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The memories of liquid triacylglycerols

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Crystallization of triacylglycerols (TAG), and other lipids, happens from the liquid into a broad range of polymorphic crystalline forms. Despite the sustained research effort over many years, it is still not possible to predict the crystalline form from first principles. In the case of mixtures, the prediction becomes disproportionately hard, even for just binary mixtures. They exhibit a very large number of seemingly anomalous crystallization behaviours. Among them, the 'memory effect' is particularly relevant. Perhaps the liquid structure holds the key to these phenomena.
A brief review of the few conceptual models proposed for the organization of TAG molecules in the liquid shows that, until a few years ago, researchers had not been able to offer a solid proposal for the liquid structures. Yet, the hypothetical structures suggested in the literature are often taken for granted.
We present here results from experiments aimed at proposing a structure of the liquid state and its influence on crystallization phenomena that are otherwise hard to explain.
Essentially, TAG molecules form clusters due to the difference in attractive forces between two regions of the molecules: the aliphatic chains, and the polar glycerol core. The clustering has been predicted by molecular dynamics and coarse-grained simulations.
Pure liquid TAG samples were examined by x-ray scattering at temperatures up to 210 ℃. Wide angle scattering (WAXS) data are consistent with the liquid phase of aliphatic molecules. Small angle scattering (SAXS) data are similar to those produced by alcohols and fatty acids, whose molecules associate via polar groups. The liquid TAG seem to form "Loose Multimers" of 5 to 9 molecules. The average number of molecules per cluster decreases with temperature and increases with molecular weight.
The 'memory effect' is observed when TAG re-crystallize from a liquid, obtained by melting crystalline TAG, and form the same structure that they had as a solid.
Differential scanning calorimetry (DSC) experiments were done with tempered pure TAG and TAG mixtures. The materials were melted and held at many [time + temperature] combinations before recrystallizing. Combinations that produced a recrystallization equal to a crystallization from a random liquid defined a time-temperature boundary. Above the boundary, the memory is erased. For pure TAG, the times and temperatures required were shorter and lower than for the mixtures. Some liquid structure of pure triacylglycerols remains after melting, which is disrupted by thermal fluctuations. In blends, it is additionally necessary to homogenize the concentration of domains of different sizes, via molecular diffusion, a much slower process.
Ultra-small angle neutron scattering (USANS) experiments were performed using tripalmitin. Data obtained from hydrogenated and deuterated samples were collected at 95 ℃. Data from the deuterated material were then obtained upon cooling from the melt, and upon melting from the crystalline state. The difference in the scattering patterns indicates the presence of different structural organization in both cases, consistent with the explanation of the 'memory effect' due to differences in the clustering of molecules in the liquid state.

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