

Self-Assembled Networks and Molecular Gels Derived from Long-Chain, Naturally-Occurring Fatty Acids

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Self-assembly of molecular gelators in a variety of liquids provides an attractive route for the construction of nanostructured materials with desired functionalities. This review focuses on correlations between structural features of gelators, specifically derivatives of long-chain, naturally-occurring fatty acids in which functional groups have been modified systematically and their gelation efficiencies in a wide range of liquids. It is shown that molecular packing at different distance scales within the gel assemblies and the microscopic and macroscopic physical properties of the gels are sensitive to even small changes in gelator structure and properties of the liquid component. Structural insights are provided to understand better the basis for the rational design of molecular gelators.

Keywords: molecular gels, fatty acids, fibrillar networks, structure-property correlations, self-assembly

1. Introduction

Molecular gels are a solid-like form of soft matter comprised of a liquid and a low concentration of a molecular gelator whose mass is typically less than 2000 Da.¹⁻⁴ The formation of molecular gels results from molecular self-assembly. Initially, driven by supersaturation, nucleation occurs between gelator molecules.⁵ The nucleating centers form one-dimensional (1D) objects usually, such as fibers, rods, ribbons, tapes, platelets and tubules.⁶ The interactions that promote preferential 1D growth include electrostatic interactions, packing constraints, H-bonding, π - π stacking, dipolar interactions, hydrophobicity or hydrophilicity, and London dispersion forces.⁷ The 1D objects may bundle into objects with larger cross-sections and interact further to form the three-dimensional (3D) self-assembled fibrillar networks (SAFiNs) that immobilize the liquid.^{3,4}

Gels are classified broadly as either hydrogels (i.e., in which the liquid component is aqueous) or organogels (i.e., in which the liquid component is organic).⁸ Hydrogels have been used in food, pharmaceutical and tissue engineering applications given their aqueous nature and, in many cases, high biocompatibility.⁹ Organogels have been investigated extensively during the past three decades because of their numerous potential applications as controlled drug delivery

devices,^{10,11} matrices for carrying chemosensors,¹² and oil recovery agents.¹³ Another category of molecular gels, metallo gels, in which metallic elements are incorporated into either the gelator or the liquid, have recently become a focus of research.^{2,14,15} Research on metallo gels can be traced back to the well-known metal-containing lithium grease gels, such as lithium stearate and lithium 12-hydroxystearate.¹⁶ The incorporation of metal ions in gelators can enhance further the ability to tune and introduce new properties into their gels, including magnetism, luminescence, molecular electronic responses, and catalytic activity.¹⁴

Molecular gels are structurally and rheologically complex systems. Although many recent studies and reviews have focused on quantitative correlations between structural features of gelators and the gelation efficiency,¹⁷⁻¹⁹ there is no paradigm for the design of molecular gels at this moment, and the prospects for one appearing in the near future are dim. Before it will be possible to predict *a priori* the ability of a system to form a gel, the relationship between structural features of gelators and their gelation properties must be well understood. Currently, the underpinnings of a gelator structure-gelation efficiency relationship have eluded many efforts of the gel community to find them. Although the gelators reported so far cover an extremely broad range of molecular structures, molecules as simple as alkanes to very complex ones containing two-

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components,^{3,4} seemingly minor additions, deletions, and transformations of functional groups on a gelator can have dramatic consequences on its ability to aggregate and on the strength of its SAFiN networks.

Derivatives of long-chain, naturally-occurring fatty acids are one class of potential gelators that has generated significant research interest.^{3,4,20,21} Long-chain fatty acids, such as (9*Z*)-octadecenoic acid (oleic acid, OA), (9*Z*,12*R*)-12-hydroxy-9-octadecenoic acid (ricinoleic acid, D-RA), and octadecanoic acid (stearic acid, SA), can be derived directly from different kinds of plant seed oils after hydrolysis of their glycerides.²²⁻²⁴ Many of these fatty acids have been examined extensively in various studies because of their importance as storage lipids and their physiological effects associated with cell stability.^{25,26} The biocompatibility, low cost, and environmentally beneficial attributes of these acids add to their attractiveness as molecular gelators. The major focus of this review is on organo-, hydro-, and metallo-gels derived from long-chain, naturally-occurring fatty acids. Studies involving this topic are summarized here to identify structure-gelation correlations and to suggest how new structural modifications may be exploited to create efficient gelators from other naturally occurring molecules.

2. Gelators and Their Gels

2.1. *n*-Alkanes

Structurally, the simplest class of molecular gelators is *n*-alkanes.²¹ They can be viewed as a structurally simpler version of long-chain fatty acids. Long *n*-alkanes are one of the major naturally occurring components of various waxes, such as Candelilla wax.²⁷ Long *n*-alkanes (with 24 to 36 carbon atoms) can gelate short *n*-alkanes and some non-hydrocarbon liquids.^{28,29} *n*-Alkanes with longer alkyl chains can form gels with a wider range of organic liquids and exhibit lower critical gelator concentrations (CGCs, the minimum amounts of a gelator necessary to make a gel at room temperature) and higher gel melting temperatures (T_g) than the *n*-alkanes with shorter chains.²⁸ The greater efficiency of the longer *n*-alkanes can be ascribed to more London dispersion forces in the SAFiNs.^{21,28} However, according to rheological, thermal and stability studies, most of the *n*-alkanes gels are weak²⁸⁻³⁰ because the London dispersion forces are much weaker on a group-to-group basis than H-bonding and dipolar interactions which are available in SAFiNs with more structurally complex gelators. Powder X-ray diffraction (XRD) studies of some long *n*-alkanes suggest that gelator molecules pack in a lamellar arrangement.^{31,32} In large part, the reason why

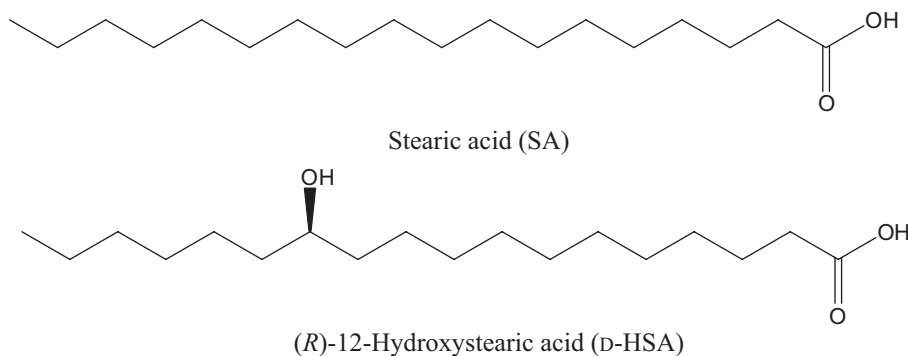
objects observed at the micrometer length scale in SAFiNs of *n*-alkane gels are platelets (i.e., 2-dimensional objects)³¹ can be ascribed to a lack of specific directional character to the London dispersion forces.

2.2. Saturated fatty acids

2.2.1. Alkanoic acids

By inserting a hetero-functional group along the alkyl chain, inter-molecular interactions other than London dispersion forces can be introduced to play an important role in the aggregation and formation of SAFiNs. For example, adding a carboxylic acid group at the terminal carbon leads to another gelator, albeit an inefficient one, octadecanoic acid (stearic acid, SA). SA is a major component of the triglycerides of many plant seed oils, especially kokum oil.³³ SA forms dimeric species in *n*-alkane solutions by inter-molecular H-bonding interactions between carboxylic acid head groups.³⁴ However, introduction of a terminal carboxylic acid head group does not aid in gelation to a great extent.^{35,36} Gelation occurs only at relatively high concentrations of SA and in a limited number of liquids.³⁷ For example, the gel of 5 wt.% SA in sunflower oil is weak mechanically, as indicated by its storage modulus (100 Pa) and low T_g value (< 40 °C).³⁵ Besides SA, alkanolic acids with chain lengths between 16 to 31 carbons are found in triglycerides of different plant seeds oils,³³ and they are known to gelate vegetable oils, including sunflower oil and lavender oil.³⁷ There are no significant differences among the gelation efficiencies of alkanolic acids with chain lengths greater than 26 carbons. Alkanolic acids with longer chain lengths can form gels at lower gelator concentrations and their gels exhibit higher melting temperatures than those with shorter chain lengths (i.e., between 16 and 26 carbons).³⁷ The increased London dispersion forces for long-chain alkanolic acids play a key role in the increased gelation efficiencies.³⁷ However, the overall ability of the alkanolic acid gels to resist plastic deformation is very weak.³⁸

Similar to alkanolic acids, 1-alkanols are not efficient gelators of vegetable oils.³⁵ A study of the gelation properties of stearic acid, stearyl alcohol, and their mixtures at different stearic acid: stearyl alcohol ratios in a vegetable oil indicates that both pure stearic acid and stearyl alcohol are inefficient gelators and both exhibit platelet-like morphology.³⁵ The morphology of the crystals changes significantly with composition, as indicated by both powder X-ray patterns and microscopy images (Figure 1). Elongated, fiber-like crystals and significantly increased hardness and elasticity (as determined by mechanical measurements) are observed at some compositions of the mixtures.³⁵



Scheme 1. Structures of two gelators based on alkanolic acids with 18 carbon atoms.

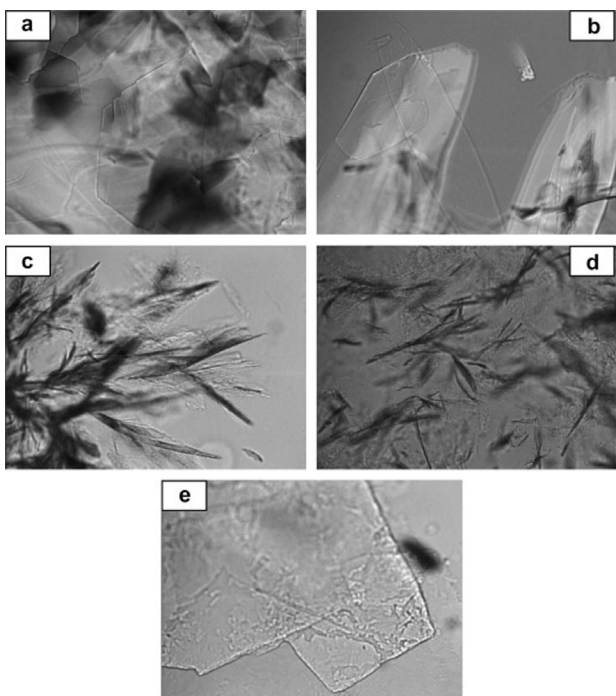


Figure 1. Polarized optical microscopy (POM) images of the crystals of stearic acid, stearyl alcohol, and their mixtures at 1:0 (a), 7:3 (b), 1:1 (c), 3:7 (d), and 0:1 (e) stearic acid:stearyl alcohol ratios in a vegetable oil; the size of each image is 0.577 mm \times 0.770 mm (from reference 35; copyright Elsevier. Reproduced with permission).

2.2.2. Hydroxyalkanoic acids

One of the best known gelators in the family of fatty acids is (*R*)-12-hydroxystearic acid (D-12HSA). It can be synthesized from castor oils, which contain up to 85% ricinoleic acids in the form of triglycerides by hydrogenation and hydrolysis. D-12HSA contains two sites suitable for H-bond donation and acceptance (Scheme 1). D-12HSA has an equivalent framework to SA but with an additional hydroxyl group at C12 in a stereospecific orientation. Based upon the difference in ranges of liquids gelled, T_g values, CGCs, storage moduli and the periods of gel stability in sealed containers at room temperature, it is clear that the introduction of a 12-hydroxyl group along the alkanoyl chain increases the gelator efficiency of SA dramatically.^{19,39,40} The

aggregates formed in most D-12HSA gels are helical fibers; they exhibit enhanced circular dichroic signals, which can be attributed to the helical arrangements of the molecules within the SAFiNs.⁴¹ Inside the fibers, hydroxyl groups on the chiral carbon atoms form inter-molecular, unidirectional H-bonds along the fiber axis (Figure 2). Similar to SA, D-12HSA molecules also pack in a head-to-head arrangement within layers of their benzene and acetonitrile derived SAFiNs, as indicated by the powder X-ray diffractograms of their gels.⁴⁰ The dimensions of the fiber cross-sections are in some ways mediated by head-to-head arrangements among carboxylic acid head groups and the diffractograms indicate repeat distances that are twice the molecular length of a D-12HSA molecule. This anchoring promotes the formation of H-bonding networks and further aids in the stability of the fibers.⁴⁰ Thus, as opposed to *n*-alkanes, London dispersion forces are not the only driving force controlling aggregation and inter-molecular orientation of the polymethylene chains of D-12HSA molecules. The inter-molecular H-bonding interactions, resulting from the presence of the carboxylic group, can aid significantly in the stabilization of the SAFiNs of SA, but not necessarily in a manner that leads to enhanced gelation efficiencies! The substantially better gelating ability of D-12HSA than that of SA is clearly related to the importance of the secondary H-bonding networks of C12 hydroxyl groups along the polymethylene chain.^{4,19,36}

Unlike most organogels with crystalline SAFiNs, those of 2 wt.% D-12HSA in silicone oil exhibit thixotropic properties after being destroyed by severe mechanical strain; they can reform and recover at least some of their viscoelastic properties without heating.¹⁹ The restoration of gel viscoelasticity after the cessation of mechanical disruption occurred within 10 s, during which time the elastic modulus was found to recover up to 70% of its initial value.¹⁹ The hypothesized mechanism for this phenomenon is that the fibers are not destroyed (completely), but at least some of the interactions which join fibers or spherulites (i.e., highly branched, small fibers emanating from a central node) are broken. After their disruption, fibers

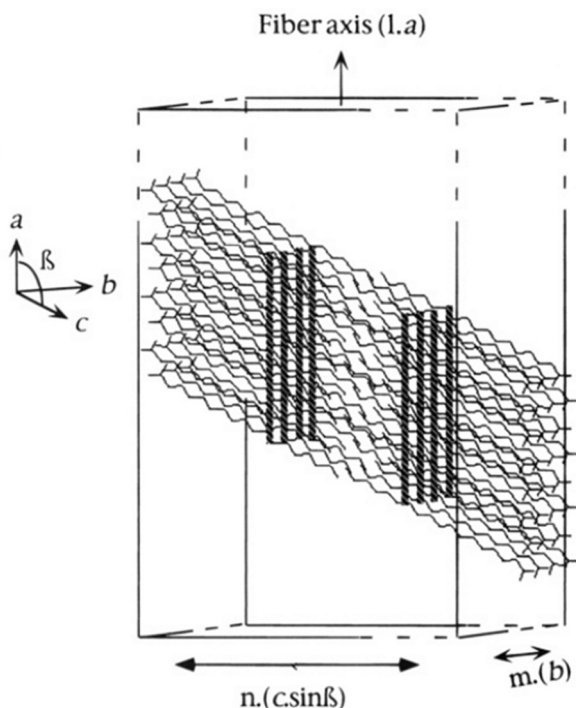


Figure 2. Structural model of the D-12HSA fibrillar or ribbon-like aggregates in organic liquids. The fiber geometry is indicated and the directions of unidirectional H-bonds are represented by the vertical lines (from reference 40; copyright American Chemical Society. Reproduced with permission).

diffuse and reform the SAFiNs via renewed contacts.¹⁹ In order to understand fully the mechanism responsible for the thixotropic behavior, the kinetic and morphological changes that occur on the micrometer distance scale, as fibers or spherulites reconnect, must be followed. However, the kinetic and thermodynamic aspects of gel formation with D-12HSA (or other gelators) via cooling from their sol phases^{21,42} are not the focus of this review; for that reason, details about them will not be discussed.

The network structure of D-12HSA gels can vary depending on the liquid in which the gel forms. For example, the wide angle spacing in XRD diffractograms (ca. 4.6, 3.9 and 4.8 Å) suggests that D-12HSA packs into triclinic polymorphs in nitriles, aldehydes and ketones, respectively. The lamellar spacing (38 to 44 Å) is less than twice the extended molecular length (46 Å) in these liquids, suggesting interdigitated networks.⁴³ In alkane and thiol liquids, D-12HSA packs into hexagonal polymorphs with a wide angle peak at ca. 4.1 Å. The spacing corresponding to the low angle peaks (ca. 54 Å) is greater than twice the extended molecular length of D-12HSA. The two different polymorphs cause differences in some microscopic and macroscopic physical properties of the gels as well. The objects in SAFiNs of D-12HSA gels in nitriles, aldehydes and ketones are spherulites and the gelator concentration needed to form gels (> 1.5 wt.%) is higher than that needed in alkanes and thiols

(ca. 1.0 wt.%), where the SAFiNs consist of non-spherulitic fiber arrays.⁴³ Whereas the alkane and thiol gels are clear (at least near their CGCs), those with aldehydes, ketones and nitriles are opaque at all concentrations examined. The different gelator packing arrangements can alter gelation efficiency. In recent reports by Rogers *et al.*,^{44,45} solubility parameters of liquids, including the $E_T(30)$ scale, Hildebrand solubility parameter, Hansen solubility parameters, and different liquid clustering techniques have been used to analyze the gelation ability of D-12HSA. The gelating abilities of enantiopure and racemic forms of 12HSA can be very different.⁴⁰ A study of both enantiopure D-12HSA and racemic DL-12HSA in mineral oil indicates that the racemate gels are not as strong as those of D-12HSA.⁴⁶ For example, the CGC of D-12HSA (< 1.0 wt.%) is lower than that of DL-12HSA (ca. 2.0 wt.%) in mineral oil.⁴⁶ The SAFiNs of D-12HSA gel are comprised of high aspect ratio helical fibers, while the objects observed in the SAFiNs of DL-12HSA gel are platelets.⁴⁶ In the same study, the physical properties of mixtures at different D-12HSA and L-12HSA ratios in mineral oil were investigated. With an increase of D-12HSA in the composition, the morphology of the SAFiNs changed from platelet-like to fibrous objects. The differences in morphology and gelation efficiency are related to the molecular packing arrangements of the carboxylic acid head groups (as well as the secondary C12 hydroxyl H-bonding networks). The Fourier transform infrared spectroscopy (FTIR) spectra in the region of carboxylic acid absorptions indicate that the carboxylic acid head groups of DL-12HSA and mixtures with D-12HSA and L-12HSA ratios at and below 90:10 exist equally as cyclic and acyclic dimers; the proportion of cyclic dimers significantly increases in D-12HSA and mixtures at and above 90:10 (Figure 3).⁴⁶ The predominance of cyclic dimers in D-12HSA promotes longitudinal growth along the secondary fiber axis (Figure 4). On the other hand, with a higher proportion of racemic DL-12HSA, the formation of acyclic dimers becomes more significant, which diminishes the formation of extended H-bonding networks but favors the growth of platelets. The polar head groups cannot be effectively shielded in the acyclic dimers from the low polarity liquid, and larger activation energies are found during the nucleation and growth of platelets than that of fibers.

Also, the appearances of positional isomers of racemic DL-nHSA ($n = 2, 3, 6, 8, 10, 12$ and 14 refers to the position of the hydroxyl group along the alkanoyl chain of the hydroxyoctadecanoic acid isomers) in mineral oil have been studied.⁴⁷ It was found that the nature and stability of the SAFiNs are very sensitive to the position of the hydroxyl group. DL-2HSA and DL-3HSA cannot form gels in mineral oil at concentrations up to 2 wt.%, whereas

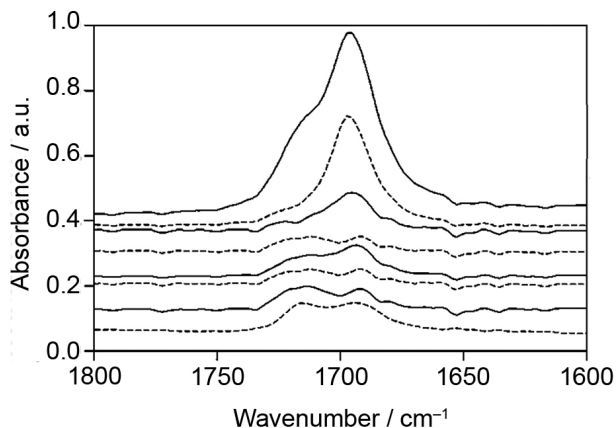


Figure 3. FTIR spectra in the region of carboxylic acid absorptions of mixtures with D-12HSA and L-12HSA ratios of 50:50, 55:45, 60:40, 70:30, 80:20, 90:10, and 95:05 (from bottom to top). The peak at ca. 1720 cm^{-1} is attributed to the acyclic dimers of carboxylic acid groups, and the peak at ca. 1700 cm^{-1} is attributed to the cyclic dimers (from reference 46; copyright Royal Society of Chemistry. Reproduced with permission).

2 wt.% DL-6HSA, DL-8HSA, DL-10HSA, DL-12HSA, or DL-14HSA in mineral oil are rheologically true gels.⁴⁷ The dispersions of DL-2HSA and DL-3HSA are comprised of separated crystals that do not interact to form a network; structures of the aggregates of the other DL-nHSA consist of a large number of small platelets and fibers that are observed to interact and form a 3D network. The data from both the FTIR spectra and powder X-ray diffractograms suggest that the carboxylic acid head groups of DL-2HSA do not form dimers and those of DL-3HSA exist only as acyclic dimers.⁴⁷ Also, there are no detectable wide angle peaks in the powder X-ray patterns that would be expected if the chains were organized within a layer.

Thus, when the secondary hydroxyl group is near the carboxylic acid head group in a DL-nHSA, the hydroxyl groups are unable to form extended H-bonding networks (Figure 5). However, the FTIR and powder X-ray patterns in the gel states of DL-6HSA through DL-14HSA indicate that the carboxylic acid head groups can form cyclic carboxylic dimers together with acyclic dimers, and the molecular pairs constitute a lamellar thickness (Figure 5). The FTIR patterns also suggest the presence of an H-bonding array between the secondary hydroxyl groups in the gels of DL-6HSA through DL-14HSA. The gels of DL-6HSA through DL-14HSA have a wide angle peak in their powder X-ray patterns corresponding to a Bragg spacing ca. 4.1 Å, which is consistent with a hexagonally packed polymorph.⁴⁸ When the secondary hydroxyl group is at least 5 carbon atoms away from the carboxylic acid head group, H-bonding networks which promote the formation of SAFiNs are established via the hydroxyl groups along the secondary axis. Therefore, in order to design an efficient molecular gelator from hydroxylated derivatives of fatty acids, there must be a relatively long distance between the hydroxyl group and the carboxylic acid head group.

2.3. Unsaturated fatty acids

Besides saturated fatty acids, unsaturated fatty acids, especially the *cis* isomers, are common constituents of natural fats and oils. *cis* Unsaturated fatty acids have been examined extensively because of their importance in cell membranes and role as macronutrients.²⁶ Typically, these molecules have very limited gelating abilities, as

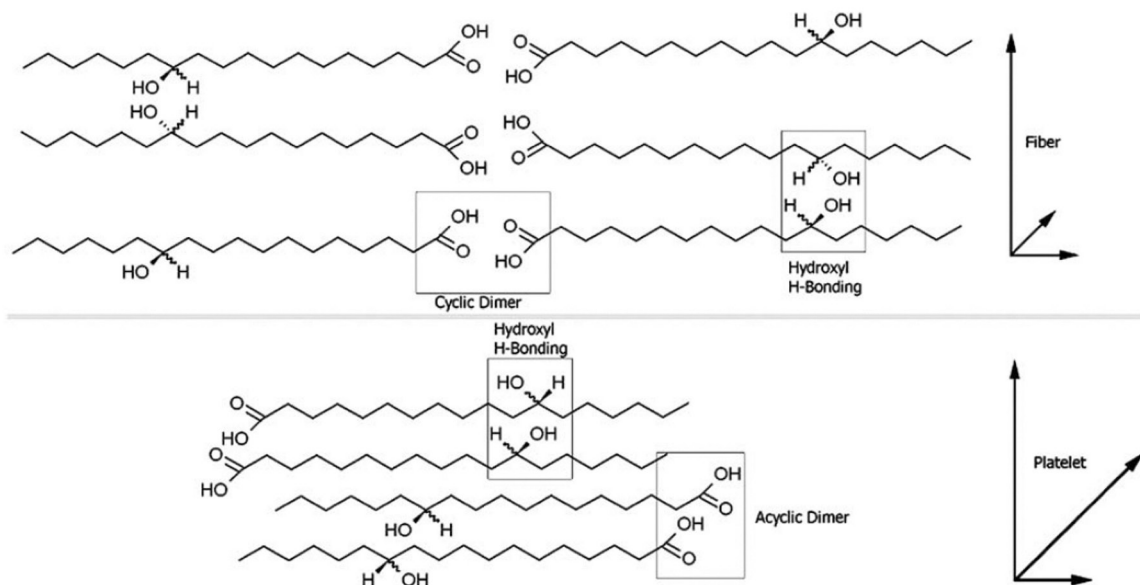


Figure 4. Possible packing modes of D-12HSA (top) and DL-12HSA (bottom) in the SAFiNs of mineral oil gels (from reference 46; copyright Royal Society of Chemistry. Reproduced with permission).

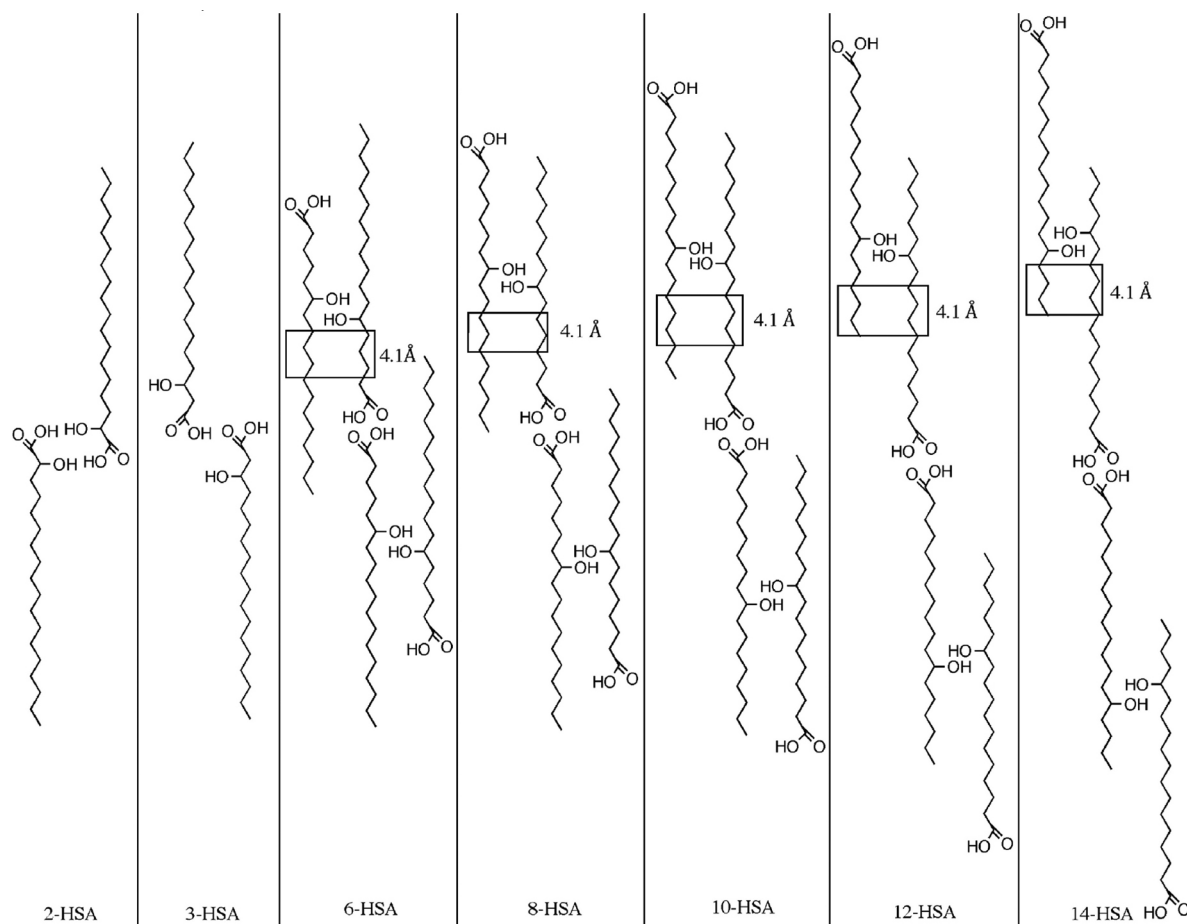


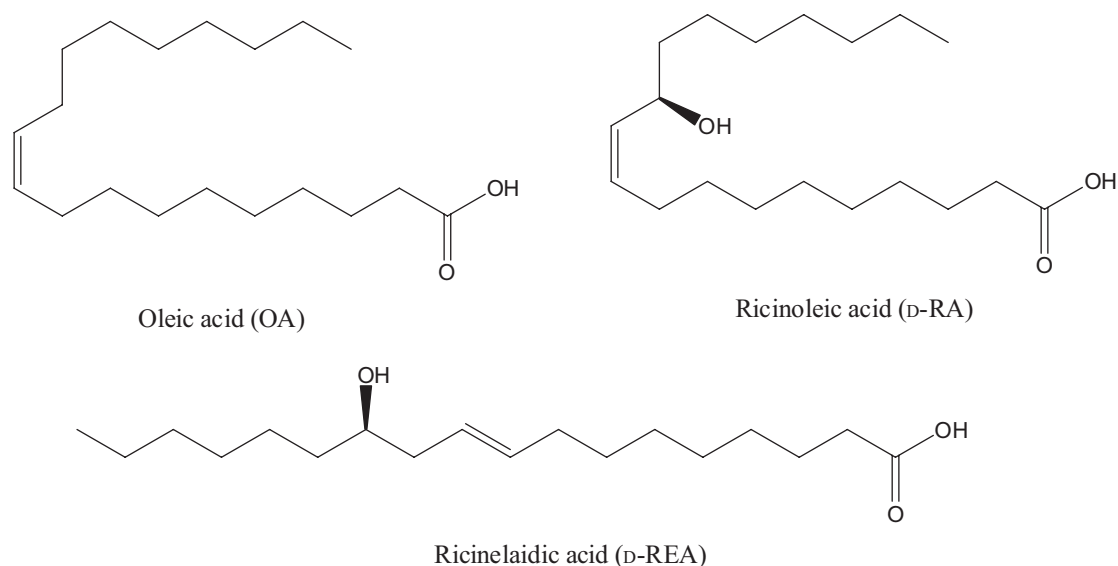
Figure 5. Proposed packing arrangements of DL-nHSA isomers in the SAFiNs of their gels/dispersions in mineral oil. Distances shown are based on X-ray measurements (from reference 47; copyright American Chemical Society. Reproduced with permission).

indicated by their low melting temperatures. The bent polymethylene chains, resulting from the presence of a *cis* double bond, limit the packing efficiency of these molecules in a crystalline lattice, but they contribute beneficially to the fluidity of cell membranes.²⁶ For the same structural reasons, OA and D-RA, molecules equivalent to SA and D-12HSA, respectively, except for the presence of a *cis* double bond, are very inefficient gelators whose melting temperatures as neat solids are below 15 °C.⁴⁹ OA can be isolated from many plant oils, especially canola oil,²² while the triglyceride of D-RA is a major component of the oil obtained from the seeds of mature castor plants.²³

The *trans* isomers of unsaturated fatty acids, however, can perform very differently as gelators from the *cis* isomers because they are able to adopt much more linear and extended conformations. For example, the *trans* isomer of the inefficient gelator D-RA (Scheme 2), (9*E*,12*R*)-12-hydroxy-9-octadecenoic acid (ricinelaidic acid, D-REA), is a much better gelator. D-REA, obtained by photoisomerization of D-RA, forms gels with relatively low polarity liquids, like alkanes, hexylbenzene and silicone

oils.⁵⁰ However, it is not as efficient as the less ‘stiff’ and saturated analogue, D-HSA.⁵⁰ The difference in gelator efficiencies and physical properties of the corresponding gels are related to their solubilities in the liquids to be gelled; in both high and low polarity liquids, the solubilities of the methyl esters of long-chain fatty acids increase with an increase in the degree of unsaturation.⁵¹ Similarly, the presence of a double bond leads to better solubility of D-REA than that of D-12HSA. In turn, the formation of D-REA gel networks is disfavored.⁵⁰

In addition, D-REA can gelate vegetable oils, such as canola oil, at concentrations higher than 2 wt.%.^{52,53} In these studies, D-REA was blended with refined, bleached, and deodorized canola oil. The neat D-REA crystallizes into spherulitic microstructures, whereas the SAFiN structures of D-REA gels in canola oil are comprised of long fibers that intertwine into twisted bundles.⁵³ In one case, the solvent interactions during nucleation and growth lead to a solid that is not amenable to form gels rheologically; in the other, the solvent interactions do allow a gel SAFiN to form. Questions dealing with the differences may be answerable eventually using Hansen solubility and related



Scheme 2. Structures of some unsaturated and hydroxylated alkanolic acids derivable from plants.

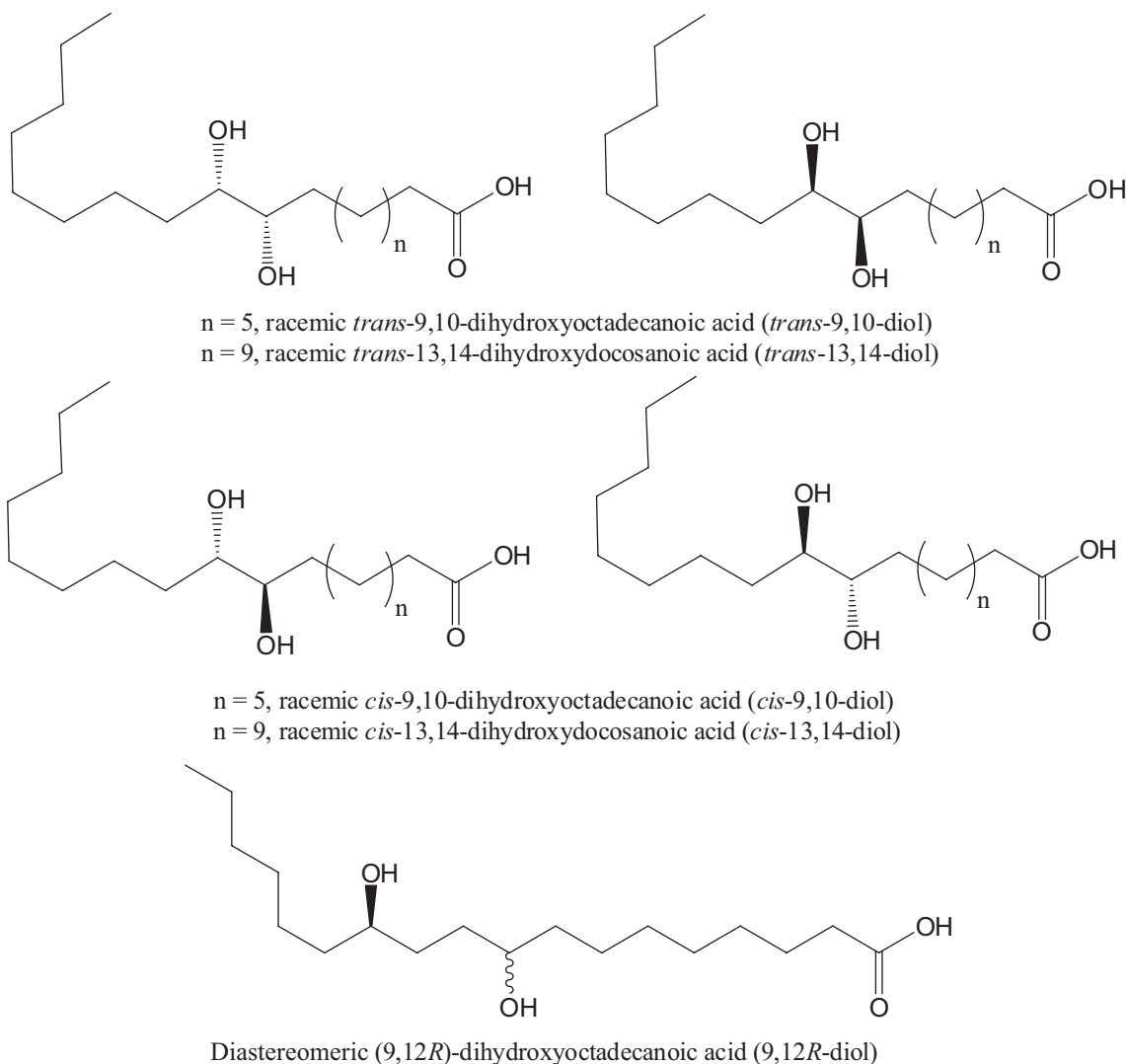
approaches that include dynamics.^{45,54} They do not as of now. The powder XRD patterns of D-REA gels indicate the presence of dimeric species associated at the carboxylic acid head groups. The physical properties of D-REA gels in vegetable oils are very dependent on concentration and temperature. The fibers become thicker and longer, and fiber clustering is more apparent when sols are incubated at higher temperatures (but below T_g) or at higher gelator concentrations.⁵² As expected, the period of time needed for gel formation decreases with an increase in gelator concentration. Both the mechanical strength and stability of the gels increase with increasing gelator concentration and decreasing incubation temperature. The elastic moduli in the linear viscoelastic region of gels of 5 wt.% D-REA in canola oil are ten times higher than those of 2 wt.% D-REA gels in the same liquid.⁵³ In addition, a fully established gel network can also be characterized by a zero slope of a frequency-dependent elastic modulus curve in the linear viscoelastic region.⁵⁵ At all concentrations examined, however, the values of elastic moduli for D-REA in canola oil gels are frequency dependent and exhibit slightly positive slopes as the frequency is increased. The networks are not very stiff and the elastic modulus of the gels can be affected by the frequency applied. The positive slopes indicate that the mixtures of D-REA in canola oil are weak gels overall.⁵²

2.4. Dihydroxyalkanoic acids

Although the presence of a *cis* double bond in unsaturated, naturally-occurring fatty acids limits gelation ability, it opens many possibilities for functional group transformations, each of which can lead to a potential

gelator. Recently, diol-based derivatives of three different unsaturated fatty acids, D-RA, OA, and erucic acid (EA), have been synthesized by one-step reactions and have been investigated as organogelators.⁵⁶ The results indicate that dihydroxyl functionality can be an important contributor to the gelation ability (or lack thereof) of fatty acids. First, diastereomeric (9,12*R*)-dihydroxyoctadecanoic acid (9,12*R*-diol, a γ -diol), in which the two hydroxyl groups are on carbon atoms separated by two methylenes, is found to form more thermally stable and mechanically stronger fibrous gels than the monohydroxylated analogue, D-12HSA. Powder XRD data and quantum calculations indicate that 9,12*R*-diol molecules are in extended conformations and the two hydroxyl groups are capable of interacting only inter-molecularly (Figure 6). The frequency and relative difference in the contributions of H-bonded OH stretching bands in the IR spectra imply that the inter-molecular H-bonds in 9,12*R*-diol gels are stronger than those in D-12HSA gels. The stronger and more extensive inter-molecular H-bonding interactions may be responsible for the SAFiN networks of 9,12*R*-diol being more robust than those of D-12HSA in each of the liquids for which direct comparisons are possible.

In addition, fiber formation by α -diols, in which the two hydroxyl groups are on adjacent carbon atoms, is primarily dependent upon diol stereochemistry. The *cis*- and *trans*-isomers of 9,10-dihydroxyoctadecanoic acid (*cis*-9,10-diol and *trans*-9,10-diol) and *cis*- and *trans*-13,14-dihydroxydocosanoic acid (*cis*-13,14-diol and *trans*-13,14-diol), have been investigated to assess the influence of the stereochemical relationship between the two hydroxyl groups on gelator efficiencies.⁵⁶ *trans* Diols are efficient gelators in aromatic liquids, while *cis* diols formed 3D



Scheme 3. Structures of some dihydroxylated fatty acid gelators.

objects that precipitated without forming SAFiNs in all the liquids investigated. The proximity of the two hydroxyl groups allows for possibilities to undergo both inter- and intra-molecular H-bonding interactions.

Results from powder XRD and modelling studies indicate that inter-molecular H-bonding networks are more favored by the *trans* diols than by the *cis* diols due to the difference in their abilities to pack efficiently. In the *trans* diols, molecules can pack in extended conformations while undergoing either inter- or intra-molecular H-bonding interactions, which leads to two inter-molecular hydroxyl H-bonds *per* molecule that can promote stabilization of the fibrillar structure. On the other hand, intra-molecular H-bonding interaction forces the *cis* diols into bent conformations; thereby, only one hydroxyl group *per* molecule can be utilized to construct a well-packed H-bonding network.⁵⁶ Thus, the dependence of gelation efficiencies on diol stereochemistry can be attributed to the

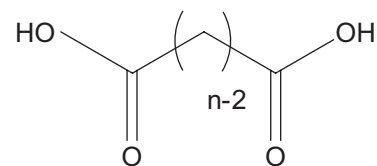
propensities to form or not to form extensive inter-molecular H-bonding networks along the alkanoyl chains. Although fiber formation is favored by the *trans* diols, the presence of intra-molecular H-bonding interactions in assemblies of *trans*-9,10-diol and the lower overall strength of H-bonding interactions (indicated by the IR frequencies) lead to a lower gelator efficiency than the γ -diol, 9,12*R*-diol, or even the monohydroxylated analogue, D-12HSA. For example, *trans*-9,10-diol forms gels in toluene only at a concentration higher than 2.1 wt.%, while the CGCs for D-12HSA and 9,12*R*-diol gels in toluene are 0.9 and 0.5 wt.%, respectively.⁵⁶

Besides H-bonding interactions, London dispersion forces between polymethylene chains of diol-based fatty acids also play an important role in promoting the formation of a fibrillar network. As noted previously with *n*-alkanes as the gelators,²⁸ elongating the alkanoyl chain length of *trans*-9,10-diol to *trans*-13,14-diol leads to improved

gelling properties.⁵⁶ The corresponding increase in London dispersion forces even result in *trans*-13,14-diol being a more efficient gelator than D-12HSA despite the presence of intra-molecular H-bonding interactions in the former.⁵⁶ As a specific comparison, the melting temperatures of gels of 5 wt.% *trans*-13,14-diol and D-12HSA in nitrobenzene are > 140 and 50 °C, respectively, and the loss tangent of the former is ten times lower than that of the latter.⁵⁶

2.5. Dicarboxylic acids

Dicarboxylic acids are another type of potential gelator derived from fatty acids; they can be produced when plant oils containing fatty acids are oxidized. Dicarboxylic acids (Scheme 4), including adipic (4 carbon atoms), suberic (6 carbon atoms) and sebacic (8 carbon atoms) acids, are capable of gelling plant oils (e.g., sunflower oil and lavender oil).³⁷ The thermal stabilities of the corresponding gels are higher than those of monocarboxylic acids of the same chain length. However, these dicarboxylic acids cannot gelate alkanes.³⁷ In addition, dicarboxylic acids with chain lengths from 5 to 13 carbon atoms form gels with crude oil at room temperature, while shorter dicarboxylic acids do not due to their insufficient solubilities in oil even at elevated temperatures.⁵⁷ Dicarboxylic acids can also harden non-liquid materials, such as bitumen, at room temperature.⁵⁷ Bitumen is a hydrophobic material obtained from crude oil distillates. The addition of 3 wt.% dodecanedioic acid increases the softening temperature

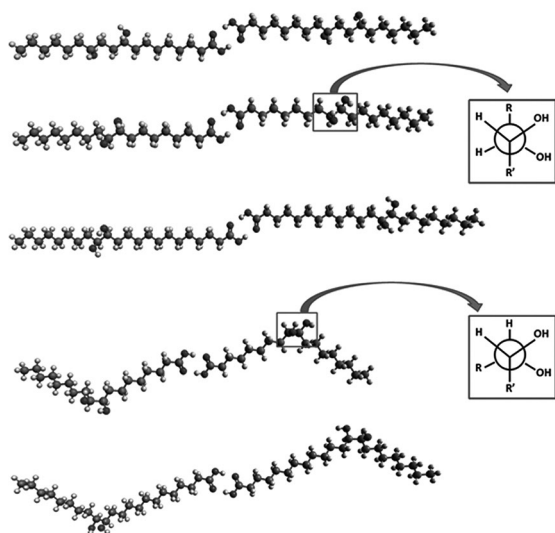


n = 4, adipic acid
n = 6, suberic acid
n = 8, sebacic acid
n = 12, dodecanedioic acid

Scheme 4. Structures of gelators: dicarboxylic acids.

of bitumen from 46 to 110 °C, and increases the hardness and elastic modulus of bitumen dramatically without increasing the melt viscosity. In the temperature range where bitumen is purely a liquid (> 46 °C, lower than the softening temperature), the network can still immobilize bitumen and the mixtures behave like typical gels. A network of micrometer-long fibers is observed (Figure 7). The corresponding IR data indicate that the free acid groups form H-bonds with one another when cooled from the softening temperature to room temperature. The formation of crystalline fibers in the mixture, mainly driven by H-bonding interactions, is directly related to the improvement of thermal and mechanical properties of bitumen. The softening temperature of the mixture alternates between odd and even carbon chain lengths of the dicarboxylic acids, but overall, the softening temperature increases with an increase in chain length.⁵⁷

(a)



(b)

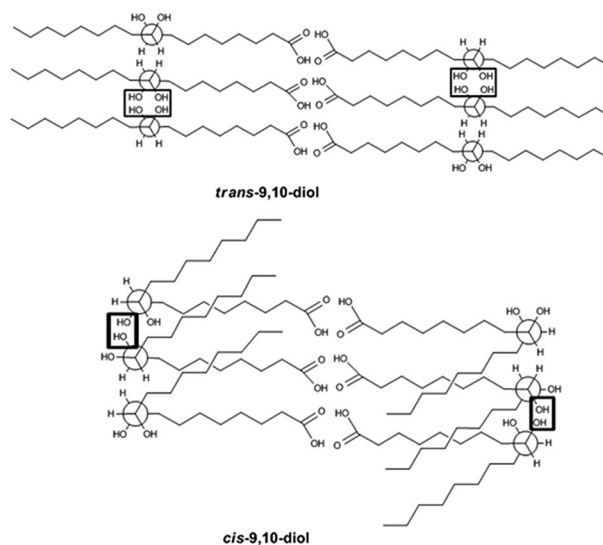


Figure 6. In (a) the proposed interacting arrangements of pairs of gelator molecules in their assemblies from geometry optimization by Gaussian using M06/6-31+G(d,p): 9,12*R*-diol, *trans*-9,10-diol, *trans*-13,14-diol, *cis*-9,10-diol, and *cis*-13,14-diol (from top to bottom). In (b) possible *cis*-9,10-diol and *trans*-9,10-diol packing modes shown in a top view (2-dimensional) projection. Inter-molecular H-bonding interactions are noted in the rectangles (from reference 56; copyright John Wiley and Sons. Reproduced with permission).

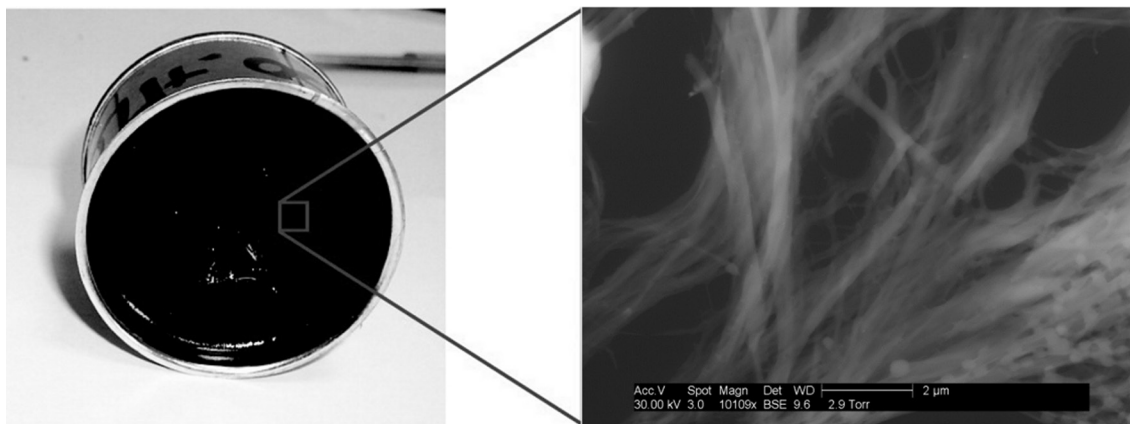


Figure 7. Photograph and scanning transmission electron microscopic image of a mixture of 6 wt.% dodecanedioic acid in bitumen at room temperature (from reference 57; copyright American Chemical Society. Reproduced with permission).

2.6. Modified carboxylic acid groups of fatty acids

In addition to the functional group transformations discussed above at various positions along the chains of fatty acids, simple modifications of the terminal carboxylic acid group can also lead to different potential gelators. For example, esterification precludes the formation of carboxylic acid dimers. In this way, various types of inter-molecular interactions, such as electrostatic and π - π stacking, can be introduced or modified. Examples of derivatives of carboxylic acids that are organogelators include waxes,^{27,58} *N*-acylethanolamines,⁵⁹ fatty acid alkyl esters,³⁷ sorbitan fatty acid monoesters,^{11,60} monoglycerides,⁶¹ and alkali metal soaps.⁶²⁻⁶⁴

Although these materials, many of which exist as mixtures with complex compositions, really merit a section of their own, only a cursory survey of examples is presented here in order to give the reader a sense of the diversity of the systems that have been examined (and the potential for new ones!).

Waxes such as rice bran, carnauba and candelilla are composed mainly of esters, fatty acids, and alkanes with different chain lengths.⁶⁵ They have been shown to form gels with different vegetable oils. For example, 1 wt.% of candelilla wax gels safflower oil.²⁷ Sorbitan monostearate, a mixture of sorbitan esters, with the stearate and palmitate esters predominating,⁶⁰ can gelate a number of organic liquids, including hexadecane, isopropyl myristate, and a range of vegetable oils, such as corn oil and olive oil. The CGC of sorbitan monostearate gel in hexadecane is ca. 1% m/m.⁶⁰ Distilled monoglycerides employed in the formation of organogels consist mainly of monostearin (up to 90%).^{33,66} One of these gels consists of 3 wt.% monoglyceride in pomegranate seed oil.⁶⁶ A 6 wt.% 1:1 monostearin:monopalmitin mixture in olive oil also forms a gel.⁶¹ However, because monostearin, monopalmitin and other derivatives of naturally occurring

fatty acids mentioned above are mixtures of different isomers,⁶⁷ it is not always clear which component of these derivatives or whether a synergistic interaction among them is most important in SAFiN formation and gelation. This is an important area for future research.

2.6.1. Fatty acid alkyl esters

Fatty acid alkyl esters are the major chemical constituents of plant wax. Bleached rice bran wax contains as much as 76% esters whose chains have an even-number (between 44 and 64) of carbon atoms.³³ Carnauba wax also consists predominantly of aliphatic esters.³³ Both bleached rice bran wax and carnauba wax are promising gelators for edible oils. As low as 0.5 wt.% rice bran wax is sufficient to form organogels with edible oils; carnauba wax forms gels at a higher CGC, 4 wt.%.⁶⁸ Although there is no direct evidence supporting that the gelation of these plant waxes is due only to fatty acid alkyl esters,³³ it is clear that pure fatty acid esters are gelators.³⁷ Methyl esters of docosanoic acid (22 carbon atoms), hexacosanoic acid (26 carbon atoms) and triacontanoic acid (30 carbon atoms) have been investigated as gelators of sunflower oil, lavender oil and diesel oil, respectively.³⁷ Both the fatty acids and their corresponding methyl esters can form gels in a similar range of liquids. However, the CGC increases upon methylation of docosanoic acid.³⁷ Without the H-bonding interactions between carboxylic acid head groups, gelation ability of 'shorter' acids is reduced.

By contrast, the CGCs of hexacosanoic acid methyl ester and triacontanoic acid methyl ester in the plant oils mentioned above are almost the same as their fatty acids counterparts.³⁷ For fatty acids with relatively long chain lengths (> 26 carbon atoms), London dispersion forces appear to play the dominant role in aggregation; the H-bonding interactions between carboxylic acid head groups may not be as important.

2.6.2. *N*-Acylethanolamines

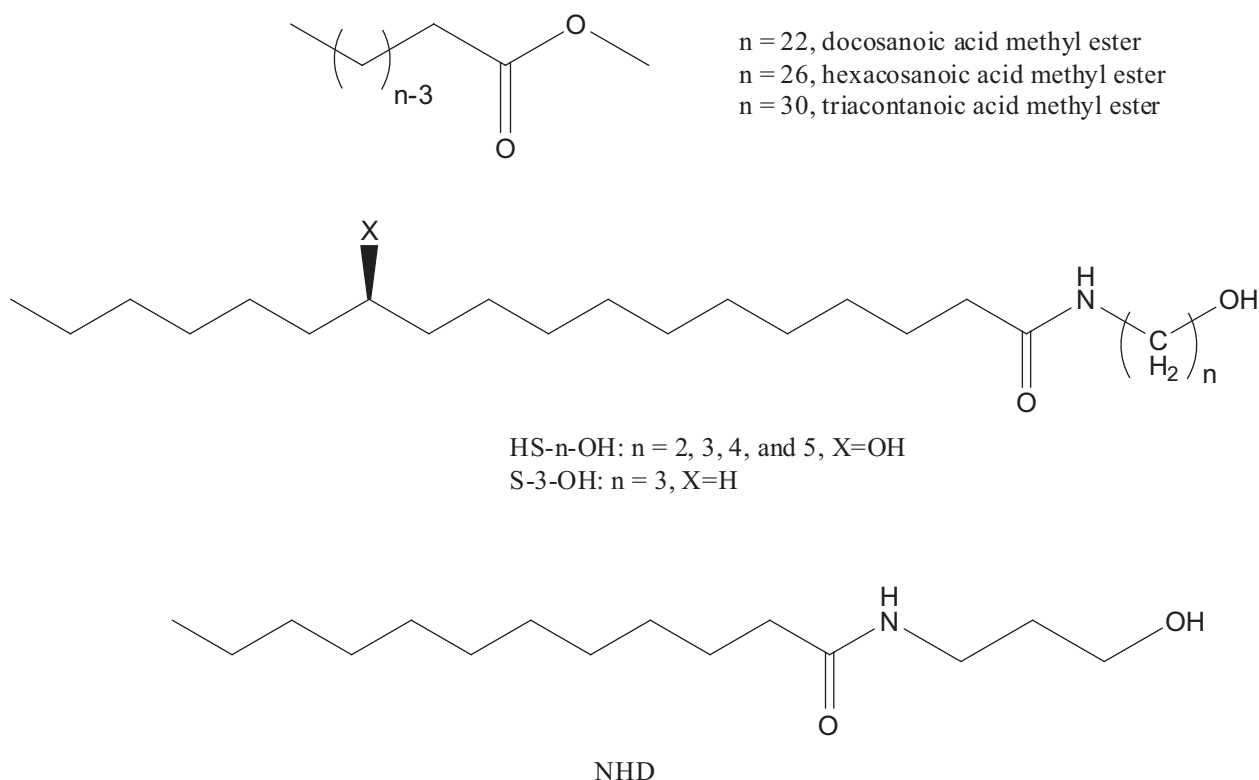
Previous studies^{19,69} and a review²⁰ have focused on derivatives of fatty acids, such as alkyl amides and aliphatic amines. They will not be discussed in detail here due to their paucity in naturally occurring compounds. *N*-acylethanolamines (NAEs) are an exception. These amphiphiles are present in a wide variety of biological membranes in animals, plants, and microbes.^{70,71} For the past two decades, NAEs have attracted the attention of researchers due to their pharmacological and medicinal properties as well as their potential in formulating liposomal systems for use in drug delivery and targeting.^{70,72}

Anandamide is one of the best known polyunsaturated NAEs. Besides its occurrence in biological membranes, it is found in chocolate and has physiological properties like that of cannabis in the brain.⁷³ The *cis* double bonds of anandamide force the chains to bend and inhibit its efficient packing in a crystalline lattice. Therefore, anandamide is a very inefficient gelator, as indicated by its low melting temperature ($-5\text{ }^{\circ}\text{C}$).⁷⁴ However, saturated NAEs and *trans* unsaturated NAEs, which may adopt extended conformations, may behave as potential gelators.

Few studies appear to have employed NAEs as molecular gelators. One involves (*R*)-12-hydroxyl-*N*-(2-hydroxyethyl)octadecanamide (HS-2-OH, Scheme 5).⁵⁹ HS-2-OH is an exceedingly efficient gelator based on the low CGCs of its gels in silicone oil, acetonitrile, CCl_4 ,

toluene ($<0.5\text{ wt.}\%$) and isostearyl alcohol (0.8 wt.%). On a micrometer distance scale, spherulites are observed in the isostearyl alcohol gel. On the nanometer distance scale, the isostearyl alcohol gel consists of non-parallel, twisted fibrous bundles with diameters ca. 100 nm. Powder XRD patterns of neat HS-2-OH and its isostearyl alcohol gel exhibit a Bragg spacing corresponding to 54.6 Å, which is consistent with twice the calculated molecular length, 54.3 Å. A possible 'head-to-tail' packing arrangement was hypothesized (Figure 8). The available inter-molecular H-bonding interactions between the hydroxyl groups along the secondary axis and those between amide and 2-hydroxyl groups on the *N*-alkyl chains can promote the formation of SAFiNs. Also, the gel of 2 wt.% HS-2-OH in isostearyl alcohol is thixotropic. Although it recovers its viscoelasticity completely within ca. 1 s after the cessation of destructive mechanical strain, formation of a gel after fast-cooling the sol phase occurs very slowly, over a period of ca. 2 days!⁵⁹

As a comparison, the gelation behaviors of the homologues, (*R*)-12-hydroxy-*N*-(ω -hydroxyalkyl) octadecanamides (HS-*n*-OH; *n* = 3, 4, and 5 refers to length of the *N*-alkyl chains), have also been reported.⁵⁹ Although the gels of all of the HS-*n*-OH in isostearyl alcohol are equally (ca. 99 %) thixotropic, their recovery times varied significantly, without an obvious correlation between the recovery times and the length of the *N*-alkyl



Scheme 5. Structures of some fatty acid ester and amide gelators.

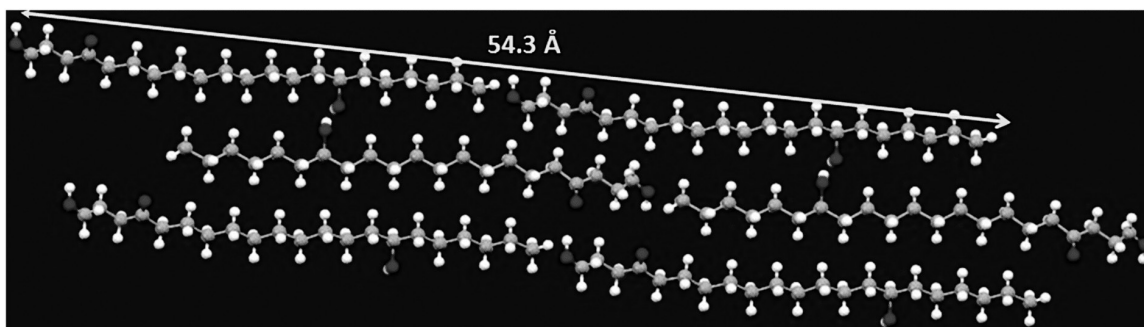


Figure 8. A possible ‘head-to-tail’ packing arrangement of HS–2–OH molecules in both the solid and isostearyl alcohol gel states (from reference 59; copyright of Royal Society of Chemistry. Reproduced with permission).

chains. However, the mechanical strength of the gels decreased with increasing length of the *N*- ω -hydroxylalkyl chains. The difference in mechanical strengths may be related to the propensities of ω -hydroxyl groups to undergo inter- or intra-molecular H-bonding interactions.

In addition, *N*-(3-hydroxypropyl)octadecanamide (S–3–OH)⁵⁹ and *N*-(3-hydroxypropyl)dodecanamide (NHD),⁷⁵ both without a hydroxyl group on the alkanoyl chains, have been investigated as organogelators. The higher CGCs and the lower T_g values of S–3–OH gels than those of HS–3–OH gels in the same liquids indicate that the absence of a 12-hydroxyl group along the alkanoyl chain decreases gelator efficiency dramatically, as it does when 12HSA is compared with SA; in both comparisons, the presence or lack of an extended inter-molecular H-bonding network along the alkanoyl chains appears to be the major factor. Whereas S–3–OH precipitated from toluene, NHD formed a gel, although at a higher CGC and a lower T_g value than found with HS–3–OH as the gelator.^{59,75} Apparently, increasing the alkanoyl chain length from 12 to 18 carbon atoms (and the attendant increase of London dispersion interactions) tips the

balance between precipitation and solvation in favor of precipitation during the transformation of the sols. Furthermore, in isostearyl alcohol, the gel with S–3–OH is not thixotropic, but the one with HS–3–OH is. This difference may be related to the inability of the S–3–OH gel to form (and reform!) H-bonding networks far from the amide head groups. However, the toluene gel with NHD is thixotropic.⁷⁵ Regardless, the very fast recovery times of some of the mechanically destroyed gels require that the destroyed gels not be comprised of 0D gelator objects (i.e., single molecules or very small aggregates of them); they must contain 1D species, large segments of spherulites, or complete spherulites which are disconnected from each other (Figure 9). In this way, re-establishment of inter-fiber (or other micro-object) connections can occur rapidly, leading to SAFiNs, via reformation of 12- and/or ω -hydroxyl H-bonding interactions.⁵⁹

2.6.3. Metal soaps

Many organometallic salts are known to be able to gelate both water^{7,14,18,76,77} and a variety of organic liquids.^{78,79} Most of the anionic ligands of these salts

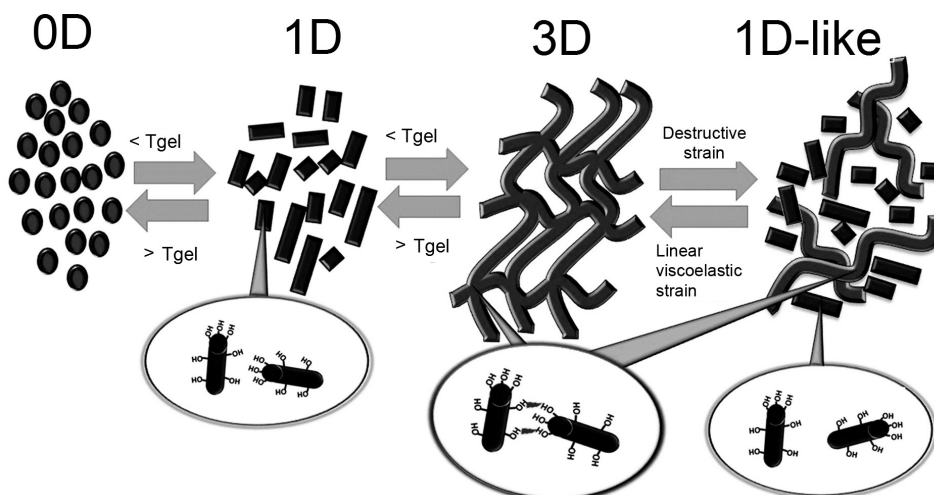


Figure 9. A possible mechanism for thermal and mechanical destruction and reformation of SAFiNs in the gels of HS–2–OH in isostearyl alcohol (from reference 59; copyright of Royal Society of Chemistry. Reproduced with permission).

contain H-bonding, aromatic motifs or flexible alkyl chains. In addition to the non-covalent interactions available to molecular gelators that are not metal-containing, metal-ligand interactions can contribute to the formation of the 3D SAFiNs of metallo-organic molecular gelators. Furthermore, these SAFiNs may respond reversibly to a broad range of external stimuli, such as UV-Vis radiation, pH and the addition of anionic species.^{77,80} For example, metal salts of long-chain fatty acids have been explored as metallo-gelators over the past several decades.^{78,81} Some of them that can gelate hydrocarbons have been used as industrial lubricants.⁸² The physical properties of these gels depend dramatically on the nature of the metal-carboxylate interactions.¹⁴ Some examples are shown in Scheme 6.

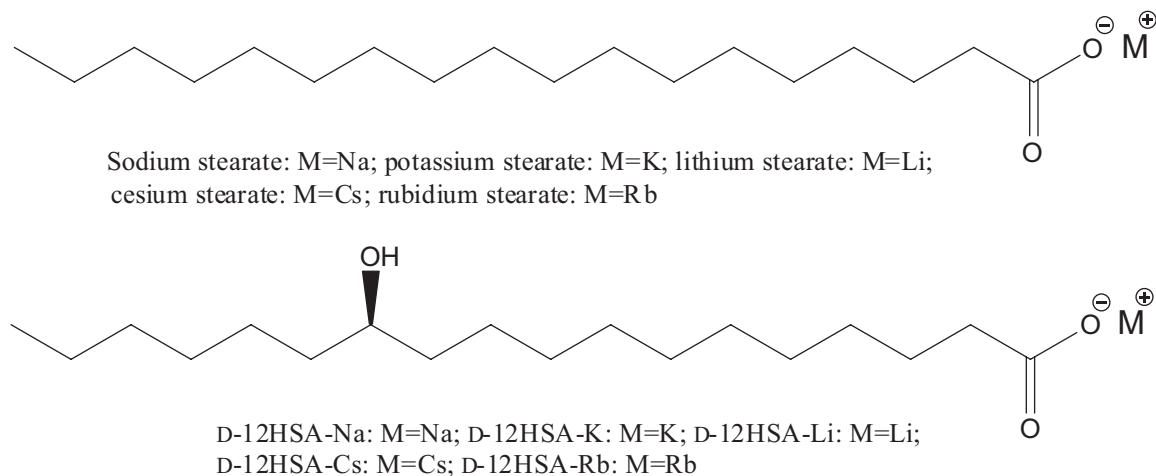
2.6.3.1. Alkali metal salts of alkanolic acids

Phase diagrams for some alkali metal salts of alkanolic acids in water have been constructed by Vincent and Skoulios.⁸³⁻⁸⁵ The amphiphilic mixtures are as gel phases in certain concentration and temperature ranges. For example, < 70% potassium stearate in water forms clear gels below 50 °C.⁸⁶ Powder XRD patterns of the potassium stearate hydrogel indicate that the thickness of the metallo-organic layers (d_a , 23.5 Å) are from fully-extended soap molecules oriented perpendicular to the layer planes and hexagonally packed within the layers. The area per polar head group (39.8 Å²) is equal to twice the cross-sectional area *per* paraffin chain (19.9 Å²). The relationship between the two areas suggests that the soap molecules pack in a head-to-tail (interdigitated) arrangement within layers (Figure 10a).⁸⁶

The formation of hydrogel phases from other alkanolates of alkali metals is dependent upon the nature of both the cation and alkanolate anion species. Different chain

lengths of alkanolate anions can lead to different gelator efficiencies. Among the hydrogels of alkanolates anions with chain lengths from 14 to 22 carbon atoms and the same cation, T_g values increase with increasing chain length.⁸³ Also, specific concentrations of potassium, rubidium, and cesium salts of alkanolates with the same chain length yield gel phases in water, while the sodium and lithium salts do not.⁸³ The T_g values of the potassium soap gels are higher than those with rubidium and cesium. Crystalline SAFiNs were present in all of the gels formed. The thicknesses of the water layers (d_w) can be calculated from the measured long spacing (d) and d_a by powder XRD (Figure 10a). The data indicate that d_w is identical for soaps with the same cation, but d_w of potassium soaps is smaller than for the rubidium and cesium soaps. The difference in thermal stabilities of the soap gels and the difference in d_w indicate that the degree of association between the carboxylate head groups and cations of the soaps is an important contributor to gelator efficiency. A gel phase may form when the relative ionization abilities of the polar head groups and the propensity of the alkyl chains to aggregate are balanced. The higher tendency of rubidium and cesium alkanolates than potassium alkanolates to ionize in water is a probable cause of the lower gel stabilities of the former. It appears that the degrees of ionization by sodium and lithium soaps are too low to reach the balance needed for gel formation.^{83,84}

A binary system consisting of an equimolecular mixture of potassium stearate and *n*-octadecanol in water was also studied by Vincent and Skoulios.⁸⁴ They observed a homogeneous gel phase at concentrations of < 92 wt.% of the organic components in water.⁸⁴ Powder XRD patterns of the gel suggest a different packing arrangement from that of the hydrogel of potassium stearate. Instead of interdigitated, uni-molecular thick lamellae, a bilayer arrangement is



Scheme 6. Structures of some monovalent metallo-organic gelators based on SA and 12HSA.

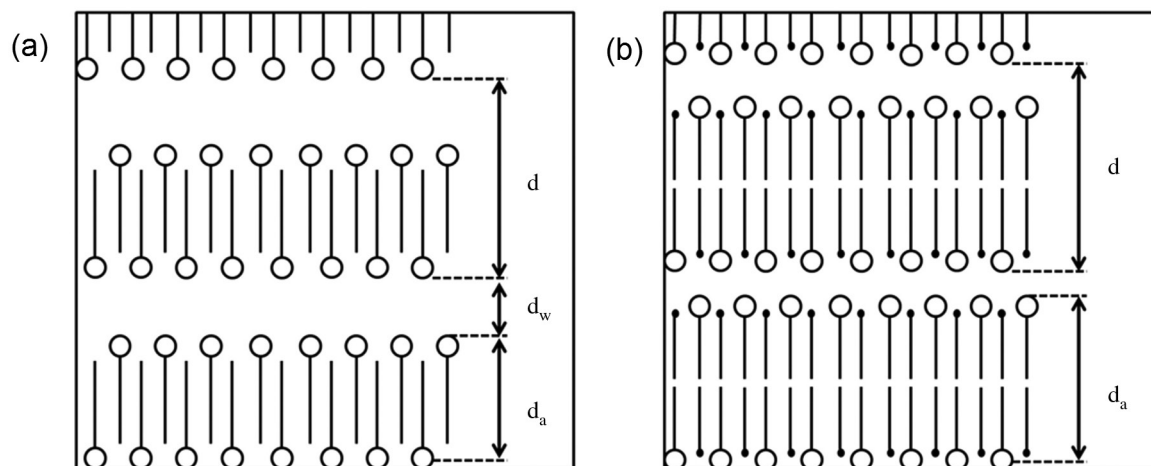


Figure 10. In (a) the schematic representation of the possible structure of alkali metal soap gel phases in water. In (b) schematic representation of the possible structure of the gel phase of an equimolar mixture of *n*-octadecanol and potassium stearate in water. The alkyl chains are indicated by lines and the circles represent the polar head groups. Adapted from references 83 and 86.

found as a result of the ability of the hydroxyl groups of *n*-octadecanol molecules to separate the negatively charged carboxylates, obviating the need for interdigitation.⁸⁴

2.6.3.2. Alkali metal salts of hydroxyalkanoic acids

Sodium, lithium, potassium, rubidium, and cesium salts of D-12HSA (D-12HSA-Na, D-12HSA-Li, D-12HSA-K, D-12HSA-Rb, and D-12HSA-Cs; Scheme 6), have been reported to be metallogelators.^{62-64,87} The gelation behavior of D-12HSA-Na has been investigated in detail in a wide range of liquids.^{62,88} Interestingly, the range of liquids that D-12HSA-Na can gelate is even broader than that of D-12HSA. For example, D-12HSA-Na forms gels in dimethyl sulfoxide, tetrahydrofuran, and dimethylformamide with excellent thermal stabilities, while D-12HSA remains a sol in these liquids at room temperature.⁶² In addition, the CGCs of many D-12HSA-Na gels are as low as 0.5 wt.%. Both the H-bonds among the hydroxyl groups and the metal-ligand interactions between the sodium cation and carboxylate appear to dictate the formation of these gels. Powder X-ray diffractograms demonstrate that D-12HSA-Na molecules pack in a bilayered lamellar arrangement. The longest *d*-spacing of the SAFiNs is ca. 49.5 Å, which is slightly longer than the sum of twice the estimated length of the fully extended anion (23.4 Å) and the van der Waals radius of a sodium cation (ca. 1.03 Å). The network formed must be non-interdigitated or very slightly interdigitated.⁶²

Mixtures of D-12HSA-Na and D-12HSA have also been studied as gelators in soybean oil.⁶⁴ The addition of even a very small amount of D-12HSA-Na to D-12HSA (1:100 molar ratio) improves the gelation ability of D-12HSA by lowering the CGC in soybean oil. Addition of D-12HSA-Na also leads to a sharp increase

in the mechanical strength of the soybean oil gels. The addition of D-12HSA-Rb, D-12HSA-Cs, and D-12HSA-K, respectively, to D-12HSA, in a 1:100 molar ratio decreases the CGCs of the soybean oil gels in the following order: D-12HSA-Rb > D-12HSA-Cs > D-12HSA-K > D-12HSA-Na. This result indicates that the alkali metal ions with smaller radii are better gelators.

Twisted fibers were observed in gels or precipitates of D-12HSA-Rb, D-12HSA-Cs, D-12HSA-K, D-12HSA-Na, and D-12HSA-Li in ethanol. However, right- or left-handed directions of twist of the fibers were found, depending on the cation attached to the anion. For example, the twist configuration is right-handed for D-12HSA-Li, and left-handed for D-12HSA-Rb and D-12HSA-Cs.⁶³ In this case, packing considerations associated with the ability of the head groups to interact with each other are more important than the chirality at C12 of the 12-hydroxyoctadecanoate chains.

2.6.3.3. Metal salts of unsaturated hydroxyalkanoic acids

A current research project at Georgetown is focused on the potential use of metal salts of D-REA as metallogelators (Scheme 6).⁵⁰ Initial experiments show that the sodium salt of D-REA (D-REA-Na) is a more efficient gelator than D-REA, and it is ambidextrous (i.e., it can gelate both water and organic liquids). Very few gelators with structures derived from fatty acids discussed here are ambidextrous. The range of organic liquids that D-REA-Na can gelate is extremely broad, including aromatic liquids, chloroalkanes, ethyl acetate, acetone, and alkanes.⁵⁰ For the liquids that both D-REA and D-REA-Na can gelate, D-REA-Na is more efficient as indicated by its lower CGCs and higher T_g values. Calcium is the only divalent cation examined with D-REA that was able to gelate some

long-chain alcohols and aromatic liquids.⁵⁰ The others, including copper, nickel, and zinc salts of D-REA, formed 3D objects that precipitated without forming SAFiNs in the liquids investigated.⁵⁰ The low solubilities of these salts make them unfavorable for gelation.

3. Summary and Outlook

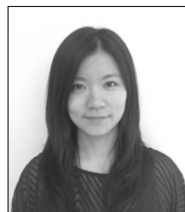
This review has focused on molecular gelators that are derived from long-chain, naturally-occurring fatty acids. Several correlations between structural features of these gelators and gelator efficiencies have been summarized. In addition, the results demonstrate that subtle structural changes in the gelators can introduce important new properties, such as thixotropy, to their gels. However, there is currently no paradigm for the design of molecular gelators or to predict the properties of their gels. Systematic and targeted studies to create structure-property correlations at different distance scales are needed.

As more and more potential and realized industrial applications are found for these nanostructured materials, the intensity of research in the field of molecular gels will continue to increase. We hope that the information provided in this review provides some insights into how other structural modifications may be exploited to create very efficient molecular gelators, whether derived from naturally occurring feedstocks or designed *de novo*.

In addition to the development of detailed structure-property correlations, many other challenges remain. The influence of thermodynamic driving forces on the nature of aggregation of gelators and the manner in which the kinetics of aggregation of gelators influence the gel networks are equally important aspects that need to be understood in order to make predictions of gelation efficiency. Although those topics have not been addressed here, the development of a truly comprehensive paradigm for molecular gels will depend on their inclusion.

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