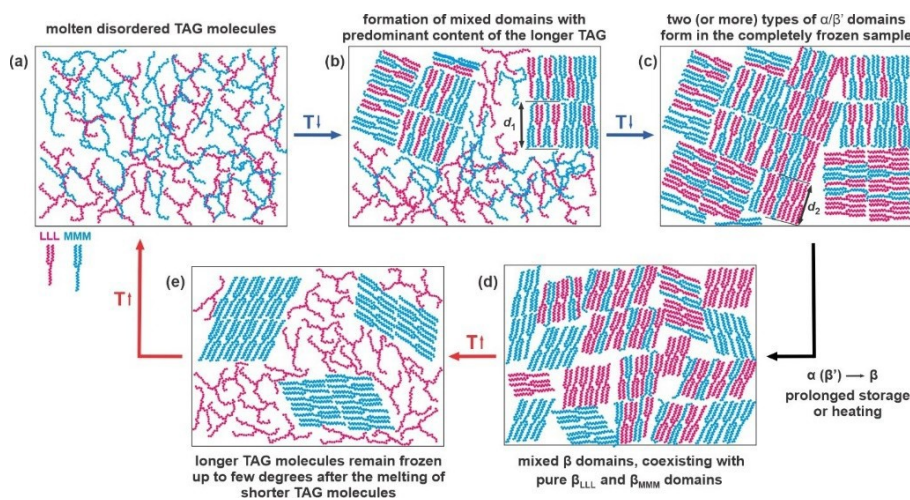
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Triacylglycerols (TAGs) are among the most abundant lipids in the food and cosmetics industries. Additionally, they are of special interest in controlled drug delivery and sustained release applications in pharmaceuticals, being a key material in the preparation of solid lipid nanoparticles. TAGs exhibit monotropic polymorphism, forming three main polymorphic forms upon crystallization -  $\alpha$ ,  $\beta'$  and  $\beta$  [1]. While the polymorphism of pure monoacid TAGs is well understood, the mixing behaviour of these relatively simple molecules remains incompletely studied, despite the prevalence of TAG mixtures in practical applications.

In this talk, we will present newly obtained results with several selected model mixtures of even-numbered monoacid TAGs, see Figure 1 [2]. The results show that two or more coexisting phases are formed upon solidification ( $\alpha$ ,  $\beta'$  and  $\beta$ ), the number of which depends strongly on the cooling rate and on the number of components in the mixture. No completely miscible  $\alpha$ - or  $\beta'$ -phases are observed. The structure of the most stable  $\beta$  polymorphs, formed upon subsequent heating of the solidified samples, does not depend on the thermal history of the samples. For all mixtures studied, we observed one-component  $\beta$  domains, coexisting with binary mixed  $\beta$  domains with composition and structure which do not depend on the specific TAG ratio in the mixture. In other words, for a mixture with  $k$  saturated TAGs we observed  $(2k-1)$  different  $\beta$  phases. These conclusions provide some predictive power when analysing the phase transition properties of TAG mixtures [2].

Furthermore, our studies with TAGs, which were emulsified as droplets in aqueous surfactant solutions, showed that the TAG polymorphism can be used to achieve a novel simple method for preparation of TAG nanoparticles with sizes down to 20 nm only by cooling and heating initially coarse emulsions, without any mechanical energy input to the system [3]. Furthermore, the TAG mixing resulted in even more interesting phenomena – the systems were able to either spontaneously disintegrate upon heating, or alternatively to engulf water from the continuous aqueous phase and form spontaneously double water-in-oil-in-water emulsion droplets upon heating [4]. The mechanism behind these non-trivial phenomena will be discussed and their applicability will be described.



**Figure 1.** Schematic presentation of the molecular rearrangements observed upon cooling and heating of binary monoacid LLL+MMM mixture.

[1] Cholakova, D. & Denkov, N. (2024). *Adv. Colloid Interface Sci.*, **333**, 103071.

[2] Cholakova, D., Tcholakova, S. & Denkov, N. (2023). *Cryst. Growth Des.*, **23**, 2075-2091.

[3] Cholakova, D., Glushkova, D., Tcholakova & Denkov, N. (2020). *ACS Nano*, **14**, 8594-8604.

[4] Cholakova, D., Glushkova, D., Pantov, M., Tcholakova, S. & Denkov, N. (2003). *Colloids Surf. A*, **668**, 131439.

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