

A Case for Discotic Liquid Crystals in Molten Triglycerides

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To date, essentially only two structural models have been proposed and debated in detail for explaining the liquid state order of triglycerides, and both invoke a form of thermotropic liquid crystalline order in triglyceride melts. These are the paralamellar model of Larsson et al. (*J. Am. Oil Chem. Soc.* **1992**, *69*, 835) and the nematic model of Cebula et al. (*J. Am. Oil Chem. Soc.* **1992**, *69*, 130). An alternative discotic model is proposed here that adequately accounts for the broad small-angle X-ray diffraction peak often observed in the liquid state of fats and oils. In this alternative model, triglyceride molecules exist in the liquid state with fully splayed chains, approximating “Y”-shapes (Y-conformers). These are loosely bound within discs that stack into flexible, relatively short cylindrical rods of colloidal dimension, which in turn assemble into rod-packings with short-range order akin to disordered versions of thermotropic discotic liquid crystalline phases in other lipidic systems.

Introduction

During the 1960s to the early 1990s, the emergence of convincing evidence for molecular ordering in triglyceride melts led to a strong consensus regarding its existence but not its structural or morphological type. The strongest evidence for the existence of supramolecular ordering in liquid triglycerides is the co-occurrence of small-angle X-ray diffraction (XRD) and neutron scattering maxima with the well-accepted $d \sim 4.6$   wide-angle scattering peak of conformationally disordered chains. The presence of broad small-angle peaks above the melting point of the highest melting polymorph present in many triglyceride systems is, however, open to interpretation, since usually only one definitive peak is observed, and so a unique structural assignment is not possible. Larsson^{3,4} first proposed ordering in the liquid state, advocating the existence of liquid–crystal-like lamellae, based on X-ray diffraction (XRD) measurements and comparison with analogous, well-characterized lipid systems. Using Raman spectroscopy and XRD, Hernqvist⁵ supported Larsson’s model, adding a proposed pathway for triglyceride crystallization from the melt. More recently, Ueno et al.⁶ used synchrotron XRD to provide new insight into the polymorphic phase transitions of *sn*-1,3-distearoyl-2-oleyl glycerol (SOS), providing very strong evidence for the existence of liquid crystallinity for triglycerides below the β' melting point, under certain conditions.

Larsson¹ and Cebula et al.² debated the explicit nature of structures occurring in the liquid state of triglycerides above the melting point of the highest melting polymorph. Larsson,^{3,4} Hernqvist and Larsson,⁷ and Hernqvist⁵ argued for a labile,

paralamellar (smectic) assembly of triglyceride molecules (Figure 1), whereas Cebula et al.,² using neutron diffraction of trilaurin melts, explicitly argued against Larsson’s lamellar model in favor of a nematic-like structure (Figure 2) comprising essentially unassociated molecules, but did not offer an explicit rationalization of the small-angle diffraction maxima. In response to Cebula et al.,² Larsson¹ countered with reasonable arguments against their nematic model and reiterated his arguments in favor of the paralamellar hypothesis, demonstrating that the neutron data was not inconsistent with a melt containing smectic order. Larsson summed up his article by stating that “...the last word on interpretation has certainly not been said.”

Larsson’s Paralamellar Model

To explain the observed small-angle diffraction maxima and coexisting $d \sim 4.5$   molten chain peak, Larsson et al.^{3–5,7} proposed that lamellar liquid crystals with short-range order (paralamellar structures) exist in triglyceride melts. The significant broadening of the small-angle peak in the liquid state was interpreted as indicating the existence of only relatively short-range order, with nanometric sized domains, in contrast to other lipidic lamellar liquid crystals such as the L_α phase of lipids and their analogues^{8,9} which often display relatively sharper small-angle peaks and corresponding higher order peaks at wider angles. Both Larsson⁴ and Hernqvist⁵ demonstrated that this molecular ordering of some triglycerides in the liquid state can persist at temperatures up to 40  C above their final melting point.

Larsson’s model for paralamellar structure in the liquid state of triglycerides also draws upon indirect evidence.⁹ They argued that similar small-angle diffraction maxima and corresponding layered freeze-fracture TEM textures observed for L_2 phases of

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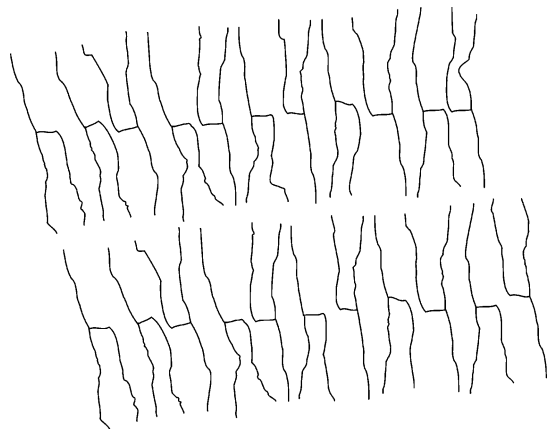


Figure 1. Proposed structure of triglycerides in the liquid state, as proposed by Larsson.

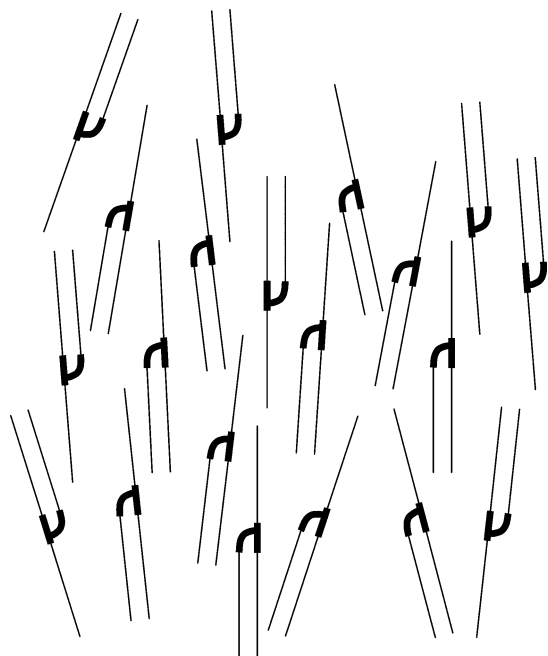


Figure 2. Proposed structure of triglycerides in the liquid state, as proposed by Cebula et al.

polar lipid melts could be used as evidence, by way of analogy, for the existence of lamellar ordering in triglyceride melts.

In his response to the work of Cebula et al.,² Larsson¹ argued against their nematic phase interpretation of triglyceride melts. The basis of their rebuttal was that nematic phases are comprised of stiff, rodlike molecules and that nematics have not been observed in lipid–water systems.

Significantly, Larsson^{3,4} reported that a “trimyristin melt exposed for a long time showed first and third ordered reflections with long spacing centered around 32 Å.” Later, Hernqvist⁵ reported trimyristin in the liquid state to have a long spacing of ~22 Å but did not report higher order reflections, only the long spacing value, and no comment to explain the discrepancy of *d*-spacings was offered by Hernqvist,⁵ nor later by Larsson.¹

Cebula et al.’s Nematic Phase: An Anisotropic, Dissociated Molecular Melt

Some uncertainty exists concerning how to interpret the structural model presented by Cebula et al.² for molten trilaurin. These authors stated that the correlations occurring laterally and at right angles to the molecular axes of the individual triglyceride molecules gave rise to the wide-angle diffraction maxima, and

this was the basis for the nematic correlations, that is, purely due to the relaxation of lamellar to nematic order, analogous to the classical rigid-molecule thermotropic liquid crystals. Thus, their definition of a nematic phase arises directly from an interpretation of the wide-angle peak and not the small-angle peak. The presence of the small-angle peak in their diffraction patterns was not crucial to their nematic argument; it was merely an indication that the structure had become nonlamellar. The authors did not interpret the small-angle peak in terms of an explicit structure other than to state that it represented a closer approach of the glycerol moieties in the nematic phase than in the lamellar phase (due to chain–chain interdigitation and/or chain-length reduction via chain melting) and that the lack of higher order reflections did not support Larsson’s lamellar interpretation. Finally, their model incorporates chair, or “h”, conformers of triglycerides.

Discotic Model for Molten Triglycerides

In constructing an alternative discotic model, we will build arguments based on the following logical progression, taking the existence of molecular aggregates in the melt, as first postulated by Larsson, as well-accepted: (1) that triglyceride molecules in the melt form Y-shaped conformers, (2) that the Y-shaped conformers are loosely bound individually within disclike volumes, (3) that disc-shaped molecules can self-assemble into discotic mesophases, and (4) that there is evidence that triglyceride molecules can associate with each other when their chains are conformationally and rotationally disordered.

The first requirement in this sequence is establishing a reasonable likelihood for the existence of the Y-shaped conformers (to the best of our knowledge, this Y-conformation has not been previously proposed). If we then accept that Y-shaped conformers are likely in triglyceride melts, then it follows fairly directly that these will probably have a time-averaged volumetric boundary that is effectively disc-shaped. Next, if we accept that triglycerides in the melt are disc-shaped, then, by analogy with other disc-shaped lipidic molecules, these likely form columnar or discotic mesophases (if any). Finally, if we show evidence that molecular cohesivity can be observed in triglyceride systems having molten chains, then it would seem reasonable that some mechanism for interdisc binding also exists.

Proposed Y-Shaped Conformation of Triglyceride Molecules in a Melt

The basis for the Y-shaped conformation is the argument that when the triglyceride chains melt, the chains splay ~120° apart, such that their free energy is minimized within the constraints set by their mutual steric hindrance (Figure 3). In a melted phase, where the longer-range attractive energies (as distinct from the very short-range (0.1 nm) soft-core steric hindrance repulsions) make a minor contribution to the free energy, minimizing the free energy is essentially maximizing the entropy.

The concept of splayed chains has been used to explain, for example, why multichain lipidic molecules form reverse thermotropic liquid crystalline phases.¹⁰ When the acyl chains of lipids such as triglycerides melt, the associated conformational and rotational freedom of the methylene units equates to a relatively larger effective chain volume. This is well-established for surfactants and lipids above their respective Krafft temperatures.

Ninham et al.^{11,12} and later Hyde (e.g., Hyde et al., 1997)¹³ formalized the analysis of molecular shape in relation to self-assembled liquid crystalline structures and their characteristic

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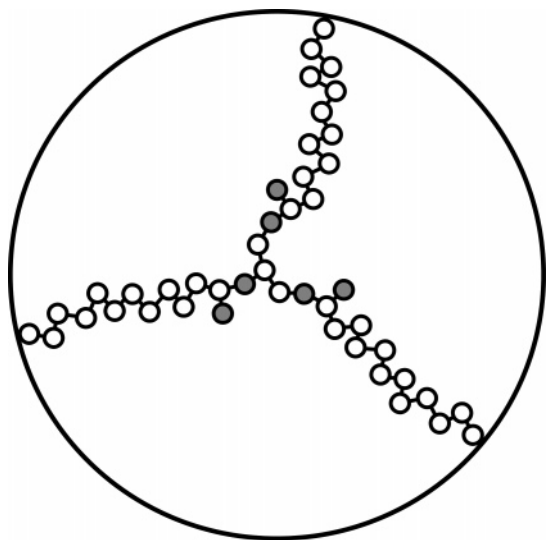


Figure 3. Proposed “Y”-conformation within each “disc”, where triglyceride fatty acid chains spread out at $\sim 120^\circ$ to each other in a single, though diffuse, plane.

interfacial geometries and topologies. These authors defined and used the surfactant packing parameter, $S (= V/al)$, as the underlying analytic expression for molecular shape in their respective contexts. Essentially, lamellar self-assemblies of lipids arise when the average value for $S = 1$ or when the chain volume (V) is equal to the headgroup cross-sectional area (a) multiplied by the effective chain length (l). Nonlamellar phases have V/al values not equal to unity. In these cases with $S \neq 1$, the average surfactant shape is that of a tapered cylinder or cone. If $S > 1$, the average molecule has a set of chains that is more bulky than the headgroup, and the opposite holds true when $S < 1$, that is, the headgroup is effectively bulkier than the chains. In the former case, and for multichain lipids, increasing temperature (or addition of a nonpolar solvent) is associated with a splaying of the chains (through increased chain volume) and a concomitant increase in S .

Examples of nonlamellar phases comprised of lipids with $S > 1$ include the thermotropic mesophases of di- and trivalent metal salts of fatty acids.^{10,14,15} In neutral divalent metal soaps, two fatty acid chains are attached to the metal via carboxylate binding. For saturated soaps, the room-temperature phase is lamellar crystalline with orthorhombic and triclinic subcells being common, as for many triglycerides. During melting of the crystalline lamellar phase of these soaps, the subcells disorder as the chains become rotationally, and then conformationally disordered, and V becomes larger and l becomes smaller, with little change in the effective headgroup area. (For the classical unsaturated metal soaps,¹⁴ the chain melting transition is at relatively high temperature ($> 100\text{--}120^\circ\text{C}$). For some branched chain soaps, the melting transition is below room temperature.¹⁰) Thus, S increases beyond unity, and for many metal soap systems, they do not remain as lamellar assemblies immediately after the chain-melting transition, as we propose for many triglyceride systems above the melting temperature of the highest melting polymorph.

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Accepting that molten triglycerides will have chains that are in a state of mutual steric repulsion, and are thus to some extent splayed apart, the likely conformation is with chains at 120° to each other. Consider an idealized lipid with three equivalent chains and a pointlike headgroup located at the center of a sphere. Pure geometric arguments lead to a conformation with a splay angle of 120° . This planar solution preserves the maximum mutual separation of the chains, for if any one chain departed from coplanarity, then this would give an average molecular shape occupying only half of the sphere. Under the constraint of maximal entropy or maximal mutual steric repulsion, the molecule would quickly rearrange to occupy a diffuse plane cutting a great circle of the sphere. For a molecule with a finite (rather than a point) headgroup similar to the glycerol moiety, and for some triglycerides with nonequivalent chains, this angle could be expected to vary a little from 120° . Given that the chains are in constant motion, the blurred locus of points occupied by the chains will define a time-averaged disc-shaped volume, with the thickness of the disc determined by the out of plane mobility of the chains. Notably, single chain lipids such as monoglycerides do not have this steric hindrance problem of arranging three chains near the headgroup. In this respect, we consider multichain lipids as the more desirable candidates for triglyceride analogues. For example, three stacked double-chain lipids with a propensity for forming inverse phases can form a similar disc structure to two stacked triglyceride molecules and so on.

In Figure 4, we show the results of a Monte Carlo computer simulation employing a model of a trilaurin molecule, with all atoms (C, H, and O) represented by soft spheres. The only interactions included were soft-core repulsive interactions, which gave rise to a *trans-gauche* energy difference in rotations about a $\text{CH}_2\text{--CH}_2$ axis. The temperature was relative to the *trans-gauche* energy barrier, E_g , of our model. Thus, low (high) temperature is defined as $k_B T \ll E_g$ ($k_B T \gg E_g$), where k_B is Boltzmann's constant. Since the intent of this simulation was to exhibit the effect of temperature upon a single trilaurin molecule, we fixed the CH group of the glycerol moiety in space, permitting neither translations nor rotations about it. Figure 4a shows the initial tuning-fork-like (“h”) conformation of trilaurin at a low temperature. The intent here was to initialize the simulated molecule in a low temperature state that was far from a Y-conformation (in order not to bias the simulation) and then to heat it and test if the equilibrium state at higher temperatures gave a Y-conformer. Figure 4b shows that this is indeed the case. The temperatures used were not intended to mimic experimental conditions but simply to make the point that, as the temperature is raised, a triglyceride can adopt a Y-conformation.

Observation of Discotic Phases in Some Analogous Thermotropic Lipid Systems

It is well-established that discotic mesophases, also known more generally as columnar or rod mesophases, are comprised of molecules, commonly multichain lipids and their derivatives, that are essentially bound within disc-shaped volumes. Giroud-Godquin¹⁶ and Bushby and Lozman¹⁷ reviewed the discotic phases, and the former included molten copper salts of fatty acids. The molecules are Cu–Cu dimers with four fatty acid chains per dimer. Upon melting, these form discotic molecules that pack into rods, with a characteristic interdisc spacing sometimes observed as a diffraction maximum. (An XRD peak

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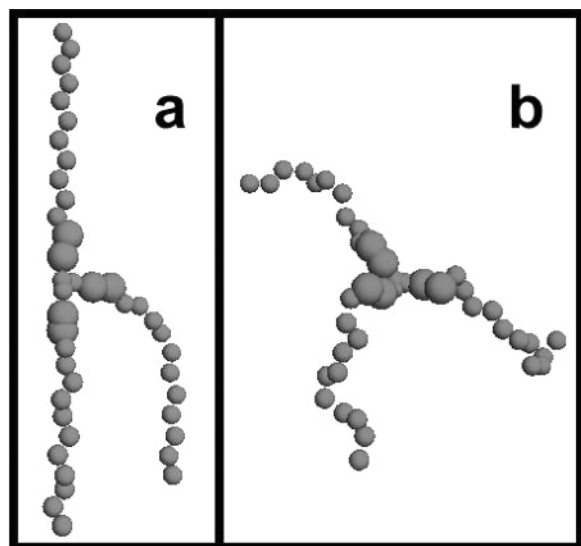


Figure 4. Model of a trilaurin molecule with the CH group of the glycerol moiety fixed in space. The pictures show typical instantaneous conformations of a Monte Carlo simulation. (a) Trilaurin molecule created in an h-conformation at a low temperature compared to the energy of *trans-gauche* isomerization, confirmed by the fact that the molecule remained close to this state for long simulation times. (b) The temperature is raised, and multiple *trans-gauche* isomerizations take place as the molecule adopts a Y-shaped conformer. Here, we show a typical conformation.

corresponding to the interdisc spacing is not expected for triglyceride discotic phases, since the triglyceride discotic phases are not as ordered as the hexagonal ($p6mm$) metal soap mesophases, nor do they have the electron density of the metal soaps. Indeed, such peaks have not been positively observed for liquid triglycerides. However, the secondary neutron scattering peak of Cebula et al.² observed near $d = 6-7 \text{ \AA}$ (interpreted by Larsson as a possible third order of a lamellar spacing) is not inconsistent with that observed for the interdisc spacing in some discotic liquid crystals.) These rods assemble into hexagonal liquid crystals. Both the discs within rods and the rods themselves pack together with chain-chain interdigitation, so that the boundaries of the discs and rods are somewhat diffuse, and relatively uniform chain packing is achieved. The same is observed for a range of the branched chain metal soaps, for example, Zn, Cu, Sr, Cd, and Ba soaps. In each of these cases, the molecules assemble (via headgroup affinities) into rods that pack into reverse hexagonal liquid crystals. For the Ca, Al, Ag, La, Ce, Tb, and Lu soaps, despite the fact that XRD was not so clearly indicative of a hexagonal phase and, in some cases, little or no birefringence was observed, the supporting evidence was strong enough for a conclusion that these were discotic liquid crystals. A continuum of well-ordered to poorly ordered discotic structures were conjectured to exist among these cases, as well as for the fully molten metal soaps of saturated fatty acids, for example, the transition metal and lanthanide soaps. In these cases, the small-angle diffraction peak of the molten metal soap was in a position more indicative of a discotic phase than a lamellar phase, and furthermore, the soaps had already passed through well-ordered lamellar and well-ordered hexagonal mesophases prior to melting. We would not expect a reversal of the transition to a lamellar phase in the melt, for example. Thus, it was concluded that the molten metal soaps have ordered melts, which are most likely discotic mesostructures with short-range order.¹⁵ The point we wish to make is that some, if not many, liquid triglycerides are analogues of the poorly ordered discotic, branched-chain metal soaps and metal soap melts.

Indeed, if we examine the expected phase transition sequence for thermotropic liquid crystals, as a function of temperature, the work of Hyde¹³ clearly predicts the following order (for constant hydrophobe volume fraction):

lamellar \rightarrow mesh (punctured lamellar) \rightarrow
 sponge (e.g., cubic) \rightarrow rod or column (e.g., hexagonal) \rightarrow
 spheres (e.g., micellar)

This sequence is predicted because of the relationship between $S = V/al$ and the differential geometry and topology of the interfaces within the molecular assemblies of lipids. If the molecule has an inherent asymmetry, for example, then some phases may not be realized. For some saturated metal soap systems,^{14,16} their phase sequence is crystalline lamellar to hexagonal liquid crystal, with no mesh or sponge in between. Because it is so well-established for liquid crystals to follow this order (in the absence of secondary factors such as relatively rigid interfaces), we must expect that, if a liquid-crystalline-like phase formed from a triglyceride melt, then it would likely be one of the phases to the right of the lamellar phase. The question is which phase. If we accept the Y-shaped conformation as likely here, then the discotic phase would be favored, since the individual molecules are more likely to pack into rods (Figure 5). This is entirely consistent with the formation of inverse hexagonal phases in other nonmetal bearing, thermotropic lipid systems, for example, those containing phosphatidylethanolamine (PE), phosphatidylglycerol (PG), or cardiolipin.¹⁸ In the case of these lipidic biomembrane constituents, their respective bulky chains and relatively small headgroups lead to average molecular shapes that will minimize the free energy of the system by forming reverse curved interfaces and thus nonlamellar, reverse liquid crystalline phases.

As a final note to this section, the microscopic surface texture of discotic, columnar, or hexagonal mesophases can resemble lamellar phases at relatively low magnification. High-resolution scanning electron microscopy (SEM) images of analogous, geometrically similar hexagonal silica mesoporous materials (synthesized using lyotropic liquid crystalline phases as templates¹⁹) demonstrate this resemblance. At higher magnification, the hexagonal rods appear aligned in layers at the fracture surfaces of these materials.²⁰ This observation decreases the importance of the freeze-fracture texture-based argument used by Larsson et al.¹ against nonlamellar phases in triglyceride melts.

A Discotic Model Can Be Used To Predict the Small-Angle XRD Peak of Molten Triglycerides

The model of Larsson is based on the generally accepted conjecture that triglycerides in the liquid state contain structures giving rise to small-angle diffraction maxima. Further, both Larsson et al. and Cebula et al. explicitly noted that the corresponding d -spacing is significantly less than two extended fatty acid chains and is thus far smaller than the repeat spacing between polar group planes in the solid lamellar phases (approximately half the long-spacing value of the corresponding α -polymorph). Accordingly, the structure of the melted phase of triglycerides is unlikely to be lamellar, even on short length scales. Here, we show that the broad small-angle diffraction maximum of molten triglycerides is more consistent with that of a discotic liquid crystalline structure.

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Fatty acid salts are used as analogues for estimating the diameter of the proposed triglyceride rods. (Metal soaps, like triglycerides, have multiple fatty acids per polar headgroup unit, are virtually insoluble in water, and have well-known thermotropic phase behavior, including discotic phases. Here, we make the reasonable assumption that the diameter and thickness of two stacked discs each comprised of triple chain molecules are the same as the diameter and thickness of three stacked discs each comprised of double chain molecules. Relatively uniform chain packing density arises by the interdigitation of chains from apposing discs, so that on average, for a triple chain lipid in a discotic phase, we could expect a 60° rotation of successive Y-conformers about the normal to their disc plane within the rod.) From the diameter of metal-soap reverse hexagonal phases, the diameter changes by $\sim 0.68\text{--}0.87$ Å per average molten methylene in the chain.¹⁰ If the molten chains in trilaurin have a similar behavior, the diameter due to the methylenes will be $\sim (12 \times 0.68) - (12 \times 0.87) = 8.2\text{--}10.4$ Å. With ~ 2 Å for the terminal methyl groups and $\sim 7 \pm 2$ Å for the glycerol backbone (including ester bonds), the estimated diameter is $\sim 15\text{--}22$ Å, which compares favorably with the observed $15\text{--}25$ Å peak reported by Cebula et al.² (The maximum is centered close to $d = 18$ Å and corresponds to an equivalent column diameter of ~ 21 Å.) Further, Hernqvist⁵ noted a broad low-angle XRD maximum for molten trimyristin (constant from ~ 70 °C to ~ 40 °C) of $d \sim 22$ Å (equivalent to a $\rho 6\text{mm}$ rod diameter of 25 Å). Using the approach employed for the trilaurin calculation above, a trimyristin rod diameter of $\sim 17\text{--}23$ Å is predicted. Thus, in both examples, the proposed model can be used for a reasonable prediction of the observed low-angle diffraction maxima. These predictions are even more reasonable if we consider that the lower temperature molten triglycerides would be expected to have slightly larger disc diameters than those predicted on the basis of the higher temperature metal soap mesophases (due to a higher percentage of *all-trans* character in alkyl chains at lower temperatures).

Seghrouchni and Skoulios²¹ reported a one-dimensional ordered rodlike mesophase between otherwise discotic (hexagonal $\rho 6\text{mm}$) thermotropic mesophases in mixtures of classical copper laurates and stearates. The XRD pattern of their intermediate phase also displays the same basic features as that of molten triglycerides. They observed a broad small-angle maximum corresponding roughly to double the length of a molten fatty acid chain, but significantly displaced (to higher 2θ) from the position expected for a lamellar phase, and a molten chain peak at $d \sim 4.6$ Å. They refer to their 1-D rod phase as a nematic phase. However, it is explicitly stressed here that this is not analogous to the nematic phase of Cebula et al.² In the latter case, the reference was to a 1-D alignment of individual molecules, whereas the former were referring to the 1-D alignment of rods comprised of stacked, disc-shaped molecules. This highlights the ongoing difficulty of devising explicit terminology to describe hierarchically structured molecular aggregates. For this reason, we have used the more geometric terms “discotic” and “rod” for supramolecular assemblies, although we in no way mean to imply that these are stiff. Indeed, it is likely that these rods are flexible and labile, undergoing various dynamic transitions, such as rotations, undulations, dilations, disconnections, fusions, and so forth, that distort their packing away from the otherwise hexagonal packing seen in the more ordered discotics. To this end, we have chosen to predict the small-angle X-ray spacings assuming a time-averaged primitive hexagonal rod-packing for the unit cell (see Table of Contents figure).

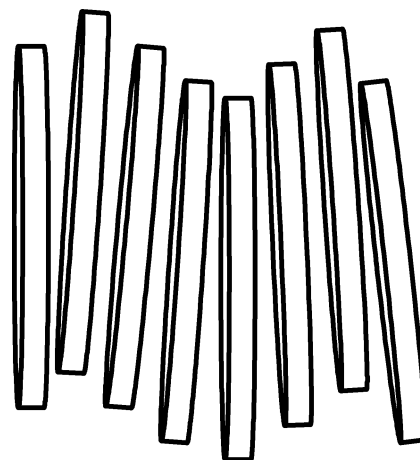


Figure 5. Proposed stacking of triglycerides in a single short column or rod, as proposed in this paper.

For conformationally disordered chains, a $d \sim 4.6$ Å peak arises due to the expansion of the crystalline subcell during melting and corresponds to a time-averaged distance of ~ 5.3 Å between the acyl chains undergoing both conformational and rotational motion. The significance of this diffraction peak has been adequately discussed by Larsson et al.^{1,3,4} and Ueno et al.⁶ in the context of triglyceride melts, and by others.⁸ However, it is worth noting that the coexistence of the $d \sim 4.6$ Å peak with small-angle peaks is generally accepted among lipid researchers as indicative of liquid crystalline order. Indeed, the study of Ueno et al.⁶ on SOS clearly demonstrates the coexistence of these wide- and small-angle peaks, indicative of liquid crystalline order at temperatures below the melting point of the highest melting polymorphs.

Intermolecular Cohesion of Triglyceride Molecules in Liquid Crystals

This section is not considered critical to our arguments for a discotic phase in molten triglycerides above the temperature of the highest melting polymorphs. However, the observation of liquid crystalline phases intermediate to the crystalline polymorphs of triglycerides⁸ is significant to the debate of structure in triglyceride melts, since these establish the existence of intermolecular cohesivity in triglycerides, despite the fact that their acyl chains are in a state of dynamic reptation. (Interestingly, and in apparent contradiction to our thesis here, Ueno et al.⁸ showed strong evidence that their intermediate liquid crystals were lamellar in structure. We argue that this is not inconsistent with our model. The reason for the lack of inconsistency is that, at the lower temperatures of Ueno et al.’s liquid crystals, significantly less conformational disordering of the triglyceride chains occurs, as compared with the case above the melting temperature of the highest melting polymorphs. Further, their small-angle spacings are much more consistent with the lengths expected for lamellar phases, as opposed to the shorter d -spacings observed above the last melting transition, which are far more consistent with that expected for discotic phases.)

It is generally accepted that lipidic systems with molten chains displaying thermotropic liquid crystalline order must have some degree of intermolecular cohesion through their headgroups to maintain their anisotropic state. Thermal motions of the molten chains associated with their inherent conformational, rotational, and positional disorder tend to disrupt headgroup ordering in liquid crystals or forbid their formation altogether, particularly as the temperature is raised. In the case of liquid crystalline metal soaps, intermolecular cohesion is mediated via various

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bridging modes of the carboxylate moieties, such that the metal charge and atomic coordination packing are satisfied. This type of binding, which allows metal soap mesophase stability up to 250–300 °C, is clearly not possible in triglycerides, where the association forces in the mesophase must be much weaker. Evidence for intermolecular cohesivity of the glycerol groups (here, analogous to headgroups) in molten triglycerides had not previously been put forward until Ueno et al.⁶ Their observation of liquid crystalline order in triglycerides below the temperature of the highest melting polymorph directly implies the existence of intermolecular cohesion sufficiently strong to overcome the disordering tendency imparted by the thermally disordered chains. However, they did not propose a mechanism. It is also beyond our intention to do so in detail here. Nonetheless, a few possible mechanisms seem plausible for future discussion.

The most likely mechanism is the polar interactions of the glycerol moieties. These could be mediated through low-level impurities or hydrolysis products and/or small hydrophilic molecules such as water (that could enable hydrogen bond bridging). A second possibility is that additive van der Waals interactions of unmolten, *all-trans* methylene groups near the glycerol moieties of adjacent discs could mediate the attraction. Last, a more subtle combination of effects amounting to an effective microphase separation of polar and nonpolar regions of the triglyceride molecules could drive the formation of ordering without specific headgroup attractions or cohesivities dominating the assembly of discs into rods.

Relationship of the Discotic Model to the Paralamellar and Nematic Models

Having put forward a new, alternative discotic model for triglyceride melts, we would like to stress the importance of not ruling out either Larsson et al.'s or Cebula et al.'s respective models. Rather, our model is offered as a structural intermediate to the previously proposed paralamellar and nematic models (providing a Y-conformer variant of the nematic model is possible). We suggest that the range of possible triglyceride melt structures spans a range of interfacial curvatures (defined by the surface of the terminal methyl groups of associated triglyceride molecules), from nearly lamellar or disordered mesh phases (closest to Larsson's model), through a bicontinuous sponge, to rod, columnar, or discotic phases, and then finally to anisotropic molecular melts (closer to a Y-conformer version of Cebula's model²). In reconciling the previous models, we suggest that nanometric lamellar or disordered meshlike domains (like Larsson's paralamellar model¹) may form at relatively low temperatures when the Y-conformer relaxes closer to a molten tuning fork or chair, and a model like an inverse micellar-like phase may be operative at relatively high temperatures when disc–disc interactions reduce associations to only a few molecules (closer to a Y-conformer version of Cebula et al.'s model²). However, given the evidence that triglyceride molecules likely exist as Y-conformers in the molten state and that their most likely assembly route is to stack in rods, we propose that discotic-

like ordered domains are more common than the previously proposed ordered domains in molten triglycerides.

Conclusion

We have presented evidence and arguments for the existence of an alternative discotic liquid-crystalline-like structure in triglyceride melts. Our proposal is based upon accepting the existence of, yet poorly understood, ordering in liquid triglyceride melts. We have presented evidence, based upon molecular shape arguments and computer simulation, that chains of a single triglyceride molecule can splay into an entropically driven Y-shape in the melt. We have argued that these Y-conformers will exhibit time-averaged cylindrical symmetry, with dislike shapes, primarily because of the approximately threefold symmetry of the chains around the central glycerol moiety. Such disc-bound triglyceride Y-conformers are morphological analogues of other well-studied multichain lipids and their derivatives that bear splayed-chain, disc-shaped constituents that also assemble into flexible cylindrical rods or columns via interdigitated stacking of discs. Also, similar to analogous multichain lipidic systems, the probably labile, cylindrical rods comprised of stacks of triglyceride Y-conformers loosely pack (also with interdigitation) into time-averaged disordered hexagonal mesophases with short range order, such that only the main small-angle diffraction maximum is observable along with the usual wide-angle peak corresponding to conformationally disordered acyl chains.

This present discotic model is consistent with the known X-ray and neutron diffraction spacings observed for molten triglycerides and can reconcile the differences between previous models by acting as a structural intermediate, in a continuum of possible melt structures. We do, however, consider that the predominant ordered domains in many, if not most, molten triglycerides, whether technical or *in vivo*, are more likely discotic rather than paralamellar or otherwise structured. Therefore, the model of discotic liquid crystalline structures presented here may be of considerable value for future basic and applied research, for example, in building fundamental and technical insight into the so-called “memory effect” during fat crystallization and in biological systems.

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Supporting Information Available: Diffraction maxima for various molten lanthanide soaps and diffraction patterns for selected metal soaps. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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