Small Angle Neutron Scattering from Voids in Crystalline Trilaurin

D.J. Cebula[a], **D.J. McClements**[b] and **M.J.W. Povey***[,b]

[a]Unilever Central Research Laboratories, Colworth House, Sharnbrook, U.K., and [b]Department of Food Science, University of Leeds, West yorkshire LS2 9JT, U.K.

Small Angle Neutron Scattering (SANS) experiments show that a high density of voids of molecular size is formed within the crystalline structure of solidified trilaurin. It is proposed that these voids are defects in the crystal structure and that ordinary metallurgical concepts of defect controlled crystal growth and material strength may be applied to trilaurin and, by analogy, other triglycerides. The presence of voids would explain the anomalous expansion of simple, saturated triglycerides on cooling. SANS experiments did not reveal evidence of liquid crystalline order in trilaurin, supercooled below its β melting point. If ordered regions do exist, their density contrast with the disordered liquid must be less than 1% (the sensitivity of the instrument) or their scale must lie outside the region between 9.3 and 63 nm.

The functional properties of edible fats (triglycerides and their mixtures) are important in many food systems (1). Properties such as texture, mouth feel and stability (of partially crystalline emulsions) depend on the size, shape and packing of the fat crystals as well as the ratio of solid to liquid fat. It is therefore important for the fat technologist to understand the mechanisms of fat crystallization and the factors which affect the properties of fats. Significant progress had been made in the elucidation of the structure of crystalline polymorphs (2), but there are still many areas of fat crystallization where a better understanding is necessary. For example, it is often assumed that saturated fats and triglycerides contract when they solidify or transform from an unstable to a more stable crystalline form. Nevertheless, Hvolby (3) reports considerable expansion (up to 20%) in many saturated triglycerides and hydrogenated fats, which he attributes to void formation. Daffler (4) has postulated that this void formation is the result of a "mock-geological folding and bending" of lamellar structures (ordered regions) present in the melt. The presence of ordered regions in the melt may also have an important effect on the type of crystals produced during solidification.

There is conflicting evidence about the existence of these lamellar structures in triglyceride melts. Measurements of the width of x-ray reflections from trimyristin melt led Larsson (2) to propose that, above the melting point, lamellar units reduce continuously in size as the temperature is increased. When the temperature is decreased, the lamellar units grow until finally crystallization takes place. Just above the melting point, Larsson determined the persistence length in the lamellar to be about 20 nm using Hosemann's paracrystal concept (5). Other data exist which support the hypothesis of liquid crystalline order in triglyceride melts. A discontinuity in the cooling curve of tristearin at 72℃ has been reported (6). Similar discontinuities have been found in viscosity data about the β melting points (7). A ^{13}C NMR study of liquid tristearin revealed a discontinuity in the spin-spin relaxation time, with a shorter T_2 in the α melt below 73℃ indicating a more rigid (ordered) structure (8). Norton *et al.* (9) have observed anomalous crystallization kinetics in triglyceride mixtures which they attribute to liquid state demixing.

Nevertheless, x-ray long-spacing data and Raman spectroscopy (10) in the C-C stretching region indicate no evidence for the ordering of triglyceride chains above the melting point. Even if these structural transitions do occur in the melt, they must be weakly energetic as none of them appear to have been recorded using techniques such as differential scanning calorimetry (DSC).

It was the intention of this work to investigate whether Small Angle Neutron Scattering (SANS) could be used to observe and to characterize ordered regions in liquid trilaurin and voids in the solid. SANS was employed since it has already been used to provide structural information about the size distribution and spatial arrangement of inhomogeneities in various materials of colloidal (11) or biological nature (12). The advantage utilized here of SANS over x-ray scattering, to which it is in many respects similar, is its ability to penetrate large samples (≈ grams), owing to the weak interaction of neutrons with matter, and to characterize larger structures (up to 400 nm), owing to the long wavelengths available.

MATERIALS AND METHODS

SANS measurements. A general introduction to the subject of neutron scattering, exemplified by studies of biological materials, is given by Jacrot (12). Neutrons are scattered by interaction with atomic nuclei and/or by the magnetic moments of atomic nuclei. Scattering may be either coherent or incoherent. Coherent scattering occurs from regular arrays of scattering centers and leads to a distinct diffraction pattern (e.g., Bragg diffraction). Incoherent neutron scattering arises from differences in scattering amplitude of different isotopes or different spin states of one or more of the elements involved. The scattering vector (Q) through which neutrons are scattered is related to the wavelength of the neutron (λ) and the angle they are scattered through (2θ):

$$Q = \frac{4\pi}{\lambda}\sin\theta \tag{1}$$

For small angle neutron scattering the relation becomes:

$$Q = \frac{4\pi}{\lambda}\,\frac{r}{D} \tag{2}$$

where, r is the displacement of the scattered wave from the incident beam at the detector and D is the distance between the scatterer and the detector. The dimensions (d) of a scatterer can be inferred from measurements of scattered intensity using the relation $d = \frac{2\pi}{Q}$ (13).

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*To whom correspondence should be addressed.

SANS was measured using the D17 diffractometer at the Institut Laue Langevin, Grenbole (14). D17 is a two axis neutron spectrometer with a multidetector for scattering experiments in the scattering vector (Q) range 0.03 to 10 nm^{-1}. The sample to detector distance was 2.78 m and the instrument was operated in small angle configuration. A nuclear reactor generates the neutrons which are guided into the experimental hall where their velocity (and hence wavelength) is selected. A neutron wavelength of 1.2 nm was used in the experiments, which is equivalent to scattering vectors (Q) of between 0.1 and 0.7 nm^{-1} for the range of angles examined.

Materials. Deuterated trilaurin was synthesized from glycerol-H (i.e., ordinary proton-containing glycerol) and deuterated lauric acid. The sample was deuterated to increase its scattering cross section with respect to neutrons (deuterons have a much larger scattering cross section than protons), thus increasing the magnitude of the observed signal. All phase transitions of the trilaurin were located prior to the SANS experiments using DSC.

RESULTS AND DISCUSSION

The deuterated trilaurin was heated to 65°C, well above its β melting point (about 41°C), for about 30 min so as to destroy any crystalline order which may have been present. It was then thermostatted at 34°C (i.e., above the α crystallization point, about 30°C), and SANS measurements were carried out every 20 min until the trilaurin crystallized ($\approx$4 hr). The melt showed no discernible scattering above that from an isotropic liquid, i.e., there was no angular dependence in the scattering pattern (Fig. 1). The slight increase in scattering below Q values of about 0.2 nm^{-1} is caused by some of the incident beam falling on the detector at small angles. There was also evidence of a change in the scattering pattern from the melt over the 4 hr period. These results suggest that there is either no liquid crystalline order in the supercooled melt or that the SANS used in this experiment was not sensitive enough to detect it or that the scale of the ordered regions lies outside of the range examined (9.3 to 63 nm).

Further SANS measurements were carried out once the trilaurin had completely crystallized (at 34°C). Strong scattering was now observed (Fig. 1)—the intensity of the scattered signal being over 100 times larger in the crystalline trilaurin than in the melt. This strong scattering can be attributed to the presence of voids (or defects), voids having large contrast in scattering length density compared with the deuterated trilaurin, in the crystalline structure. The results in Figure 1 show scattering from voids with correlation lengths ($= \frac{2\pi}{Q}$) between 9.3 nm (at high Q) and 63 nm (at low Q). In addition there is probably a significant number of voids larger than 63 nm which do not appear in Figure 1 because they scatter at too low Q values to be seen in this particular experiment.

To examine this hypothesis of defect scattering, deuterated trilaurin melt held for an hour at 50°C was quenched in ice. In metal and polymer crystallization, quenching produces a higher number of smaller defects than a sample allowed to cool slowly. This phenomenon was observed in the quenched crystallize trilaurin (Fig. 1). The scattering at large Q values was greater from the quenched sample than from the sample allowed to crystallize at 34°C. Further confirmation that the voids were defects was obtained when the quenched sample was annealed by raising the temperature to 35°C, holding it for 30 min, then cooling to 25°C. The number of scattering entities at 9.4 nm reduced whilst those at 63 nm increased, consistent with disproportionation of defects. Voids of this size range are not altogether surprising if they are regarded as defects in the formation of crystals, whose unit cell size in the case of triluarin is about 0.35 × 3 × 0.2 nm^3. The SANS measurements carried out in this work only give a qualitative indication of the size distribution of the voids; nevertheless, they clearly demonstrate

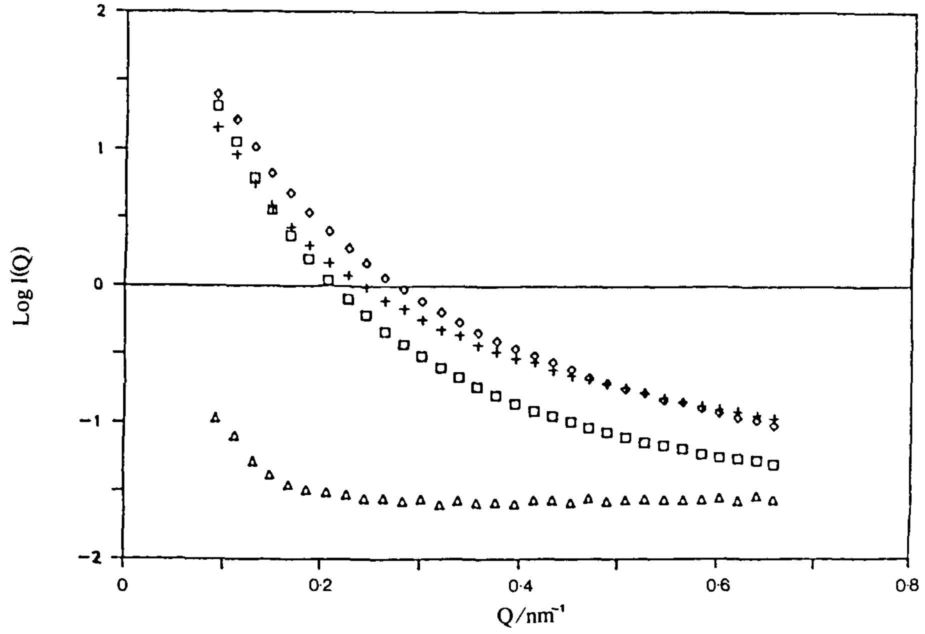

FIG. 1. Variation of relative intensity with momemtum transfer for trilaurin melt (△), trilaurin crystallized at 34°C (□), quenched trilaurin (+) and annealed trilaurin (◇).

the usefulness of SANS for characterizing voids in crystalline triglycerides. More detailed SANS experiments, over a wider Q range, will provide quantitative information about void size distributions. Such experimental testing will be the subject of future work.

The authors could find no evidence of other workers who had attempted to characterize voids in crystalline fats. However, the presence of voids would explain the high attenuation of ultrasound in solid trigylcerides (15) and the anomalous expansion of simple even triglycerides observed by Hvolby (3). Defects in crystalline triglycerides, caused by the incorporation of surfactants in the melt, are believed to play an important role in regulating polymorphic transitions (16). SANS may prove a useful technique for examining these defects.

We conclude that the voids observed in our SANS experiments should be understood as defects in the otherwise regular crystalline structure of trilaurin. The presence of defects in crystalline triglycerides may have great significance in controlling and modifying the functional properties of edible fats. In metals and polymers, defects effect the rate of crystallization, crystal habit and material strength. By applying the understanding of the role of defects developed in metallurgy and polymer science, the study of the functional properties of fats could be greatly improved.

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