SELF-ASSEMBLY INTO SOFT MATERIALS OF MOLECULES DERIVED FROM NATURALLY-OCCURRING FATTY-ACIDS

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ABSTRACT

The self-assembly of molecular gelators has provided an attractive route for the construction of nanostructured materials with desired functionalities. A well-defined paradigm for the design of molecular gels is needed, but none has yet been established. One of the important challenges to defining this paradigm is the creation of structure-property correlations for gelators at different distance scales. This dissertation centers on gaining additional insights in the relationship between small changes in gelator structures derived from long-chain, naturally-occurring fatty acids and the properties of the corresponding gels. This approach offers a reasonable method to probe the rational design of molecular gelators.

Thus, results from the investigation of molecular gels with a wide range of liquids and several structurally related molecular gelators are reported. The structures of the initial, naturally occurring fatty acids, each with a cis-double bond, were modified systematically to include the trans-isomer of one and its ammonium carboxylate salts, dihydroxyl derivatives, and an α-diketo compound and its metal carboxylate salts. A variety of physical, thermal, structural, molecular packing and mechanical properties of the gels have been studied in detail and compared for each type of gelator. Some important correlations have been made between the changes in gelator structure, the nature of the liquids gelated or not gelated, and the properties of the gels. One of the most important insights gained from these structure-property correlations is that differences in molecular packing arrangements and the magnitudes of the driving forces for nucleation and one-dimensional growth of the molecular gelators are key factors that modulate the efficiency of
gelation.

In addition, the kinetics of gel formation, and the stimulus-responsiveness of the corresponding gels have been examined in some cases. Some organogels of the α-diketo derivative and its metal salts respond to both thermal and mechanical stimuli in ways that include significant changes in their luminescent properties. Mechanisms for both the formation and the change in the physical properties of these gels have been proposed.

Although a general paradigm for prediction of what constitutes an efficient gelator has not been successfully created here, and the possibility for finding one even in the next decade is extremely low, the systematic structure-property correlations presented here constitute an important advance in that quest. They are useful to understand better the design of molecular gelators and their gels, including more complicated systems.
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<table>
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<tr>
<td>0D, 1D, 2D, 3D</td>
<td>zero dimensional, one dimensional, two dimensional, three dimensional, respectively</td>
</tr>
<tr>
<td>9,12R-diol</td>
<td>diastereomeric mixture of (9,12R)-dihydroxyoctadecanoic acid</td>
</tr>
</tbody>
</table>
| 12DREA | ethane-1,2-diammonium ricinela
date |
| 14DREA | butane-1,4-diammonium ricinela
date |
| 18DREA | octane-1,8-diammonium ricinela
date |
| 10-KSA | 10-oxooctadecanoic acid |
| \( \delta \) | overall energy density for Hansen parameters |
| \( \delta_d \) | dispersion force interaction component for Hansen parameter |
| \( \delta_h \) | H-bonding interaction component for Hansen parameter |
| \( \delta_p \) | dipole-dipole interaction component for Hansen parameter |
| \( \Delta H \) | Enthalpy change |
| AFM | atomic force microscopy |
| ATR | attenuated total reflection |
| AIE | aggregation-induced emission |
| C4REA | 1-butylammonium ricinela
date |
| C10REA | 1-decylammonium ricinela
date |
| C18REA | 1-octadecylammonium ricinela
date |
| CD | circular dichroism |
| CG | clear gel |
| CGC | critical gelator concentration |
| cis-9,10-diol | cis-9,10-dihydroxyoctadecanoic acid |
| cis-13,14-diol | cis-13,14-dihydroxydocosanoic acid |
| D-12HSA | \((R)\)-12-hydroxystearic acid |
| D-12HSA-M | metal salts of \((R)\)-12-hydroxystearic acid |
| DL-\( n \)HSA | racemic \( n \)-hydroxystearic acid where \( n \) refers to the position of the hydroxy group along the alkanoyl chain of the hydroxyoctadecanoic acid isomers |
| DLS | dynamic light scattering |
| DODA | 9,10-dioxoctadecanoic acid |
| DODA-Ca | calcium(II) 9,10-dioxoctadecanoate |
| DODA-Cu | copper(II) 9,10-dioxoctadecanoate |
DODA-M • x H₂O 9,10-dioxo-octadecanoic acid metal salt hydrate
DODA-Ni nickel(II) 9,10-dioxo-octadecanoate
DODA-Ni • H₂O nickel(II) 9,10-dioxooctadecanoate monohydrate
DODA-Zn zinc(II) 9,10-dioxooctadecanoate
DODE methyl ester of 9,10-dioxooctadecanoic acid
D-RA (9Z,12R)-12-hydroxy-9-octadecenoic acid (ricinoleic acid)
D-REA (9E,12R)-12-hydroxy-9-octadecenoic acid (ricinelaidic acid)
DS destructive strain
DSC differential scanning calorimetry
EA erucic acid
FT-IR Fourier-transform infrared spectroscopy
Gʹ storage modulus
Gʺ loss modulus
GC-MS gas chromatography–mass spectrometry
GP gelatinous precipitate
HS-ν-OH (R)-12-hydroxy-N-(ω-hydroxyalkyl)octadecanamides, where n = 3, 4, and 5 refer to the length of the N-alkyl chain
HSPs Hansen solubility parameters
I insoluble
J coupling constants from NMR
L-12HSA (S)-12-hydroxystearic acid
LVR linear viscoelastic region
NAEs N-acyl ethanolamines
NHD N-(3-hydroxypropyl)dodecanamide
NMO N-methylmorpholine N-oxide
NMR nuclear magnetic resonance
OA (9Z)-octadecenoic acid (oleic acid)
OG opaque gel
P precipitate
PAA poly(acrylic acid)
PG partial gel
POM polarizing optical microscopy
PXRD powder X-ray diffraction
\( R_g \) radius of gyration
\( R_h \) hydrodynamic radius
S solution
\( s, d, t, q, m \) in NMR singlet, doublet, triplet, quartet, and multiplet multiplicity from NMR
S-3-OH \( N-(3\text{-hydroxypropyl})\text{octadecanamide} \)
SA stearic acid
SAFiN self-assembled fibrillar network
SANS small angle neutron scattering
SAXS small angle X-ray scattering
SEM scanning electron microscopy
SLS static light scattering
Sus suspension
TEM transmission electron microscopy
\( T_c \) onset temperature of gelator solidification from DSC
\( T_g \) gel melting temperature
TG translucent gel
TGA thermal gravimetric analysis
\( T_{gc} \) onset temperature of gel formation from DSC
\( T_{gm} \) onset temperature of gel melting from DSC
\( T_m \) onset temperature of gelator melting from DSC
TMS tetramethylsilane
\textit{trans}-9,10-diol \textit{trans}-9,10-dihydroxyoctadecanoic acid
\textit{trans}-13,14-diol \textit{trans}-13,14-dihydroxydocosanoic acid
UV/Vis ultraviolet/visible
WAXS wide-angle X-ray scattering
WG weak gel
1 INTRODUCTION

1.1 Introduction to molecular gels

1.1.1 Soft matter

Soft material, or soft matter, is a general term for materials that are physically compliant to the touch but are neither liquids nor incompressible solids. Such materials are common in daily life and cover an extremely broad range of systems, ranging from relatively hard plastics and rubbers to liquid-like materials, such as colloids or polymer solutions. According to Pierre-Gilles De Gennes, soft matter is a class of materials that exhibits “a large response to small perturbations”. In other words, soft matter can undergo large deformations in response to diverse external stimuli, such as temperature, mechanical force, pH, salinity, and enzymes. The energies of these stimuli that are needed to greatly affect the structure of soft matter can be as low as $k_B T$, where $k_B$ is the Boltzmann constant ($1.38 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$) and $T$ is the temperature in Kelvin. These energies are much lower than those needed to alter the structure of crystalline solids at room temperature.

Another characteristic of soft matter is that they have some degree of self-assembled ordering, although it is typically short-range in comparison to that of crystalline solids. Self-assembly is a spontaneous molecular ordering process resulting from the balance between entropic and inter-molecular forces. An exciting emerging field of materials science is the utilization of soft materials to design new classes of active devices, such as implantable biomedical sensors, soft robots, organic electronics, and adaptive optics.
1.1.2 Gels

Gels are a viscoelastic solid-like form of soft matter comprised of a liquid and a low concentration of a gelator.\textsuperscript{9-11} Gels are colloidal in nature due to the dispersion of the gelator (the solid continuous phase) within a liquid (the liquid dispersed phase). Although the majority component of gels is the liquid, gels still behave like solids rheologically by immobilizing the bulk liquid within a 3-dimensional (3D) network of smaller subunits joined together through chemical or physical interactions. Gels can be classified as polymeric and molecular based on the structure of the gelator. The 3D network of polymer gels is typically formed by units linked by covalent bonds,\textsuperscript{12,13} whereas molecular gel networks are formed by weak non-covalent interactions among molecules whose mass is typically less than 2000 Daltons.\textsuperscript{9,14-20}

The discussion here will focus on molecular gels, which can, as mentioned above, be formed by weak non-covalent interactions. Molecular 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).\textsuperscript{12} Another category of molecular gels, metallogels, in which metallic elements are incorporated into either the gelator or the liquid, have recently become a focus of research.\textsuperscript{17,21,22} Based upon their appearances, molecular gels can be subdivided into clear, translucent, and opaque gels. When light encounters clear gels, almost all of it passes directly through them and the objects behind the gels can be seen clearly. Whereas none of the light passes through an opaque gel. Translucent gels are semi-transparent; only some of the light passes through them and the light is scattered as it passes through. Therefore, objects on the other side of a translucent gel appear fuzzy and unclear.
Figure 1.1 Appearances of an opaque gel of 2 wt % (R)-12-hydroxystearic acid in silicone oil (left), a translucent gel of 2 wt % (R)-12-hydroxystearic acid in decane (middle), and a clear gel of 2 wt % (R)-12-hydroxystearic acid in toluene (right).

1.1.3 Gelation efficiency and its characterization

Understanding how to evaluate the efficiency of gelation and the corresponding complex chemical and physical properties of the materials is necessary in order to be able to design molecular gels. There are many criteria that can be used to define ‘efficiency’. Among them are:

1. the range of liquids in which gelation occurs;
2. the critical gelator concentration (CGC): the minimum amounts of a gelator that is necessary to make a gel at room temperature;
3. the gel melting temperature ($T_g$): the temperature at which the gel-to-sol or sol-to-gel transition occurs;
4. the yield strain: the crossover point between the storage modulus ($G'$) and the loss modulus ($G''$) during a strain sweep;
5. the loss tangent ($G''/G'$): the ratio between $G''$ and $G'$ in the linear viscoelastic region (LVR, a regime in which both moduli are independent of strain);
(6) the lifetime of the gel at room temperature under conditions where the liquid component does not evaporate or change due to humidity;

In this work, a combination of these criteria is employed to assess the efficiency of gelation. A larger range of liquids gelated and a lower CGC value indicate higher gelation ability. A higher $T_g$ value implies higher thermal stability of the network. Both yield strain and loss tangent are measures of mechanical strength of the gel. A higher yield strain suggests stronger resistance of the gel to breaking at high strains, whereas a lower loss tangent value indicates higher solidity of the material. The stability of the network can be determined by its lifetime at room temperature.

Investigation of the efficiency of gelation and the functionality of molecular gels requires an array of interdisciplinary approaches and instrumental techniques that covers different aspects of physical and chemical properties of molecular gels. By integrating pieces of information obtained, a clear understanding of corresponding molecular gel system can be gained. Differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), the falling ball method,\textsuperscript{24} and inverse flow method\textsuperscript{25} have been adapted for the study of the thermal stability of molecular gels. Rheology is one of the most important techniques for the study of mechanical properties. Techniques such as polarizing optical microscopy (POM), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM) have been used to visualize the morphology of molecular gels at different distance scales. However, due to the limitations of SEM and TEM under non-vacuum environments, the liquid in wet gels has to be removed by increasing the temperature or decreasing the pressure to create xerogels when they are being examined by these techniques. The formation of xerogels occurs with large shrinkage and/or destruction of the initially formed gel. In order to avoid the risks of
changing the morphology of the gel, cryo-SEM\textsuperscript{26} and cryo-TEM\textsuperscript{27} have been introduced to the soft materials community.\textsuperscript{10,18,23,28} Powder X-ray diffraction (PXRD), dynamic light scattering (DLS), static light scattering (SLS), small angle neutron scattering (SANS), and small angle X-ray scattering (SAXS) have been adapted to extract information about the morphologies of aggregates at different distance scales also and the molecular packing arrangement of gelators in their 3D self-assembled fibrillar networks (SAFiNs). Fourier-transform infrared spectroscopy (FT-IR), Raman spectroscopy, nuclear magnetic resonance (NMR) spectrometry, ultraviolet/visible (UV/Vis) absorption spectroscopy, fluorescence spectroscopy, circular dichroism (CD) spectroscopy, and other analytical techniques used in chemistry and physics are currently in use or being developed to probe the changes in the type and the strength of interactions that drive sol-to-gel transitions.

Alongside the need for understanding the physical and chemical properties of molecular gels, how to design molecular gel systems with different degrees of gelation efficiency and desired functionalities is a question that has become central to the field. The ability, \textit{a priori}, to design and exploit molecular gel systems will depend on gaining a deep understanding of four main factors: (1) the manner in which the thermodynamic driving forces associated with supersaturation influence the nature of aggregation of gelators; (2) how the kinetics of aggregation of gelator molecules affects the eventual gel networks; (3) how the characteristics of the molecular structure of the gelator lead to stronger or weaker gel SAFiNs; and (4) influence of a liquid on gelation. Further explanations of these factors will be covered throughout this chapter. Each of the four factors mentioned above provides a partial answer to the question: How can one predict gelation ability? Although many recent studies have focused on each of the four factors (vide infra), none seems to have encompassed the four to an extent that permits good predictability
about a potential molecular gel system with novel (rather than related) gelator structures. Thus, currently, no paradigm for the design of molecular gels exists; the study of molecular gels remains an empirical science. Only through systematic and targeted studies is a paradigm likely to emerge.

1.1.4 Formation of a molecular gel

1.1.4.1 Self-assembly model

A molecular gel is usually prepared by heating a gelator in a liquid until the solid dissolves, and then cooling the solution/sol to a temperature that is below $T_g$. The formation of molecular gels can be explained by the well-accepted self-assembly model which emphasizes the molecular self-assembly of the gelator at more than one time regime and distance scale. Initially, driven by supersaturation, nucleation occurs between gelator molecules. The nucleating centers form one-dimensional (1D) objects usually, such as fibers, rods, ribbons, tapes, platelets and tubules via inter-molecular non-covalent interactions. 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. The non-parallel 1D objects may bundle into objects with larger cross-sections and interact further to form the 3D SAFiNs that immobilize the liquid by surface tension, capillary forces and related interfacial interactions. Due to the reversible nature of non-covalent interactions, the vast majority of molecular gels undergo thermally reversible gel-to-sol transformations. Figure 1.2 is a cartoon representing the thermally reversible formation of molecular gels.

The molecular formation process is a discontinuous transition from a liquid state containing isolated molecules or small aggregates of the gelator to a gel state with the
mechanical properties of a highly disordered solid-like state. The molecular gel formation process is also a pseudo-equilibration between solubilization and aggregation.\textsuperscript{33} When the driving force for aggregation is much larger than that for solubilization, gelators will form precipitates instead of gels. Obviously, solutions will not form either precipitates or gel networks if the driving force for phase separation is low. Only when the driving forces for aggregation and solvation are balanced are entangled networks and gels formed.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Cartoon representation of self-assembly model for a thermally reversible, sol-to-gel transition in molecular gels.}
\end{figure}

\subsection*{1.1.4.2 Nucleation-growth model}
In order to dissect the components of the kinetics and thermodynamic driving forces during aggregation and SAFiNs formation, a nucleation-growth model has been utilized in many molecular gel systems.\textsuperscript{34-38} According to POM and PXRD studies, most molecular gels have crystalline SAFiNs.\textsuperscript{38-41} Based on the nucleation-growth model, the formation of crystalline SAFiNs is initiated from the nucleation of gelator molecules, and is followed by alternating
growth and branching of fibers (Figure 1.3). When the interfacial structural mismatch between the growing crystalline fibers and the nucleating phase occurs, fiber branching will take place.\textsuperscript{36} There are two types of nucleation, homogeneous nucleation and heterogeneous.\textsuperscript{36} Homogeneous nucleation is defined as the nucleation in the interior of a uniform substance without preferential nucleation sites.\textsuperscript{36} Heterogeneous nucleation starts at nucleation sites on certain substrates, the occurrence of which reduces the nucleation barrier.\textsuperscript{36} The kinetics of surface nucleated transformation in 2D and 3D finite systems have been studied by Weinberg.\textsuperscript{42} The nucleation-growth model proposed by Weinberg is suitable for systems in which nucleation occurs solely at the boundary edge, such as the walls and surfaces of a mixture. In surface nucleated transformations, nucleation completes prior to growth.\textsuperscript{42} The transformation of a region includes expansion of the existing domains near the surface as well as nucleation-growth of new domains at new boundary edges.

![Cartoon representation of SAFiN formation through nucleation, growth, and branching of fibers. The building blocks of the entire network represented here are spherulites (highly branched, small fibers emanating from a central node).](image)

**Figure 1.3** Cartoon representation of SAFiN formation through nucleation, growth, and branching of fibers. The building blocks of the entire network represented here are spherulites (highly branched, small fibers emanating from a central node).

### 1.1.4.3 Isodesmic and cooperative models

The isodesmic and cooperative models, originally established to describe polymerization, can also be used to probe the formation of molecular gels.\textsuperscript{43,44} In isodesmic assembly, each
molecular-scale building unit adds onto a growing, existing fiber with the same affinity. Isodesmic growth is characterized by high polydispersity, and during it, the number and the length of the aggregated species gradually increase.\textsuperscript{45} Isodesmic self-assembly has been reported for linear self-assembly of organic molecules.\textsuperscript{46} In the cooperative growth model, an initial nucleation step occurs with lower binding affinity before chain elongation or growth. Subsequent chain elongation proceeds more rapidly than the initial nucleation.\textsuperscript{43} Once nucleation occurs, a distribution of small aggregates elongated objects will be present throughout the self-assembly process.\textsuperscript{43}

1.1.4.4 Thermodynamics and kinetics

Regardless which model is used to explain gel formation, the thermodynamic driving force (i.e., supersaturation) plays an important role in affecting nucleation, fiber growth and branching.\textsuperscript{47} Several efforts to control the structure of the fiber networks in a gel and the physical properties of the gel by regulating the chemical potential difference between the crystalline phase and the solution/sol phase have been reported.\textsuperscript{48-51} By doing that, the thermodynamic driving force for the formation of new phases (i.e., crystalline SAFiNs) will be altered. One of the main approaches that have been used to tune the thermodynamic driving force is to regulate the temperature at which the gel forms from a sol. At a lower temperature, the rate of nucleation becomes greater due to a higher degree of supersaturation. Then, the growth of highly branched fibers is favored and smaller spherulitic (colloidal) aggregates are formed. At a higher temperature, the thermodynamic driving force for nucleation becomes weaker, which facilitates 1D growth of fibers with less branching and more elongated assemblies. One example of the temperature-induced change in morphology is reported for n-alkane gels of (5\textit{R})-cholestan-3\textbeta-yl
N-(2-naphthyl)-carbamate, where spherulitic objects were observed when the gels were prepared by incubation at lower temperatures, and elongated fibers were seen in gels prepared by incubation at higher temperatures.\textsuperscript{50} By regulating the temperature, the degree of super-cooling will be modulated and, thereby, lead to a controllable structure of the fiber networks in the molecular gel.

Also, the kinetics of nucleation, growth and branching at different time and distance scales is another important aspect of gelation; it offers insights into the mechanisms leading to SAFiNs. The kinetic behavior and its relation to the corresponding SAFiN structure have gained great research attention over the past decades.\textsuperscript{30,42,46,52-54} Because molecular gels usually form very rapidly after the temperature of a sol has been lowered to below \( T_g \), the processes accompanying aggregation, especially the initial steps, are frequently difficult to follow. The development of gels in which the sol-to-gel transition process occurs on time scales of a few minutes to hours is important to allow the processes to be followed by easily employed kinetic techniques.

Investigation into the kinetics of formation requires techniques that can probe the change in a certain aspect of the aggregation process and can respond on a much faster time scale than the changes at different stages of aggregation in the target system. Dynamic rheological techniques, sensitive to the change in viscoelasticity, are the most common used to acquire kinetic data during the gelation process because they are suitable for almost all molecular gel systems with a relative fast response time. Based on the availability of changes in other physical properties during the sol-to-gel transition, CD, fluorescence, POM, SANS, DLS, and many other techniques have also been adapted for kinetic studies of specific molecular gel systems.

In an attempt to dissect the components of the kinetic and thermodynamic driving forces
during aggregation, models that involve fiber branching induced by mismatch nucleation have been applied.\textsuperscript{40,46-48,54-60} Among them, the Avrami model\textsuperscript{50,61,62} and the Dickinson model\textsuperscript{63} have gained popularity to study gelation processes.\textsuperscript{50,51,62,64}

The Avrami model (equation 1.1), although originally developed to describe the crystallization of polymer melts and other precipitation phenomena, can be used to extract information about the relevant nucleation and growth kinetics of the SAFINs. For example, Liu and coworkers analyzed the kinetics of formation of the SAFINs of \textit{N}-lauroyl-\textit{L}-glutamic acid di-\textit{n}-butylamide in propylene glycol using Avrami theory.\textsuperscript{61} They devised a model for correlating kinetics and network structure which provided information about the interplay between nucleation, fiber growth, branching, and inter-fiber interactions.\textsuperscript{61}

\begin{equation}
\ln(-\ln(1 - X)) = \ln K + n \ln t
\end{equation}

\(X = \frac{I(t) - I(0)}{I(\infty) - I(0)}\) is the volume fraction of gel phase at time, \(t\). \(I(0)\) is the onset value of a rapid change in a variable recorded by a particular technique that represents a particular physical property of the system (e.g., \(G'\) in rheology), \(I(\infty)\) is the plateau value (i.e., the maximum \(G'\) achieved after long times), \(K\) is a temperature-dependent parameter similar to a rate constant, and \(C\) is a constant. The Avrami exponent \(n\) in equation 1.1 reflects the type of nucleation (i.e., heterogeneous or homogeneous) and the dimensionality of crystal growth.\textsuperscript{62} Because gel formation may not be describable by one mode of aggregation and growth, the diagnostic value of \(K\) may be greater than that of \(n\). The Avrami model is based upon two assumptions: (1) nucleation occurs either heterogeneously or homogeneously over the entire untransformed portion of the material, and (2) the small domains of the separated gel phase grow independently.\textsuperscript{62,64} The Avrami model is not applicable in systems where neither of these two conditions is operative.
The Dickinson model (equation 1.2), which was originally developed to describe the kinetics of weak gelation particles,\textsuperscript{63} provides information about the fractal structure features of the resultant crystalline SAFiN of the gel.\textsuperscript{38,51}

\[ \ln X = C + \frac{3-D_f}{D_f} \ln t \]  

(1.2)

As in the Avrami model, \( X = \frac{I(t) - I(0)}{I(\infty) - I(0)} \) is the volume fraction of gel phase at time, \( t \). The mass fractal dimension, \( D_f \), is one of the most important defining parameters of a fractal object. It pertains to the dimensionality of the SAFiN objects. Typically, for linear network structures, 1.0 \( < D_f < 1.5 \);\textsuperscript{51} for less compact network structures, 1.5 \( < D_f < 2.0 \);\textsuperscript{51} and for highly compact network structures, 2.0 \( < D_f < 3.0 \).\textsuperscript{65,66}

A recent study by Mallia et al. utilized both the Avrami and the Dickinson models to probe the aggregation and gelation processes of \( N \)-acyl ethanolamines in isostearyl alcohol.\textsuperscript{64} By correlating the Avrami exponent with the mass fractal dimension, a quantitative understanding of kinetics–structure correlation of gel networks that are formed under different degree of supersaturation could be achieved. Furthermore, correlating the Avrami exponent with the mass fractal dimension is also helpful for understanding the roles of thermodynamics and kinetics in the control of nucleation, fiber growth, branching, and bundling and in how they govern the structural and physical properties of molecular gels.

\subsection*{1.1.5 Structure-property correlations}

Although the many studies on gelation formation have provided valuable insights into some of the parameters controlling gelation, they do not address interactions at the molecular
level. Understanding the characteristic molecular structure of gelators that may promote successful gelation is one of the important challenges to the rational design of molecular gels. The gelators reported so far cover an extremely broad range of molecular structures—molecules as simple as alkanes to very complex ones containing two-components. However, currently, no paradigm for prediction of efficient gelator with novel molecular structures exits and the prospects for one appearing in the near future are dim. The development of any new gelators with novel molecular structures that are capable of forming SAFiNs still requires a significant effort by screening a large number of compounds in a variety of liquids. However, some relationship between structural features of gelators and their gelation properties can be gleaned from systematic and targeted studies of structural analogues of a known gelator. Many recent studies and reviews have focused on quantitative correlations between structural features of gelators and the gelation efficiency. 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. Studies on gelators that are derived from long-chain, naturally-occurring fatty acids will be discussed at length in Section 1.2.

1.1.6 Influence of the liquid

Besides interactions between gelator molecules, gelator-liquid interactions and the bulk properties of the liquid must be considered when discussing the nucleation and growth processes. Numerous attempts have been made, with varying degrees of success, to correlate gelation abilities with physical properties of liquids. A recent review by Lan et al., has examined different liquid clustering techniques to probe this subject in great detail. However, it
is almost impossible to know *a priori* which solvent parameters will lead to the desired self-assembly.

Endeavors to correlate molecular gelation with a variety of bulk properties of the liquid have been made by characterizing the liquid as a macroscopic continuum. Parameters such as dielectric constant and refractive index can assess the physical properties of the liquid. Specifically, dielectric constant can be used to probe the polarity of the liquid, whereas refractive index is related to the molar polarizability of a liquid. For example, the Hildebrand solubility parameter is derived from the cohesive energy density of the liquid and relies solely on the enthalpy. It reflects the total forces that hold liquid molecules together. Reichardt’s $E_T(30)$ solvent parameter is another parameter that is a good indicator of the polarity of a liquid. Reichardt’s $E_T(30)$ value is measured by the change in absorption band of a solvatochromic dye dissolved in that liquid. Previous studies have shown some weak correlations between gel properties of some trehalose-based gelators and both the Hildebrand and Reichardt’s $E_T(30)$ solvent parameters. However, most of these parameters that represent the bulk property of a liquid show very limited utility in prediction of gelation capabilities. It implies that the bulk property of a liquid is an insufficient criterion to judge when a gel will or will not be formed; specific liquid-gelator interactions at the molecular level must be considered as well, and how they affect the nucleation and aggregation phenomena as a function of time.

Many efforts have been made to develop multi-term parameters to separate the contributions of individual interactions and define the liquid contributions more accurately. For example, Kamlet-Taft solubility parameters dissect the property of a liquid into polarizability, hydrogen-bond donating, and hydrogen-bond accepting terms. Catalan’s solubility parameters characterize a liquid with regards to its polarizability, solvent acidity, and solvent basicity.
utilizing different series of probe molecules from those of the Kamlet-Taft solubility parameters.\textsuperscript{83}

Recently, Hansen solubility parameters (HSPs), widely accepted in polymer science, have been adapted to evaluate gelation behavior in many systems with different types of gelators.\textsuperscript{74-76,84,85} In this method, the overall energy density ($\delta$) of a liquid or a gelator is separated into dispersion force ($\delta_d$), H-bonding ($\delta_h$), and dipole-dipole ($\delta_p$) interaction components (equation 1.3).\textsuperscript{73,75,76,86}

\begin{equation}
\delta = \sqrt{\delta_d^2 + \delta_p^2 + \delta_h^2}
\end{equation} \hspace{1cm} (1.3)

Typically, the HSPs of the gelator are unknown and can be estimated by two different methods. First, the HSPs of the gelators can be calculated by the group-contribution method.\textsuperscript{87} The group-contribution method includes various first-order and second-order groups and it is used to predict properties (e.g., HSPs) of organic compounds by accumulating the functional group properties.\textsuperscript{87} However, a shortcoming of HSPs calculated from group contributions is that stereo and positional isomers are not distinguished.\textsuperscript{86} Another way to estimate the HSPs of the gelator is through Hansen Space, using the three parameters as axes empirically (Figure 1.4).\textsuperscript{74,75} A program that can be used to plot Hansen Space is MATLAB HSP 3D Plotting and Fitting Program developed by Diehn \textit{et al.} from UMD Complex Fluids and Nanomaterials Lab.\textsuperscript{75} A Hansen sphere of a particular phase in Hansen Space is built and minimized to contain most, if not all, liquids within that phase category. There are two approaches adopted to establish Hansen spheres, concentric- and discrete-spheres.\textsuperscript{75} The concentric-spheres approach uses the average of the solution points as the initial center of all spheres, while the discrete-spheres approach uses the average of the data points from each class as the initial center of its own Hansen sphere.\textsuperscript{75}
HSPs for the gelator can be calculated as the center of any sphere constructed from concentric-spheres approach or the center of the gel sphere constructed from discrete-spheres approach.\textsuperscript{75} How to choose between these two approaches may vary among systems.\textsuperscript{74,86,88} Theoretically, liquids whose Hansen parameters are inside the gel sphere should form a gel with that particular gelator.\textsuperscript{86} Many successful cases have demonstrated that the liquids gelated by a particular gelator have similar HSPs with few exceptions.\textsuperscript{71,74-76} By comparing the HSPs of different gelators and the range of HSPs of the gel spheres, it becomes possible to analyze and understand the factors responsible for gel formation. Therefore, HSPs have the potential to become a useful tool for understanding and predicting the formation of different phases when a potential gelator and a liquid are mixed.\textsuperscript{74,88} However, as mentioned, it is almost impossible to make accurate predictions of gel formation on the basis of only one solvent parameter theory. Continuous efforts have to be made to develop relationships between numerous solvent parameters in order to further increase the accuracy of gelation predictions.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{hansen_sphere.png}
\caption{Schematic illustration of the route for establishment of a Hansen sphere in Hansen Space. The black open circles represent the HSPs of liquids that a form a specific phase (i.e.,...}
\end{figure}
solution, gel, or precipitate) with a gelator. The green closed circle represents the center of the Hansen sphere and the black circle represents the limit of the sphere.

1.2 Naturally-occurring fatty acids and their gels

As mentioned in section 1.1.5, it is necessary to create correlations between molecular structure of gelator and the physical properties of the corresponding molecular gels in order to gain an understanding of how to design molecular gelators in a rational way. The range of known gelator structures is extremely broad. Derivatives of long-chain, naturally-occurring fatty acids are one class of molecular gelators that have generated significant research interest. They are among the gelators with the simplest molecular structures, containing no more than two functional groups on an n-alkyl chain. Long-chain fatty acids, such as (9Z)-octadecenoic acid (oleic acid, OA), (9Z,12R)-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. 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. The structural simplicity, biocompatibility, low cost, and environmentally beneficial attributes of these acids add to their attractiveness as molecular gelators. The major focus of this dissertation is on organo-, hydro-, and metallo-gels derived from long-chain, naturally-occurring fatty acids. Previous studies involving this topic are summarized here.
1.2.1 *n*-Alkanes

Structurally, the simplest class of molecular gelators is *n*-alkanes. 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. Long *n*-alkanes (with 24 to 36 carbon atoms) can gelate short *n*-alkanes and some non-hydrocarbon liquids. *n*-Alkanes with longer alkyl chains can form gels with a wider range of organic liquids and exhibit lower CGCs and higher *T*gs than the *n*-alkanes with shorter chains. The greater efficiency of the longer *n*-alkanes can be ascribed to more London dispersion forces in the SAFiNs. However, according to rheological, thermal and stability studies, most of the *n*-alkanes gels are weak 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. PXRD studies of some long *n*-alkanes suggest that gelator molecules pack in a lamellar arrangement. In large part, the reason why objects observed at the micrometer length scale in SAFiNs of *n*-alkane gels are platelets (i.e., 2D objects) can be ascribed to the importance of London dispersion forces among vicinal extended alkanes that promotes 2D growth.

1.2.2 Alkanoic fatty acids

By inserting a hetero-functional group along the chain of an *n*-alkane, 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, SA. SA is a major component of the triglycerides of many plant seed oils, especially kokum oil. SA forms dimeric species in
alkane solutions by inter-molecular H-bonding interactions between carboxylic acid head groups. However, introduction of a terminal carboxylic acid head group does not aid in gelation to a great extent. Gelation occurs only at relatively high concentrations of SA and in a limited number of liquids. For example, the gel of 5 wt % SA in sunflower oil exhibits platelet-like morphology and it is weak mechanically, as indicated by its low $G'$ value (100 Pa) and low $T_g$ value (< 40 °C). Besides SA, alkanoic acids with chain lengths between 16 to 31 carbon atoms are found in triglycerides of different plant seed oils, and they are known to gelate vegetable oils, including sunflower oil and lavender oil. There are no significant differences among the gelation efficiencies of alkanoic acids with chain lengths greater than 26 carbons. However, alkanoic 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). The increased London dispersion forces for long-chain alkanoic acids play a key role in the increased gelation efficiencies. However, the overall ability of the alkanoic acid gels to resist plastic deformation is very weak.

**Scheme 1.1** Structures of two gelators based on alkanoic acids with 18 carbon atoms.
1.2.3 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 oil, 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 1.1). 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 gelated, $T_g$ values, CGCs, viscoelasticity, 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.\(^{70,108-110}\) 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.\(^{111}\) Inside the fibers, hydroxyl groups on the chiral carbon atoms form inter-molecular, unidirectional H-bonds along the fiber axis (Figure 1.5). Similar to SA, D-12HSA molecules also pack as dimers 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.\(^{110}\) 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.\(^{110}\) 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.¹⁹,⁷⁰,¹⁰⁵

Figure 1.5 Structural model for 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. Reprinted with permission from ref 110. Copyright (1994) American Chemical Society.

The network structure of D-12HSA gels can vary depending on the liquid in which the gel forms. For example, the wide angle spacing of D-12HSA in PXRD diffractograms, ~4.6, 3.9 and 4.8 Å in nitriles, aldehydes and ketones, respectively, suggests that it packs into triclinic polymorphs. The lamellar spacings in these liquids, 38 to 44 Å, are less than twice the extended molecular length (46 Å), suggesting interdigitated networks or molecules with bent conformations.¹¹² In alkane and thiol liquids, D-12HSA packs into hexagonal polymorphs with a
wide angle peak at ~4.1 Å. The spacing corresponding to the low angle peaks (~54 Å) is greater than twice the extended molecular length of \textit{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 \textbf{D-12HSA} gels in nitriles, aldehydes and ketones are spherulites and the gelator concentration needed to form opaque gels (> 1.5 wt %) is higher than that needed in alkanes and thiols (~1.0 wt %), where the SAFiNs consist of non-spherulitic fiber arrays.\textsuperscript{112} The different gelator packing arrangements can alter gelation efficiency.

The gelating abilities of enantiopure and racemic forms of \textbf{12HSA} can be very different.\textsuperscript{110} A study of both enantiopure \textbf{D-12HSA} and racemic \textbf{DL-12HSA} in mineral oil indicates that the racemate gels are not as strong as those of \textbf{D-12HSA}.\textsuperscript{113} For example, the \textit{CGC} of \textbf{D-12HSA} (<1.0 wt %) is lower than that of \textbf{DL-12HSA} (ca. 2.0 wt %) in mineral oil.\textsuperscript{113} The SAFiNs of \textbf{D-12HSA} gel are comprised of high aspect ratio helical fibers, while the objects observed in the SAFiNs of \textbf{DL-12HSA} gel are platelets.\textsuperscript{113} In the same study, the physical properties of mixtures at different \textbf{D-12HSA} and \textbf{L-12HSA} ratios in mineral oil were investigated. With an increase of one \textbf{12HSA} enantiomer 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 to the secondary C12 hydroxyl H-bonding networks). The FT-IR spectra in the region of carboxylic acid absorptions indicate that the carboxylic acid head groups of \textbf{DL-12HSA} and mixtures with \textbf{D-12HSA} and \textbf{L-12HSA} ratios at and below 90:10 exist equally as cyclic and acyclic dimers; the proportion of cyclic dimers significantly increases in neat \textbf{D-12HSA} and in enantiomeric mixtures at and above 90:10 (Figure 1.6).\textsuperscript{113} The predominance of cyclic dimers in enantiomerically pure \textbf{12HSA} promotes longitudinal growth along the
secondary fiber axis (Figure 1.7). 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.

Figure 1.6 FT-IR spectra in the region of carboxylic acid absorptions of mixtures with D-12HSA: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 ~1720 cm\(^{-1}\) is attributed to the acyclic dimers of carboxylic acid groups, and the peak at ~1700 cm\(^{-1}\) is attributed to the cyclic dimers. Reproduced from ref 113 with permission of the Royal Society of Chemistry.
Figure 1.7 Possible packing modes of D-12HSA (top) and DL-12HSA (bottom) in the SAFiNs of mineral oil gels. Reproduced from ref 113 with permission of the Royal Society of Chemistry.

Also, the appearances of SAFiNs of positional isomers of racemic DL-nHSA (where \( n = 2, 3, 6, 8, 10, 12 \) 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.\(^\text{114}\) 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 2 wt \% DL-6HSA, DL-8HSA, DL-10HSA, DL-12HSA, or DL-14HSA in mineral oil are rheologically true gels.\(^\text{114}\) 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 FT-IR 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.\(^\text{114}\) 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 1.8). However, the FT-IR and PXRD data 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 1.8). The FT-IR 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 ~4.1 Å, which is consistent with (but not definitive proof of) a hexagonally packed polymorph.115 Thus, 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. These data indicate that there must be a relatively long distance between the hydroxyl group and the carboxylic acid head group of hydroxylated derivatives of fatty acids in order for them to be efficient molecular gelators.
1.2.4 Unsaturated fatty acids

Besides saturated fatty acids, especially the cis isomers of unsaturated fatty acids are common constituents of natural fats and oils. However, their intrinsically bent shapes, even in extended conformations, make them less attractive as gelators. The trans isomers of the same unsaturated fatty acids are potentially more efficient gelators because they are able to adopt...
linear and extended conformations. For example, \((9E,12R)-12\text{-hydroxy-9-octadecenoic acid, D-REA}\), is a much better gelator than the inefficient \((cis)\) molecule, D-RA (Scheme 1.2). D-REA, blended with refined, bleached, and deodorized canola oil, forms gels in vegetable oils, such as canola oil, at concentrations higher than 2 wt %\(^{116,117}\). The SAFiN structures of D-REA gels in canola oil are comprised of long fibers that intertwine into twisted bundles.\(^{117}\) The PXRD 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.\(^{116}\) 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.\(^{117}\) 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.\(^{118}\) 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.\(^{116}\)
Scheme 1.2 Structures of some unsaturated hydroxyalkanoic acids derivable from plants.

1.2.5 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, including adipic (4 carbon atoms), suberic (6 carbon atoms) and sebacic (8 carbon atoms) acids, are capable of gelating plant oils (e.g., sunflower oil and lavender oil).\textsuperscript{106} 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.\textsuperscript{106} 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.\textsuperscript{119}

Dicarboxylic acids can also harden non-liquid materials, such as bitumen, at room temperature.\textsuperscript{119} Bitumen is a hydrophobic material obtained from crude oil distillates. The
addition of 3 wt % dodecanedioic acid increases the softening temperature of bitumen from 46 to 110 °C, and increases the hardness and elastic modulus of bitumen dramatically without increasing the melt viscosity.\textsuperscript{119} 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 1.9).\textsuperscript{119} 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.\textsuperscript{119} 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.\textsuperscript{119}

\begin{align*}
\text{HO} & \quad \overset{(\quad)}{\text{O}} \quad \text{OH} \\
\text{O} & \quad \text{O} \\
\text{n=4, adipic acid} & \\
\text{n=6, suberic acid} & \\
\text{n=8, sebacic acid} & \\
\text{n=12, dodecanedioic acid} & 
\end{align*}

\textbf{Scheme 1.3} Structures of some dicarboxylic acid gelators.

\textbf{Figure 1.9} Photograph and scanning transmission electron microscopic image of a mixture of 6 wt % dodecanedioic acid in bitumen at room temperature. Reprinted with permission from ref 119. Copyright (2009) American Chemical Society.
1.2.6 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.\textsuperscript{102} Carnauba wax also consists predominantly of aliphatic esters.\textsuperscript{102} 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 %.\textsuperscript{120} Although there is no direct evidence supporting that the gelation of these plant waxes is due only to fatty acid alkyl esters,\textsuperscript{102} it is clear that pure fatty acid esters are gelators.\textsuperscript{106}

![Scheme 1.4 Structures of some alkyl fatty acid methyl ester gelators.](image)

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.\textsuperscript{106} 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.\textsuperscript{106} Without the H-bonding interactions between carboxylic acid head groups, gelation ability of the corresponding esters 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 acid counterparts.\textsuperscript{106} 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.

1.2.7 N-acylethanolamines

Previous studies\textsuperscript{70,121} and a review\textsuperscript{89} 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. \textit{N-acylethanolamines (NAEs)} are an exception. These amphiphiles are present in a wide variety of biological membranes in animals, plants, and microbes.\textsuperscript{122,123} For the past two decades, \textbf{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.\textsuperscript{122,124}

Anandamide is one of the best known polyunsaturated \textbf{NAEs}. Besides its occurrence in biological membranes, it is found in chocolate and has physiological properties in the brain like that of cannabis.\textsuperscript{125,126} The \textit{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 °C).\textsuperscript{127} However, saturated \textbf{NAEs} and \textit{trans} unsaturated \textbf{NAEs}, which may adopt extended conformations, may behave as gelators.

Few studies appear to have employed \textbf{NAEs} as molecular gelators. One involves \textsuperscript{(R)-12-hydroxyl-N-(2-hydroxylethyl)octadecanamide (HS-2-OH, Scheme 1.5).}\textsuperscript{64} \textbf{HS-2-OH} is an exceedingly efficient gelator based on the low \textit{CGCs} of its gels in silicone oil, acetonitrile, CCl\textsubscript{4}, toluene (< 0.5 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 ~ 100
nm. PXRD 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 extended molecular length, 54.3 Å. A possible ‘head-to-tail’ packing arrangement was hypothesized (Figure 1.10). 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.

Scheme 1.5 Structures of some homologues of N-acylethanolamine gelators.

Figure 1.10 A possible ‘head-to-tail’ packing arrangement of HS-2-OH molecules in both the solid and isostearyl alcohol gel states. Reproduced from ref 64 with permission of the Royal Society of Chemistry.
As a comparison, the gelation behaviors of the homologues, \((R)-12\text{-hydroxy-}N-(\omega\text{-hydroxyalkyl})\text{octadecanamides (HS-}n\text{-OH); where} n = 3, 4, \text{ and 5 refers to length of the } N\text{-alkyl chains), have also been reported.}^{64}\text{ The mechanical strength of the gels decreased with increasing length of the } N\omega\text{-hydroxylalkyl chains. The difference in mechanical strengths may be related to the propensities of } \omega\text{-hydroxyl groups to undergo inter- or intra-molecular H-bonding interactions.}

In addition, \(N\text{-}(3\text{-hydroxypropyl})\text{octadecanamide (S-3-OH)}\)^{64} \text{ and } N\text{-}(3\text{-hydroxypropyl)dodecanamide (NHD),}^{128} \text{ both lacking a hydroxyl group on the alkanoyl chains, have been investigated as organogelators. The higher } CGCs \text{ and the lower } T_g \text{ values of } S\text{-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 } 12\text{HSA 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 \text{ and a lower } T_g \text{ value than found with HS-3-OH as the gelator.}^{64,128} \text{ 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.}

\subsection{1.2.8 Metal soaps}

Metal salts of long-chain fatty acids have been explored as metallogelators over the past several decades.\textsuperscript{129,130} \text{ Some of them that can gelate hydrocarbons have been used as industrial}
lubricants. The physical properties of these gels depend dramatically on the nature of the metal-carboxylate interactions. Some examples are shown in Scheme 1.6.

Scheme 1.6 Structures of some monovalent metallo-organo gelators based on SA and D-12HSA.

1.2.8.1 Alkali metal salts of alkanoic acids

Phase diagrams for some alkali metal salts of alkanoic acids in water have been constructed by Vincent and Skoulios. The amphiphilic mixtures are gel phases in certain concentration and temperature ranges. For example, <70 % potassium stearate in water forms clear gels below 50 °C. PXRD 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 1.11). The formation of hydrogel phases from other alkanoates of alkali metals is dependent upon the nature of both the cation and alkanoate anion species. Different chain lengths of
alkanoate anions can lead to different gelator efficiencies. Among the hydrogels of alkanoate anions with chain lengths from 14 to 22 carbon atoms and the same cation, $T_g$ values increase with increasing chain length.\textsuperscript{133} Also, specific concentrations of potassium, rubidium, and cesium salts of alkanoates with the same chain length yield gel phases in water, while the sodium and lithium salts do not.\textsuperscript{133} 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 PXRD (Figure 1.11). 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 alkanoates than potassium alkanoates 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.\textsuperscript{133,134}
Figure 1.11 Schematic representation of the possible structure of alkali metal soap gel phases in water. The alkyl chains are indicated by lines and the circles represent the polar head groups. Adapted from ref 133.

1.2.8.2 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 1.6), have been reported to be metallogelators.137-142 The gelation behavior of D-12HSA-Na has been investigated in detail in a wide range of liquids.137,143 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.137 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. PXRD 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.\(^{137}\)

Mixtures of D-12HSA-Na and D-12HSA have also been studied as gelators in soybean oil.\(^{142}\) 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 direction is right-handed for D-12HSA-Li, and left-handed for D-12HSA-Rb and D-12HSA-Cs.\(^{141}\) 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.
1.3 Molecular gels as stimuli-responsive materials

1.3.1 Definition and classification of stimulus-responsive gels

As mentioned in section 1.1.4, the vast majority of molecular gels undergo a thermally reversible sol-to-gel transition due to the non-covalent nature of the gelator interactions. Besides being responsive to temperature changes, some molecular gels respond to other external stimuli, such as ultrasound, mechanical force, light, addition of ionic species, enzymes, and pH. The loss and gain of non-covalent interactions can be manipulated by external stimuli, allowing for the tuning of the physical properties of the gel. The reversible change in properties on the macroscopic distance scale can be traced to structural reorganizations of aggregates on the microscopic distance scale. The design of gels in which the physical and chemical properties can be changed systematically is very appealing.

When the chemical moieties of the gelators are capable of light-induced conformational and/or chemical changes, the sol-to-gel transition can be tuned by changing the wavelength of the light applied. For example, trans-cis photo-isomerization of the azobenzene groups has been shown to be the cause of the sol-to-gel phase transition in azocholesterol-derived molecular gels. The transition was reversed by using wavelengths that cause selectively the cis-trans or trans-cis isomerizations.

For gelators containing functional groups that are sensitive to the pH of their environment, deprotonation or protonation may remove or create important interactions vital to the gel properties and/or gel formation. For example, Das et al. showed how pH control of gelation of a dipeptide-based gelator can be used to entrap compounds such as dyes. The formation of the sodium salt by increasing the pH improved the gelating ability of the dipeptide in both organic liquids and in water.
When an enzyme-cleavable moiety is incorporated into a gelator, the gel can be tuned using the catalytic properties of enzymes.\textsuperscript{164,165} For example, Xu \textit{et al.} investigated an amino acid derivative which could be converted from an inefficient gelator into a hydrogelator by enzymatic dephosphorylation in the presence of a phosphatase enzyme.\textsuperscript{166}

Recently, molecular gels with multi-stimuli responsive properties have been developed.\textsuperscript{167-172} They require careful integration between the molecular structure of the gelator and the environment of the non-covalent interactions. Molecular gels derived from a $D$-gluconic acetal-based gelator, 2,4-(3,4-dichloro)benzylidene-$N$-octyl-$D$-gluconamide, is one example with multi-stimuli responsive properties.\textsuperscript{173} The gels displayed controllable phase transitions upon application of chemical (i.e., base, anions) and physical (i.e., ultrasound, mechanical) stimuli (Figure 1.12). In particular, anion responsiveness was found by adding tert-butyl halides; the original gel networks were broken, probably due to the formation of halide-$\text{HNCO}$ H-bonds. Reformation of the gels was achieved by adding methanol to recover the original hydrogen bonding networks. Similarly, adjusting the pH can also reversibly trigger the sol-gel transition through the formation and deformation of OH-$\text{HNCO}$ H-bonds.

Besides chemical stimuli, some gels are also responsive to physical stimuli, including ultrasound and mechanical force. Mechanical force is one of the major stimuli which have been used to probe molecular gels in this dissertation. Studies on mechano-switchable gels will be discussed at length in Section 1.3.2.
Reversible gel-to-sol transitions of a chloroform gel of 2,4-(3,4-dichloro)benzylidene-$N$-octyl-$D$-gluconamide by a variety of chemical and physical stimuli. Reproduced from ref 174 with permission of the Royal Society of Chemistry.

1.3.2 Mechanical-responsive gels

As mentioned above, in some molecular gels, the assembly/disassembly of the SAFiN can be controlled by specific stimuli. Specifically, some materials that are thixotropic and capable of self-healing after being damaged have been developed recently.\textsuperscript{51,150,175} Thixotropic materials can regain their viscoelasticity after cessation of destructive mechanical force. Although many thixotropic materials comprised of covalently crosslinked polymers or supramolecular polymers are known,\textsuperscript{150,175-177} relatively few thixotropic molecular gels that have crystalline SAFiNs have been reported.\textsuperscript{64,128,178,179} Most crystalline molecular gels can only regain their viscoelasticity after being heated to their sol phases and recooled. Two recent reviews by Yu et al. and Mallia et al., have described different types of molecular gels that are responsive to mechanical stimuli and assessed some useful structural characteristics of the gelators capable of forming thixotropic molecular gels.\textsuperscript{180,181} However, the ability to design molecular gelators whose gels are thixotropic continues to be a challenge.
Many of the thixotropic molecular gels reported so far are derived from metallo-gelators. 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-gelators. The coordination of a metal ion to a ligand can introduce or increase luminescent, catalytic, and magnetic properties. Recently, a few metallo-molecular gels have been reported to exhibit self-healing properties based on the reversible formation of metal-ligand coordination; the functional groups of their ligands include aromatic rings, host-guest type interactions, or peptides and sugars with strong hydrogen-bonds. However, very few of the metallogels that can respond reversibly to mechanical stimuli have very simple ligand structures, such as those that are fatty acid based.

Examples of thixotropic molecular gels derived from fatty acids with crystalline SAFiNs are even rarer. It is desirable to find the fundamental design principles for making new thixotropic gels derived from naturally-occurring, readily-available compounds. The gels of D-12HSA in silicone oil are among the few crystalline thixotropic molecular gels derived from naturally-occurring fatty acids; at 2 wt % of gelator, they reform and recover at least some of their viscoelastic properties without heating. The restoration of gel viscoelasticity occurred within 10 s after the cessation of mechanical disruption and the elastic modulus was found to recover up to 70% of its initial value. The hypothesized mechanism for this phenomenon is that the fibers are not destroyed completely, while at least some of the interactions which join fibers or spherulites are broken. After their disruption, fibers diffuse and reform the SAFiNs via renewed contacts.

Another system involves the N-acylethanolamine-based gelators, HS-n-OH (Scheme 1.5), introduced in section 1.2.7. Although the gels of all of the HS-n-OH in isostearyl alcohol
are equally (~99 %) thixotropic, their recovery times varied significantly, without an obvious correlation with the length of the N-alkyl chains. Although 2 wt % HS-2-OH in isostearyl alcohol can recover its viscoelasticity completely within ~1 s after the cessation of destructive mechanical strain, after removing the hydroxyl group on the alkanoyl chain of HS-3-OH, the gel with the resultant gelator, S-3-OH, is not thixotropic in isostearyl alcohol. 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. Mallia et al. proposed a possible mechanism for mechanical destruction and reformation of SAFiNs in the gels of HS-n-OH in isostearyl alcohol. The very fast recovery times of some of the mechanically destroyed gels require that the destroyed gels contain 1D species (rather than reverting to 0D species) that are large fragments of spherulites or complete spherulites which are disconnected from each other. In this way, re-establishment of inter-fiber (or other micro-object) connections can occur rapidly, leading to SAFiNs.

1.3.3 Changes in physical properties

The reversible sol-to-gel transitions can lead to significant changes in mechanical, thermal, optical and, in some cases, electronic and luminescent properties of the materials. For example, the transition from gel-to-sol can lead to a decrease in the elastic modulus and viscosity as well as to different morphologies of the materials. Also, the formation of SAFiNs in some organogels that contain a luminogen can lead to enhanced and blue-shifted emissions. These gels are aggregation-induced emissive (AIE) materials. The luminescent properties of these materials can be controlled by external stimuli (i.e., temperature changes) during their transitions from sols to gels. Several types of luminescent gels have been designed previously, such as quantum dot-silica gel glasses, carbon dot gel glasses, nanoparticle
organogels, and molecular gels. Among them, the functional groups of most molecular gels include aromatic hydrocarbons, hydrogen bonds, and organometallic motifs. The AIE behavior of these molecular gels can be rationalized on the basis of the gelators experiencing motional restrictions in the SAFiNs. The change in the physical properties of the materials during gel-to-sol transition not only can lead to promising applications, but also can provide feasible tools to monitor the kinetics of the phase transitions.

1.4 Applications

A major reason why interest in molecular gels has increased at a nearly exponential pace during the last 3 decades is their numerous potential and realized industrial applications. They can be found in many areas, such as sensors, cosmetic carriers, templates for materials synthesis, food additives, and lubrication. Specifically, hydrogels have been used in food, pharmaceutical and tissue engineering applications given their aqueous nature and, in many cases, high biocompatibility. Organogels have been investigated extensively during the past three decades because of their numerous potential applications as controlled drug delivery devices, matrixes for carrying chemosensors, and oil recovery agents. The possible magnetism, luminescence, molecular electronic responses, and catalytic activity of metallo-gels also have potential applications in materials science. For example, Jadhav et al. investigated the phase-selective gelation of a naturally-occurring sugar-based gelator, mannitol dioctanoate, and its use as solidifier for oil spill. Gelation of diesel oil occurred instantly after mixing a solution of mannitol dioctanoate in ethanol with a diesel oil/water mixture. The diesel oil gel layer was then separated from the mixture and the gelator was recovered quantitatively by distilling off the diesel fuel. This is one of the examples that
provides promising approach for the treatment of oil spills utilizing the different gelation abilities of a gelator in water and in oil.225

Stimulus-responsive molecular gels have potential applications in many fields, such as organic light emitting diodes,226-228, chemosensors,229,230 drug delivery units,159,231 and biosensors.145 For example, Lin et al. developed an anion sensor array based on the difference in AIE behavior of metallo-gels derived from 3,4,5-tris(hexadecylox)benzo-hydrazide.232 The AIE behavior of a 3,4,5-tris(hexadecylox)benzo-hydrazide gel in DMF was lost upon addition of several metal ions (N.B., Cu²⁺, Hg²⁺, Fe³⁺, Cr³⁺, and Zn²⁺). These metallo-gels sensed selectively CN⁻, SCN⁻, S²⁻, and I⁻ by the competitive coordination of the gelator to different metal ions, and anions in ways that led to different emission characteristics.

Most applications of molecular gels have been envisaged because of their abilities to trap and immobilize large volumes of liquid using gelators with low molecular masses and their different responses to environmental stimuli. The development of molecular gels suitable for these and other applications will continually be appealing.

1.5 Statement of problem

As more and more potential and realized industrial applications are found for molecular gels, the ability, a priori, to design molecular gelators and to predict their gelating abilities in specific liquids will continue to be a primary challenge in the field of molecular gels. Therefore, systematic and targeted studies to create structure-property correlations, and to understand the influence of the liquids on the kinetics and thermodynamics of gel formation are critically needed. The body of work described in this dissertation provides some of this information by focusing on the rational design of molecular gelators derived from long-chain, naturally-
occurring fatty acids. Specifically, the goal of this work is to understand the effects that small changes in functional groups on gelators derived from OA and D-RA have on the structural, mechanical, kinetic, and thermodynamic properties of their gels.

1.6 Scope of this work

This dissertation reports detailed studies on a series of molecular gelators, each derived from naturally-occurring cis-unsaturated fatty acids, and the properties of their gels. Typically, cis-unsaturated fatty acids have very limited gelating abilities, as indicated by their low melting temperatures. The bent polymethylene chains, introduced by introduction 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.\textsuperscript{233} 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 are below 15 °C.\textsuperscript{234,235} However, the presence of a C=C double bond in OA and D-RA opens many possibilities for functional group transformations, each of which can lead to a somewhat different potential gelator.

OA can be isolated from many plant oils, especially canola oil,\textsuperscript{91} while the triglyceride of D-RA is a major component of the oil obtained from the seeds of mature castor plants.\textsuperscript{92} Several structural features added to OA and D-RA have been investigated and covered in the following chapters, including dihydroxyl, α-diketo functionalities, metal carboxylate salts, and ammonium carboxylate salts. Several structure-property correlations, including some involving important stimulus-responsive properties, have been developed. In addition to the development of detailed structure-property correlations, the influence of thermodynamic driving forces, kinetics of aggregation and the influence of liquids on the gel networks and gelation efficiency have been
covered in some of the studies. The information provided in this dissertation provides some useful 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*. It gives several steps toward the sought paradigm but it does not supply one.

**Scheme 1.7** Flow chart for gelators investigated in this dissertation.
2 GENERAL EXPERIMENTAL PROCEDURES AND SYNTHESSES

2.1 Reagents

Ethanol (Sigma-Aldrich, 200 proof, anhydrous, 99.5 %), 1-octanol (Sigma Aldrich, >99 %), isostearyl alcohol (Nissan Chemical, >99 %, FO 180), acetonitrile (Fisher Scientific, certified A.C.S), acetone (Sigma-Aldrich, HPLC, 99.8 %), hexamethylphosphoramide (Aldrich Chemicals, 99 %), N,N-dimethylacetamide (Sigma-Aldrich, 99 %), methyl-2-pyrrolidone (Sigma-Aldrich, anhydrous, 99.5 %), methyl salicylate (Fisher Scientific, reagent grade), tetrahydrofuran (THF, Sigma-Aldrich, anhydrous, >99 %), ethyl acetate (Sigma-Aldrich, HPLC, 99.7 %), dichloromethane (Fisher, HPLC grade, 99.7 %), chloroform (Fisher Scientific, 99.6 %), carbon tetrachloride (Fisher, HPLC 99.9 %), toluene (EMD Chemicals, 99.8 %), o-xylene (Aldrich, anhydrous, 97 %), p-xylene (Aldrich, HPLC 99+ %), m-xylene (Aldrich Chemicals, anhydrous, >99 %), n-butylbenzene (Aldrich, 99+ %), n-hexylbenzene (Aldrich, 97 %), benzonitrile (Matheson Coleman & Bell Manufacturing Chemists, 98 %), nitrobenzene (Sigma, 99 %), chlorobenzene (Alfa Aesar, certified A.C.S, 99.5 %), hexanes (Fisher, 98.5 %), decane (Sigma Aldrich, >99 %), octane (Sigma Aldrich, 98 %), dodecane (Sigma Aldrich, >99 %), silicone oil (tetramethyltetraphenylsiloxane, Dow silicone oil 704 from Dow Chemical Company, Midland, MI), safflower oil (Coral International, San Luis Potosi, Mex.; high in triolein), deionized water (pH 5.3), CDCl₃ (D, 99.9 %; Cambridge Isotope Laboratories, Inc.), DMSO-d₆ (D, 99.9 %; Cambridge Isotope Laboratories, Inc.), CD₃OD (D, 99.9 %; Cambridge Isotope Laboratories, Inc.), and silica gel (Sorbent Technologies®, silica gel standard grade: porosity 60 Å, particle size: 230 x 400 mesh) were used as received. Dimethyl formamide (DMF,
Fisher Scientific, certified A.C.S.) and methanol (Fisher Scientific, certified A.C.S.) were purified by literature methods.236

2.2 Instrumentation

$^1$H-NMR and $^{13}$C-NMR spectra were recorded on a Varian Inova 400 MHz Spectrometer operating at 400 MHz (100 MHz for $^{13}$C). MestReNova v5.2.4-3924 software from Mestrelab Research was used to analyze the spectra. Data from the $^1$H-NMR and $^{13}$C-NMR spectra are reported as chemical shifts in ppm, referenced to tetramethylsilane (TMS), with the corresponding integration values for the proton spectra. Coupling constants ($J$) are reported in Hertz (Hz). Standard abbreviations indicating multiplicity are: s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). FT-IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer, using an attenuated total reflection accessory (ATR) for neat solids, and a liquid cell having NaCl windows and a lead foil spacer that was sealed with Teflon plugs for gels and other non-solid samples. The IR stretching peaks of the gels were identified by subtracting empirically the IR spectra of the liquids from those of the gels. Gas chromatography–mass spectrometry (GC-MS) measurements were obtained on a Shimadzu GC-17A gas chromatograph connected to a Shimadzu QP-5000 mass spectrometer using a 0.25 μm SGE BPX5 (15 m× 0.25 mm) column and a flame ionization detector. Elemental analyses were performed on a Perkin-Elmer 2400 CHN elemental analyzer using acetonilide as a calibration standard.

DSC studies were performed on a TA DSC200 instrument using hermetically-sealed aluminum pans against an empty reference cell. Transition temperatures from DSC, including gelator melting, gel melting, gelator solidification, and gel formation temperatures ($T_m$, $T_{gm}$, $T_c$, and $T_{gc}$, respectively), are reported at the onsets of endotherms (on heating) and exotherms (on
cooling) with heating and cooling rates of 10 °C/min. The enthalpies of the transitions for the neat gelators have been measured as well. The enthalpies of the gelators in the gels have been normalized to ‘neat’ concentrations by dividing 100x the observed heats by the effective SAFiN concentrations as wt %s (i.e., the total added wt % of gelator minus the CGC). TGA of the neat solids were performed on a TA 2910 differential scanning calorimeter interfaced to a TA Thermal Analyst 3100 controller while a slow stream of nitrogen was flowed through the instrument cell. The heating rate was 20 °C/min.

Melting points of all solids and POMs of gels were recorded on either a Leitz 585 SM-LUX-POL microscope equipped with crossed polars, a Leitz 350 heating stage with a full-wave plate, a Photometrics CCD camera interfaced to a computer or with an automated Nikon Eclipse Ti-E inverted microscope, equipped with a Linkam PE100-NIF inverted Peltier heating/cooling stage with a full-wave plate.

AFM images were recorded at room temperature in an open system on a NTEGRA Prima scanning probe microscope (from NT-MDT) mounted on an inverted Nikon Eclipse Ti-S fluorescence microscope using a non-modified or a hydrophobically modified NSG30 silicone tip (force constant, 22-100 N/m; NT-MDT). The hydrophobically modified NSG30 silicone tip was prepared by dipping a NSG30 silicone tip in a 10 mM dichlorodimethylsilane in toluene solution for 1 h, followed by washing sequentially with chloroform, 2-propanol and water. The tip was then heated to 150 °C for 30 min.\(^\text{237}\) Semi-contact mode was used and the scan rate was 0.1 Hz. The setpoint and the gain were set at different values for each sample. The setpoint was adjusted in between 3.8 to 11.2 nA, and the gain was adjusted between 0.1 and 0.8. Gels were deposited directly onto a glass substrate, reheated to their solution/sol phase, and (when necessary) liquid was added to maintain the concentration within 5 wt % after heating.
PXRD patterns of the neat solids were obtained either on a Rigaku R-AXIS image plate system with Cu Kα X-rays (λ = 1.54 Å) generated by a Rigaku generator operating at 46 kV and 40 mA with the collimator at 0.3 mm for 2 h or a Rigaku RAPID image plate system with Cu Kα X-rays (λ = 1.54 Å) at 30 kV and 20 mA. Two detectors were used in the Rigaku R-AXIS image plate system. The diffraction data at 2θ between 1.5° and 10° were collected for 12 h using a scintillator detector; data at 2θ between 5° and 50° were collected for 30 min using a D/Tex Ultra detector. PXRD patterns of the gels were recorded using the Rigaku RAPID image plate system. The gel samples used for PXRD studies were prepared by flame-sealing hot solutions/sols in 0.5 mm glass capillaries (W. Müller, Schönwalde, Germany) and allowing them to cool to room temperature. The diffractions were collected for 10 h for the gels. Diffraction data of the liquids used for the gels were also collected for 10 h in 0.5 mm glass capillaries. The diffraction peaks of the gels were identified by subtracting empirically the diffractograms of the liquids from those of the gels.\textsuperscript{238} Materials Data JADE (version 5.0.35) PXRD pattern processing software was used to for data processing and analysis. During the unit cell indexing, two conditions for a possible fit were enforced: (1) the window of difference in 2θ between the diffraction peaks and the indexed peaks could be no more than 0.2 degree; (2) all diffraction peaks had to be present in the indexed patterns.

Rheological measurements were performed on an Anton Paar-Physica MCR 302 strain-controlled rheometer using Peltier temperature-controlled parallel plates (25 mm diameter) at a gap of 0.5 mm. Samples were heated between the rheometer plates to a temperature at which solution/sols were formed, cooled to 0 °C (at 20 °C /min), equilibrated at 0 °C for 5 min, warmed to 20 °C, and then incubated in place for 20 min to reform the gels before commencing data collection. The linear viscoelastic regions of the gel samples were determined by measuring $G'$
(associated with energy storage), and \( G'' \) (associated with the loss of energy), as a function of the strain amplitude at a constant frequency (1 Hz). Then, the moduli were measured from 100 to 1 Hz at a constant strain in the linear viscoelastic region. Both strain sweeps and angular frequency sweeps were measured for three aliquots of each sample and averaged. The difference between the averaged value and the value in each run is represented by the error limits.

2.3 Procedures

2.3.1 Preparation and preliminary classification of samples.

A mixture of a gelator and a liquid was flame-sealed in a glass tube (5 mm i.d.) and heated in boiling water or an oil bath until a solution/sol was obtained; systems in which the gelator did not dissolve after heating were referred to as “insoluble” (I). The hot solution/sol was placed in an ice-water bath for 10 min and finally kept at room temperature for 1 h. For fast-cooled samples, the glass tubes were then placed directly into an ice-water bath for 10 min and were warmed to room temperature for 1 h. For slow-cooled samples, the hot mixtures were kept in the water or oil bath while it returned slowly to room temperature by removing the heating unit. Systems in which only a solution/sol remained after heating and cooling were considered “solutions” (S). If the gelator dissolved after heating, but precipitated when cooled, the sample was deemed a “precipitate” (P). Then, either the inverse flow method\(^{24}\) or the falling ball method\(^{25}\) was used to determine qualitatively the nature of the samples.

*Inverse flow method:*

If the sample did not flow perceptibly with or without gentle tapping after being inverted, it was an “opaque” (OG), “translucent” (TG) or “clear” (CG) gel. If the sample did not flow without gentle tapping, but flowed after being tapped, the sample was considered a “weak gel”
(WG). When a part of the sample flowed perceptibly and the rest of the sample did not, the sample was designated as a “partial gel” (PG). If a gel-like mixture was formed after cooling, but flowed slowly when the tube was inverted, the sample was considered a gelatinous precipitate (GP). Finally, if a potential gelator dissolved on heating and formed an inhomogeneous particle suspension that flowed when inverted on cooling, the sample was denoted as a suspension (Sus).

**Falling ball method:**

Each tube was opened, a steel ball (4 mm diameter; 250 mg) was carefully placed on the surface of the mixture, and the tube was flame-sealed again. Gelation was considered to have occurred qualitatively if the sample supported the ball at room temperature. The sample was an “opaque” (OG), “translucent” (TG) or “clear” (CG) gel.

### 2.3.2 Critical gelator concentrations and gel melting temperatures

CGC and $T_g$ ranges (*vide infra*) were also determined by either the inverse flow method$^{24}$ or the falling ball method$^{25}$. A CGC was determined from samples with different concentrations of a gelator in a liquid. Data are reported for different gelator concentration increments, as indicated by the error limits of the CGCs. $T_g$ values were determined by heating 5 wt % gels in flame-sealed capillaries at a rate of 2 °C/min.

**Inverse flow method:**

The glass tube was inverted. The gel melting temperature ranges are between when a sample began to flow and when it fell completely under the influence of gravity. The lowest concentration at which the sample did not flow perceptibly at room temperature was considered the CGC.

**Falling ball method:**
A steel ball (4 mm diameter; 250 mg) was carefully placed on the surface of the mixture. The lowest concentration at which the ball did not fall was considered the CGC. The gel melting temperature ranges reported are between when the ball began to fall and when it arrived at the bottom of the tube under the influence of gravity.
3 STRUCTURAL AND SOLUBILITY PARAMETER CORRELATIONS OF
GELATION ABILITIES FOR DIHYDROXYLATED DERIVATIVES OF LONG-
CHAIN, NATURALLY OCCURRING FATTY ACIDS

3.1 Introduction

As described in Chapter 1, creating structure-property correlations at different distance scales is one of the most important challenges to the rational design of molecular gelators. To understand the factors that lead to efficient gelation, it is necessary to compare the effects that small changes in functional groups of gelators have on gel structure at different distance scales and the corresponding properties of the gels.

Fatty acid-derived molecular gelators, as described in Section 1.2, have been studied extensively. An example is the well-known and very efficient, saturated fatty acid gelator, \((R)\)-12-hydroxystearic acid (\(D-12\text{HSA}\)).\(^{108,110,113,239,240}\) Starting from the unsaturated, naturally-occurring fatty acids, such as oleic acid (\(\text{OA}\)), ricinoleic acid (\(\text{D-RA}\)), and erucic acid (\(\text{EA}\)), many potential gelators with different functionality that are structurally related to \(D-12\text{HSA}\) can be developed. Among different functional group types, hydroxyl groups have been invoked as important contributors to the ability of saccharides to act as gelators.\(^{241}\) However, to the best of our knowledge, no diol-based molecular gelators, besides those synthesized from \(\text{D-RA, OA, and EA}\) here, have been derived from fatty acids. In this research, we have used the unsaturation of the initial acids to introduce a second hydroxyl group. The addition of the second hydroxyl group may aid fiber formation by introducing additional inter-molecular H-bonding interactions. Conversely, it may impede fiber formation by weakening the inter-molecular H-bonding via...
strong intra-molecular interactions. This work illuminates cases in which a second hydroxyl group, in proximity to the first, aids and impedes fiber network formation.

Here, the influence of the location and the orientation of a second hydroxyl group on gelation efficiency has been investigated by comparing the comportment of a 9:1 diastereomeric mixture of (9,12R)-dihydroxyoctadecanoic acid (9,12R-diol, in which a second hydroxyl group has been added to the D-RA structure), and two racemic molecules derived from OA, the cis- and trans- isomers of 9,10-dihydroxyoctadecanoic acid (cis-9,10-diol and trans-9,10-diol). Similarly, the gelating abilities of the racemic isomers of cis- and trans-13,14-dihydroxydocosanoic acid (cis-13,14-diol and trans-13,14-diol), homologues of cis-9,10-diol and trans-9,10-diol, have been synthesized from EA and used to assess the influence of an elongated alkyl chain on gelator efficiency. Although physical properties, such as the elasticity of gels, can be influenced by the nucleation and the enhancement of fiber branching, most of the experimental conditions to make the gels were held constant in order to isolate the relationship between structure and gelation properties. The results have been analyzed comparatively, and they can be rationalized on the basis of models for inter-molecular interactions among the gelator molecules. The work described throughout this chapter has been published.
Scheme 3.1 Structures of OA, EA, D-RA and gelators derived from them.

3.2 Experimental Section

3.2.1 Materials

Ricinoleic acid (D-RA, 89%; Wako Chemical Co.), oleic acid (OA, Sigma-Aldrich, 90%), erucic acid (EA, TCI America, 90%), methyl erucate (Sigma-Aldrich, ≥99%), osmium tetroxide (Sigma-Aldrich, 2.5% wt. in tert-butyl alcohol), formic acid (Alfa Aesar, 97%), N-methylmorpholine N-oxide (NMO) monohydrate (Alfa Aesar, >98%), mercuric acetate (Fisher, certified A.C.S), sodium tetraborate decahydrate (Fluka, >99.5%), sodium borohydride (Aldrich, 99%), Celite 545 (Sigma Aldrich), hydrogen peroxide (Fisher, 30%, certified ACS), dichlorodimethylsilane (Sigma Aldrich, >99.5%), and silica gel (Sorbent Technologies®, silica gel standard grade: porosity 60 Å, particle size: 230 x 400 mesh) were used as received. All solvents and other chemicals used for syntheses and gelation studies are listed in Chapter 2.
Trans-9,10-diol, trans-13,14-diol, cis-9,10-diol, and cis-13,14-diol were supplied by Prof. Mukund P. Sibi of the Department of Chemistry, North Dakota State University, Fargo, ND. Trans-9,10-diol and trans-13,14-diol were synthesized from OA and EA, respectively; cis-9,10-diol, and cis-13,14-diol were synthesized from methyl oleate and methyl erucate, respectively. Details concerning the syntheses, purifications, and characterizations of these diols have been reported.242

For trans-9,10-diol: 52 % yield, mp 135.1-138.6 °C. (lit:243 95 °C). 1H NMR (CD3OD, 400 MHz) chemical shifts (ppm): 0.92 (t, 3H, CH3, J = 8 Hz), 1.32 (m, 20H, CH2-CH2), 1.51 (m, 4H, -CH(-OH)CHH′- and -CH2-CH2-COOH), 1.62 (m, 2H, -CH(-OH)CHH′-), 2.24 (t, 2H, CH2-COOH, J = 8 Hz), 3.38 (m, 2H, -CH(-OH)CH2-). 13C NMR (CD3OD, 100 MHz) chemical shifts (ppm): 13.0 (1C, CH3), 22.3, 25.5, 25.7, 29.0, 29.1, 29.3, 32.5 (14C, CH2), 73.9 (2C, CHOH), 178.9 (1C, COOH). HRMS: calculated for C18H36O4Na+: 339.2506; found: 339.2506.

For trans-13,14-diol: 75 % yield, mp 182.8-185.6 °C. (lit:244 100 °C). 1H NMR (CD3OD, 400 MHz) chemical shifts (ppm): 0.92 (t, 3H, CH3, J = 8 Hz), 1.31 (m, 28H, CH2-CH2), 1.51 (m, 4H, -CH(-OH)CHH′- and -CH2-CH2-COOH), 1.62 (m, 2H, -CH(-OH)CHH′-), 2.24 (t, 2H, CH2-COOH, J = 8 Hz), 3.38 (m, 2H, -CH(-OH)CH2-). 13C NMR (CD3OD, 100 MHz) chemical shifts (ppm): 13.0 (1C, CH3), 22.3, 25.5, 25.7, 29.0, 29.1, 29.3, 32.5 (14C, CH2), 73.9 (2C, CHOH), 178.9 (1C, COOH). HRMS: calculated for C22H44O4Na+: 395.3132; found: 395.3137.

For cis-9,10-diol: 90 % yield, 125.8-128.8 °C (lit:245 127-128 °C). 1H NMR (CD3OD, 400 MHz) chemical shifts (ppm): 0.92 (t, 3H, CH3, J = 8 Hz), 1.34 (m, 20H, CH2-CH2), 1.59 (m, 6H, -CH(-OH)CH2- and -CH2-CH2-COOH), 1.62 (m, 2H, -CH(-OH)CHH′-), 2.30 (t, 2H, CH2-COOH, J = 8 Hz), 3.36 (m, 2H, -CH(-OH)CH2-). 13C NMR (CD3OD, 100 MHz) chemical shifts
(ppm): 13.0 (1C, CH₃), 22.3, 24.7, 25.5, 25.6, 28.8, 29.0, 29.3, 29.5, 31.7, 32.1, 32.2, 33.5 (14C, CH₂), 74.5, 74.6 (2C, CHO), 176.3 (1C, COOH). HRMS: calculated for C₁₈H₃₅O₄ [M-H]: 315.2530; found: 315.2521

For cis-13,14-diol: 68% yield, 129.9-131.4 °C (lit: 245 131-132 °C). ¹H NMR (CD₃OD, 400 MHz) chemical shifts (ppm): 0.92 (t, 3H, CH₃, J = 8 Hz), 1.34 (m, 26H, CH₂-CH₂), 1.60 (m, 6H, -CH(-OH)CH₂- and -CH₂-CH₂-COOH), 2.29 (t, 2H, CH₂-COOH, J = 8 Hz), 3.36 (m, 2H, -CH(-OH)CH₂-). ¹³C NMR (CD₃OD, 100 MHz) chemical shifts (ppm): 13.0(1C, CH₃), 22.3, 24.7, 25.6, 28.8, 29.0, 29.2, 29.3, 29.4, 29.5, 31.7, 32.2, 33.6, (18C, CH₂), 74.6 (2C, CHO), 176.4 (1C, COOH). HRMS: calculated for C₂₂H₄₄O₄Na⁺: 395.3132; found: 395.3125.

3.2.2 Instrumentation and sample preparation

3.2.2.1 Hansen Space Correlations and Spheres

The overall energy density (δ) of each liquid or gelator is separated into dispersive (δ_d), polar (δ_p), and H-bonding (δ_h) interaction components (as discussed in Section 1.1.6, eq 1.3). ⁷³,⁷⁵,⁷⁶,⁸⁴,²⁴⁶ These HSPs for the neat liquids were taken from the literature (Table 3.6). ⁸⁶ The Hansen Space was plotted using MATLAB HSP 3D Plotting and Fitting Program from UMD Complex Fluids and Nanomaterials Lab. ⁷⁵ HSP values for each gelator were calculated as the center of the spheres constructed from the data points. For the purpose of these analyses, the samples of gelators in different liquids were separated into soluble (S), gel (G), and precipitated (P) categories; suspensions were treated as “precipitates”.

Other common instrumentation and general procedures are described in Chapter 2.
3.2.3 Synthesis

**9,12R-diol** was synthesized from ricinoleic acid by oxymercuration (Scheme 3.2).\(^\text{247}\)

Scheme 3.2 Synthesis of **9,12R-diol**.

Mercuric acetate (2.136 g, 6.702 mmol) was dissolved in 6 mL of H\(_2\)O. Ricinoleic acid (1.997 g, 6.701 mmol) was dissolved in 6 mL of THF. The solution was then added to the mercuric acetate-water solution. The mixture was stirred at 20 °C for 40 min. Aqueous sodium hydroxide (6 mL, 3M) was added at 20-25 °C. NaBH\(_4\) (0.128 g, 3.37 mmol) was then dissolved in the aqueous NaOH (6 mL, 3M) and then added to the reaction mixture dropwise over 10 min at 20-22 °C. The mixture was stirred at 20 °C for an additional 20 min and then mixed with 5 g Celite for 10 min. After filtration, the filtrate was acidified with 2 M HCl to pH~2. The THF was removed on a rotary evaporator (20 mmHg) at 50 °C. The aqueous solution was extracted with 15 mL of CH\(_2\)Cl\(_2\). The organic phase was washed twice with 15 mL of deionized water and once with saturated aqueous NaCl solution. After drying with Na\(_2\)SO\(_4\) overnight, the CH\(_2\)Cl\(_2\) was removed on a rotary evaporator (20 mmHg) at 30 °C. The crude product (0.863 g) was recrystallized thrice from chloroform and diethyl ether to yield 0.219 g (11 %) of **9,12R-diol** as a white powder, mp 84.7-86.9 °C (lit:\(^\text{247}\) 78-82 °C). IR (\(\nu_{\text{max}}/\text{cm}^{-1}\)): 2600-3500 (broad, COOH), 3411 (broad, O-H stretching), 2918 (C-H stretching) and 1701 (COOH, C=O stretching). \(^1\)H NMR (CDCl\(_3\), 400 MHz) chemical shifts (ppm): 3.95 or 3.63 (m, 2H, 2 diastereomers, integration ratio 1:9, -CH\(_2\)CH(-OH)CH\(_2\)-), 2.33-2.37 (t, 2H, CH\(_2\)-COOH, J = 7.6 Hz), 1.63 (m, 4H, -CH\(_2\)(HO-))HCCH\(_2\)CH\(_2\)CH(-OH)CH\(_2\)-), 1.45 (m, 6H, -CH\(_2\)(-OH)HCCH\(_2\)CH\(_2\)C(-OH)HCH\(_2\)-)}
and \(-\text{CH}_2\text{-CH}_2\text{-COOH}\), 1.27-1.31 (m, 16H, \text{CH}_2\text{-CH}_2), 0.8 (t, 3H, \text{CH}_3, J = 6.6 \text{ Hz}). \text{Elemental Analysis (\%)} calculated for \text{C}_{18}\text{H}_{36}\text{O}_4: \text{C}, 68.31; \text{H}, 11.46; \text{N}, 0.00; \text{found}: \text{C}, 68.05; \text{H}, 11.84; \text{N}, 0.12.

3.3 Results and discussion

In this study, the range of liquids gelated was the major criterion employed to determine the ‘efficiency’ of the gelators, although several thermodynamic, structural, and dynamic (N.B., rheological) techniques were used as well. Also, the relationship between liquids and a gelator was explored using Hansen solubility parameters.\textsuperscript{75}

3.3.1 Gelation properties

The gelation properties of 5 wt \% \text{D-12HSA, 9,12R-diol, cis-9,10-diol, trans-9,10-diol, cis-13,14-diol, and trans-13,14-diol}, in a wide range of organic liquids, are summarized in Table 3.1. No detectable phase separation was noted for > 8 months in any of the samples that produced gels stored at room temperature in sealed vials.
Table 3.1 Appearances,[a] $T_g$ values (°C) of fast-cooled gels with 5 wt % gelator,[b] and CGCs (wt %) in different liquids.[c]

<table>
<thead>
<tr>
<th>liquid[d]</th>
<th>D-12HSA</th>
<th>9,12R-diol</th>
<th>cis-9,10-diol</th>
<th>trans-9,10-diol</th>
<th>cis-13,14-diol</th>
<th>trans-13,14-diol</th>
</tr>
</thead>
<tbody>
<tr>
<td>dimethyl sulfoxide (DMSO)</td>
<td>S[e]</td>
<td>S</td>
<td>S</td>
<td>P</td>
<td>S</td>
<td>Sus</td>
</tr>
<tr>
<td>dimethylformamide (DMF)</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>P</td>
<td>P</td>
<td>S</td>
</tr>
<tr>
<td>acetone (ACT)</td>
<td>S</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>S</td>
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<tr>
<td>methanol (MOH)</td>
<td>S[e]</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>ethanol (EOH)</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
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<tr>
<td>1-octanol (OOH)</td>
<td>S[e]</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>Sus</td>
<td>Sus</td>
</tr>
<tr>
<td>ethyl acetate (EAC)</td>
<td>S</td>
<td>GP</td>
<td>Sus</td>
<td>P</td>
<td>P</td>
<td>P</td>
</tr>
<tr>
<td>hexamethylphosphoramide (HMP)</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>N,N-dimethylacetamide (NDM)</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>CG 64-66,</td>
<td>S</td>
<td>OG 114-117,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.8(0.3)</td>
<td>S</td>
<td>0.70(0.05)</td>
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<tr>
<td>methyl-2-pyrrolidone (MP)</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>CG 87-89,</td>
<td>S</td>
<td>OG 119-122,</td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
<td>0.4(0.2)</td>
<td>S</td>
<td>0.6(0.1)</td>
</tr>
<tr>
<td>methyl salicylate (MS)</td>
<td>TG 46-49, 0.40(0.05)</td>
<td>OG 60-62, 0.35(0.05)</td>
<td>GP</td>
<td>Sus</td>
<td>GP</td>
<td>OG 138-141, 0.7(0.1)</td>
</tr>
</tbody>
</table>
### Table 3.1 (cont.)

<table>
<thead>
<tr>
<th>liquid$^{[d]}$</th>
<th>D-12HSA</th>
<th>9,12R-diol</th>
<th>cis-9,10-diol</th>
<th>trans-9,10-diol</th>
<th>cis-13,14-diol</th>
<th>trans-13,14-diol</th>
</tr>
</thead>
<tbody>
<tr>
<td>toluene (TOL)</td>
<td>CG 44-45,$^{[e]}$</td>
<td>OG 57-59,</td>
<td>P</td>
<td>OG 63-66,</td>
<td>P</td>
<td>P</td>
</tr>
<tr>
<td></td>
<td>0.90(0.05)</td>
<td>0.50(0.05)</td>
<td></td>
<td>2.1(2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>o-xylene (OXL)</td>
<td>CG 36-38, 1.4(0.1)</td>
<td>CG 57-59,</td>
<td>P</td>
<td>OG 101-104,</td>
<td></td>
<td>OG 112-114,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.50(0.05)</td>
<td></td>
<td>1.4(0.2)</td>
<td>Sus</td>
<td>0.18(0.02)</td>
</tr>
<tr>
<td>p-xylene (PXL)</td>
<td>CG 35-37, 1.6(0.1)</td>
<td>OG 61-62, 1.3(0.1)</td>
<td>P</td>
<td>GP</td>
<td>Sus</td>
<td>CG 114-117, 0.35(0.05)</td>
</tr>
<tr>
<td>m-xylene (MXL)</td>
<td>CG 38-40, 1.4(0.1)</td>
<td>OG 60-62, 1.4(0.2)</td>
<td>P</td>
<td></td>
<td>OG 90-92, 0.9(0.1)</td>
<td>Sus</td>
</tr>
<tr>
<td>n-butylbenzene (BBN)</td>
<td>CG 44-46, 1.8(0.1)</td>
<td>OG 68-70, 1.7(0.1)</td>
<td>P</td>
<td></td>
<td>OG 50-54, 2.7(0.3)</td>
<td>Sus</td>
</tr>
<tr>
<td>nitrobenzene (NTB)</td>
<td>OG 44-45, 0.30(0.05)</td>
<td>OG 57-59, 0.20(0.05)</td>
<td>P</td>
<td>OG 121-123, 0.6(0.1)</td>
<td>Sus</td>
<td>OG 138-139, 0.30(0.05)</td>
</tr>
<tr>
<td>chlorobenzene (CHB)</td>
<td>CG 46-48,$^{[e]}$ 0.7(0.1)</td>
<td>OG 54-56, 0.30(0.05)</td>
<td>P</td>
<td>OG107-109, 2.2(0.3)</td>
<td>Sus</td>
<td>TG 120-122, 0.7(0.1)</td>
</tr>
<tr>
<td>benzonitrile (BZN)</td>
<td>CG 37-39, 1.0(0.1)</td>
<td>CG 45-47, 0.30(0.05)</td>
<td>Sus</td>
<td>OG118-120, 0.60(0.05)</td>
<td>Sus</td>
<td>TG 118-120, 0.50(0.05)</td>
</tr>
<tr>
<td>CHCl₃ (CHF)</td>
<td>S</td>
<td>OG 34-36, 1.1(0.1)</td>
<td>P</td>
<td></td>
<td>P</td>
<td>P</td>
</tr>
<tr>
<td>liquid[^d]</td>
<td>D-12HSA</td>
<td>9,12R-diol</td>
<td>cis-9,10-diol</td>
<td>trans-9,10-diol</td>
<td>cis-13,14-diol</td>
<td>trans-13,14-diol</td>
</tr>
<tr>
<td>-----------</td>
<td>---------</td>
<td>-----------</td>
<td>---------------</td>
<td>-----------------</td>
<td>----------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>CH$_2$Cl$_2$ (DCM)</td>
<td>OG 28-29, 1.6(0.1)</td>
<td>OG 37-39, 0.3(0.1)</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>P</td>
</tr>
<tr>
<td>CCl$_4$ (CTC)</td>
<td>OG 41,[^e] 0.4(0.05)</td>
<td>OG 62-64, 0.3(0.05)[^f]</td>
<td>Sus</td>
<td>Sus</td>
<td>Sus</td>
<td>Sus</td>
</tr>
<tr>
<td>acetonitrile (ATN)</td>
<td>OG 45-48,[^e] 1.8(0.1)</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>P</td>
</tr>
<tr>
<td>decane (DCN)</td>
<td>TG 62-63, 0.4(0.05)</td>
<td>P</td>
<td>Sus</td>
<td>P</td>
<td>P</td>
<td>P</td>
</tr>
<tr>
<td>octane (OCT)</td>
<td>TG 60-62,[^e] 0.4(0.05)</td>
<td>P</td>
<td>Sus</td>
<td>P</td>
<td>P</td>
<td>P</td>
</tr>
<tr>
<td>dodecane (DOD)</td>
<td>TG 64-65,[^e] 0.3(0.05)</td>
<td>P</td>
<td>Sus</td>
<td>P</td>
<td>P</td>
<td>P</td>
</tr>
<tr>
<td>hexanes (HXN)</td>
<td>TG 59-60,[^e] 0.4(0.05)</td>
<td>P</td>
<td>Sus</td>
<td>P</td>
<td>P</td>
<td>P</td>
</tr>
<tr>
<td>silicone oil</td>
<td>OG 73-74,[^e] 0.3(0.05)</td>
<td>P</td>
<td>P</td>
<td>I</td>
<td>GP</td>
<td>S</td>
</tr>
<tr>
<td>water</td>
<td>I[^e]</td>
<td>I</td>
<td>I</td>
<td>I</td>
<td>I</td>
<td>I</td>
</tr>
</tbody>
</table>

[^a] OG = opaque gel, CG = clear gel, TG = translucent gel, S = solution, P = precipitated, I = insoluble, Sus = suspension, GP = gelatinous precipitate; see Chapter 2 for details.  
[^b] Based on the falling ball method.  
[^c] Numbers in parentheses are the error limits of the CGCs.  
[^d] Acronyms for the liquids are listed in parentheses.  
[^e] From ref 70.  
[^f] Gel formed slowly when the concentration was below 1.5 wt %; the appearance of the sample was recorded 12 h after completion of the fast-cooling process.
Previous studies have found that the gelating properties of enantio-pure and racemic forms of D-12HSA\textsuperscript{113} can be very different. Regardless, some comparisons of the gelating abilities among D-12HSA and 9,12\textit{R}-diol (which are optically active), and \textit{trans}-9,10-diol (which is not) are made here. 9,12\textit{R}-Diol has high solubility in alcohols, DMSO and DMF, which is similar to that of D-12HSA. 9,12\textit{R}-Diol was able to gelate both high- and low-polarity aprotic aromatic liquids, as well as chloroalkanes. As indicated by the \textit{CGC} values, 9,12\textit{R}-diol is a more efficient gelator than D-12HSA in these liquids, but it was unable to gelate alkanes (although D-12HSA could). It appears that the increased polarity from the two hydroxyl groups of 9,12\textit{R}-diol decreases its ability to be solvated efficiently by low polarity liquids such as alkanes and, thus, the propensity to form precipitates is enhanced.

The optically-inactive diols display different gelator efficiencies as a result of the diastereomeric relationships between the hydroxyl groups and the influence of elongating the alkyl chain. The importance of \textit{\alpha}-diol (i.e., diols on adjacent carbon atoms) stereochemistry is clearly demonstrated by our observations that \textit{trans}-9,10-diol and \textit{trans}-13,14-diol formed gels in aromatic liquids, while \textit{cis}-9,10-diol and \textit{cis}-13,14-diol did not gelate any of the liquids investigated (Table 3.1). The solubility of both racemic \textit{cis}-9,10-diol and \textit{cis}-13,14-diol in various solvents are low. They stayed insoluble or precipitated even when the concentration was as low as 0.5 wt \%. \textit{Trans}-13,14-diol, with its longer alkyl chain (and, thus, greater London dispersion interactions), is a more efficient gelator than \textit{trans}-9,10-diol; it gelated more liquids and with lower \textit{CGCs}. An analogous example of this phenomenon is found in the aggregation of \textit{n}-alkanes: the longest \textit{n}-alkanes are the most efficient gelators.\textsuperscript{97} However, \textit{trans}-9,10-diol did not gelate as many liquids as the \gamma-diol (i.e., in which the two hydroxyl groups are on carbon atoms separated by two methylenes), 9,12\textit{R}-diol, or D-12HSA. Also, where direct comparisons
were possible, the CGC values of trans-\textbf{9,10-diol} were higher than those of \textbf{9,12R-diol} and \textbf{D-12HSA}. This may be rationalized in terms of the presence of intra-molecular H-bonding interactions in assemblies of trans-diols, which would impede the formation of SAFiNs. This hypothesis will be examined further in the discussion of molecular packing of the diols (\textit{vide infra}).

\subsection*{3.3.2 Thermal stability of gels}

The $T_g$ values of gels of \textbf{9,12R-diol}, \textbf{trans-9,10-diol}, and \textbf{trans-13,14-diol} in nitrobenzene are plotted as a function of gelator concentration in Figure 3.1. The $T_g$ values increase with increasing gelator concentration until a “plateau” region is reached, at which point $T_g$ (and the mechanical strength) no longer increases significantly with increasing gelator concentration. In this region, the basic structures and interactions of the SAFiN network are reasonably well established.\textsuperscript{18} For \textbf{9,12R-diol}, \textbf{trans-9,10-diol}, and \textbf{trans-13,14-diol}, the “plateau” concentration regions are reached at approximately 2, 3, and 2 wt %, respectively. Note that the plateau region is reached at $< 2$ wt % of \textbf{D-12HSA} in its silicone oil gel.\textsuperscript{70} Based upon these data, the experiments reported in Table 3.1 were conducted at 5 wt % gelator (i.e., within the “plateau” concentration region for all of the gels formed).
Figure 3.1 $T_g$s of nitrobenzene gels as a function of concentrations of $9,12R$-diol (black), $trans-9,10$-diol (green) and $trans-13,14$-diol (red). Vertical bars refer to when the ball first penetrated the gel surface and when the ball touched the bottom of the tube. The lines are visual aids only.

The thermal stability of a gel is dependent upon the nature of the liquid and the gelator, as well as the concentrations of each.\textsuperscript{70} The $T_g$ values of gels containing the diols are higher than those of the corresponding D-12HSA gels in each of the liquids for which direct comparisons are possible, and they follow the trend: D-12HSA $< 9,12R$-diol $< trans-9,10$-diol $< trans-13,14$-diol. Except for the $T_g$ values of $9,12R$-diol (68-70 °C) and trans-$9,10$-diol (50-54 °C) in $n$-butylbenzene, the same trends are found for the $T_g$ values for the 5 wt % gels and the melting temperatures ($T_{mp}$) of the neat gelators (Figure 3.2). Although this correlation only suggests similar molecular packing within the SAFiNs and neat solid phases of the gelators,\textsuperscript{31} X-ray diffraction data present a more compelling case for this assertion (vide infra). The exceptions may be due to the higher CGC of trans-$9,10$-diol that reduces the fraction of gelator within its SAFiNs.
Figure 3.2 Trends of the melting points of the neat gelators ($T_{mp}$) or of their 5 wt % gels in various liquids ($T_g$) by the falling ball method. $T_{mp}$ of gelators (■), $T_g$ of nitrobenzene gels (▼), and $T_g$ of o-xylene gels (◆). Gelator molecules are sequenced from left to right with increasing melting temperatures. Temperature ranges of vertical bars for $T_g$ refer to when the ball first penetrated the gel surface and when the ball touched the bottom of the tube.

DSC thermograms of neat gelator powders and the corresponding 5 wt % nitrobenzene gels are shown in Figure 3.3. Transition temperature ranges, the transition enthalpies for gelators and the normalized enthalpies for gels are listed in Table 3.2. The melting temperatures from the DSC thermograms ($T_{gm}$) of the fast-cooled gels are the same (within experimental error) as the $T_g$ values from the falling ball method. The correspondence indicates that the critical decrease in mechanical strength of these gels occurs when the networks melt rather than when the “junction zones” (i.e., the intersecting points between gelator strands in a SAFiN) are lost, leaving the fibers basically intact.\textsuperscript{11}
Figure 3.3 DSC thermograms of the 9,12R-diol, trans-9,10-diol and trans-13,14-diol neat powders, and their 5 wt % fast-cooled gels in nitrobenzene.

Table 3.2 Melting temperature (\(T_m, ^\circ C\)), solidification temperature (\(T_c, ^\circ C\)), and enthalpies (\(\Delta H, J/g\)) of neat gelator powders, and melting temperature (\(T_{gm}, ^\circ C\)), formation temperature (\(T_{gc}, ^\circ C\)) and normalized enthalpies (\(\Delta H, J/g\)) of nitrobenzene gels with 5 wt % gelator from DSC thermograms.\(^a\)

<table>
<thead>
<tr>
<th>gelator</th>
<th>neat powders</th>
<th>gels</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>heating</td>
<td>cooling</td>
</tr>
<tr>
<td></td>
<td>(T_m)  (\Delta H)</td>
<td>(T_c)  (\Delta H)</td>
</tr>
<tr>
<td>9,12R-diol</td>
<td>84.7  132</td>
<td>64.0  117</td>
</tr>
<tr>
<td>trans-9,10-diol</td>
<td>138  123</td>
<td>120  121</td>
</tr>
<tr>
<td>trans-13,14-diol</td>
<td>176  50.7</td>
<td>164  46.8</td>
</tr>
</tbody>
</table>

\(^a\) Averages of data from second and third heating and cooling cycles.
3.3.3 Rheological properties

Gels of 9,12R-diol in nitrobenzene were chosen to investigate the role of gelator concentration on the rheological properties. Only concentrations higher than the CGC, 0.6 wt %, were explored. At 1.0, 1.5, 2.0, and 5.0 wt %, $G'$ is higher than $G''$ over large ranges of strain, and both moduli remain almost invariant in the linear viscoelastic regions over the entire ranges of the frequency sweeps (Figure 3.4). This behavior is consistent with the samples being true gels. However, the gels were broken mechanically at distinct yield strains. Furthermore, with an increase in gelator concentration from 1.0 to 2.0 wt %, the yield strain increased while the loss tangent decreased (Figure 3.5). As expected, the mechanical strengths of the 9,12R-diol in nitrobenzene gels increased with increasing gelator concentrations. Although the loss tangent is slightly lower and $G'$ is slightly higher at 5 wt % than at 2 wt %, there is no obvious difference in the yield strains. The similarity of these values at the disparate gelator concentrations can be attributed to both gels being in the “plateau” region, at which the basic structures and interactions of the 3D network do not change considerably. The similarity of the trends for mechanical strength and thermal stability with gelator concentration suggests that the two are related. Before reaching the “plateau” region, the energy needed to melt or break the SAFiN networks (indicated by $T_g$ or yield strain, respectively) increases with increasing gelator concentration.
Figure 3.4 Log-log plots of rheological data for 5, 2, 1.5, and 1 wt % 9,12-\textit{R}-diol in nitrobenzene gels. (a) Strain sweeps (frequency = 1 Hz); (b) angular frequency sweeps (strain = 0.01 %).

Figure 3.5 Yield strain and loss tangent of gels of 9,12-\textit{R}-diol in nitrobenzene as a function of gelator concentration. Vertical bars refer to the standard deviation of data from three measurements.
The previously reported rheological properties of D-12HSA gels at room temperature\textsuperscript{108,109} are used as a comparison to those of 5 wt % gels of 9,12\textit{R}-diol, \textit{trans}-9,10-diol, and \textit{trans}-13,14-diol (Figure 3.6). The gels of 5 wt % 9,12\textit{R}-diol in nitrobenzene are less brittle than those of D-12HSA, as indicated by the greater resistance of the former to break at high strains (Figure 3.1a). The lower value of loss tangent of the gels of 9,12\textit{R}-diol in nitrobenzene (Table 3.3) indicates that the added hydroxyl group at the position \(\gamma\) to the 12-hydroxyl group of D-12HSA improves the mechanical properties of the gel.\textsuperscript{118} Also, the 9,12\textit{R}-diol gels are more stable thermally and their CGCs are lower than those of the corresponding D-12HSA gels in each liquid where a direct comparison is possible (Table 3.1). Thus, adding a second hydroxyl group at a position \(\gamma\) to the initial hydroxyl group of D-12HSA improves gelator efficiency.

The data in Figure 3.6 and Table 3.1 demonstrate that the distance between the two hydroxyl groups affects gelator efficiency. For example, nitrobenzene gels of the \(\gamma\)-diol, 9,12\textit{R}-diol, are mechanically stronger than those of the \(\alpha\)-diol, \textit{trans}-9,10-diol; the former have a higher yield strain and lower loss tangent (Table 3.3), as well as a lower CGC.

As indicated by the loss tangents and yield strains, gels of \textit{trans}-13,14-diol are less mechanically fragile than the those of \textit{trans}-9,10-diol (Table 3.3). As discussed above, \textit{trans}-13,14-diol gelated a larger range of liquids with lower CGCs and higher thermal stabilities than \textit{trans}-9,10-diol. Because the energies needed for mechanically breaking and melting a gel network are related, the trend of the thermal stabilities also infers that the \textit{trans}-13,14-diol gels are stronger mechanically. Both gelators contain two hydroxyl groups that are separated by the same number of carbon atoms and have the same stereochemical orientation. They differ only in the length of their polymethylene chains. The greater London dispersive interactions available to
**trans-13,14-diol** molecules within their SAFiNs appear to be responsible for the differences observed.

![Figure 3.6](image)

**Figure 3.6** Log-log plots of strain sweeps (a: frequency = 1 Hz) and angular frequency sweeps (b: strain = 0.01 %) for 5 wt % gels at 25 °C. D-12HSA (▲, △), 9,12R-diol (★, ☆), **trans-9,10-diol** (▼, ▽) and **trans-13,14-diol** (■, □) in nitrobenzene. *G'* are closed symbols and *G''* are open symbols.

**Table 3.3** *G'*, *G''*, loss tangent (at 0.01 % strain), and yield strain of gels in nitrobenzene.\[^{[a]}\]

<table>
<thead>
<tr>
<th>gelator (5 wt %)</th>
<th><em>G'</em> (Pa)</th>
<th><em>G''</em> (Pa)</th>
<th>loss tangent</th>
<th>yield strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-12HSA</td>
<td>285000±62400</td>
<td>30900±9900</td>
<td>0.11±0.01</td>
<td>5.7±1.6</td>
</tr>
<tr>
<td>9,12R-diol</td>
<td>950±220</td>
<td>90±10</td>
<td>0.09±0.01</td>
<td>78.8±2.0</td>
</tr>
<tr>
<td><strong>trans-9,10-diol</strong></td>
<td>136000±21700</td>
<td>50400±5500</td>
<td>0.37±0.03</td>
<td>29.3±6.2</td>
</tr>
<tr>
<td><strong>trans-13,14-diol</strong></td>
<td>335700±1200</td>
<td>14500±200</td>
<td>0.043±0.001</td>
<td>47.4±3.0</td>
</tr>
</tbody>
</table>

[^{[a]}]: Error limits are based on averages of 3 runs with different aliquots.
3.3.4 **Morphologies from POM and AFM measurements**

The morphologies of gels consisting of 2 wt % of each of the diols in nitrobenzene were investigated by POM. After formation by both the fast- and slow-cooling processes, fibrous SAFiNs were observed (Figure 3.7). As expected, the slow-cooled gels possessed longer fibers than the fast-cooled ones. The degree of super-saturation (and, thus, the thermodynamic driving force for phase separation) during the nucleation and fiber growth processes is smaller during slow cooling, and the frequency of crystallization mismatches, leading to branching and shorter fibers, is reduced in the final SAFiN. Furthermore, both fast- and slow-cooled gels of trans-13,14-diol in nitrobenzene are more translucent and have the smallest objects among the 3 diols for which gels were found, while both fast- and slow-cooled gels of trans-9,10-diol in nitrobenzene are opaque and have the largest objects. However, the objects in all of the POMs appear to be bundles of many fibers.

![Figure 3.7](image_url) **Figure 3.7** POMs of gels consisting of 2 wt % gelator in nitrobenzene: 9,12R-diol (a, d); trans-9,10-diol (b, e); and trans-13,14-diol (c, f) after fast-cooling (a, b, c) or slow-cooling (d, e, f) their solutions/sols to room temperature.
AFM images of the gels were recorded as well (Figure 3.8). Because drying the samples to create xerogels risks changing SAFiN morphology,\textsuperscript{121,250} we have opted to sacrifice some resolution in order to examine the unadulterated gels \textit{in situ}.

Many efforts have been made to optimize parameters used in AFM measurements considering the sticky and brittle nature of the gel samples. Different tips, including NSG03 (0.35-6.1 N/m), NSG10 (3-37 N/m), and NSG30 (22-100 N/m), were tested for the gel samples. Theoretically, tips with higher force constants are more suitable for soft matter since they are less likely to be trapped by the sample.\textsuperscript{237} However, tips with higher force constants may damage the surface features of a sample during scanning. It was found that using NSG10 can lead to an improvement in image quality compared to using NSG03, while NSG30 performs similar to NSG10. In order to get a complete scan of the sample surface with little contamination of the tip, the tip was modified to make it more hydrophobic. Based on the trials with all these tips, hydrophobically modified NSG30 was selected to be the tip for all the dihydroxyl derivative nitrobenzene gels. Ideally, besides tip selection, only three parameters--setpoint, gain, and scan rate--need to be adjusted within the scan process. The setpoint is basically a measure of the force applied by the tip to the sample. In the semi-contact mode used in these experiments, the setpoint shows a certain deflection of the cantilever, which is maintained by the feedback electronics to keep the force constant.\textsuperscript{244} When applying a larger force to the sample, better images could be obtained. However, larger forces lead to more wear on the tip and the sample. The value of gain determines the sensitivity of AFM to sample height variations. If the gain is set too high, AFM becomes sensitive to random noise which can make the system unstable. If the gain is set too low, the AFM will be sluggish and may not catch some feature changes of the surface. The scan rate is normally set to be low in order to decrease the degree of tailing. Fortunately, AFM images
at different regions on the surfaces of each gel samples were successfully recorded after different parameter optimizations. However, attempts to record images of slow-cooled gels were unsuccessful because some of the liquid evaporated during sample preparations.

**Figure 3.8** AFM images at room temperature of fast-cooled gels consisting of 2 wt % gelator in nitrobenzene: (a) **9,12R-diol**; (b) **trans-9,10-diol**; and (c) **trans-13,14-diol**.

**Table 3.4** The average lengths, diameters, and their standard deviations for fibrous objects from fast-cooled 2 wt % gelator in nitrobenzene gels from images recorded by POM and AFM. [a]

<table>
<thead>
<tr>
<th>gelator</th>
<th>length (POM), µm</th>
<th>diameter (POM), µm</th>
<th>diameter (AFM), nm</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>9,12R-diol</strong></td>
<td>4.99±1.44</td>
<td>0.42±0.09</td>
<td>73±9</td>
</tr>
<tr>
<td><strong>trans-9,10-diol</strong></td>
<td>4.93±1.18</td>
<td>0.47±0.12</td>
<td>80±10</td>
</tr>
<tr>
<td><strong>trans-13,14-diol</strong></td>
<td>4.97±1.42</td>
<td>0.28±0.07</td>
<td>54±8</td>
</tr>
</tbody>
</table>

[a] Data from polarizing optical microscopy are based on measurements of at least 30 objects. Data from atomic force microscopy are based on measurements of 10 fibers for gels of **9,12R-diol** and gels of **trans-9,10-diol**, and on 6 fibers for gels of **trans-13,14-diol**.

The fast-cooled nitrobenzene gels examined in Figure 3.8 consist of non-parallel fibrillar objects, some of which appear to be in larger twisted bundles. Although it is clear that the objects
have a range of diameters and lengths (Table 3.4), the resolution of the images is insufficient to conclude whether the narrowest ones are single fibers or smaller bundles of yet smaller fibers. At 2 wt % gelator, the measured diameters of the narrowest fibers are $\sim 73$ nm ($9,12R$-diol), $\sim 80$ nm ($trans$-$9,10$-diol), and $\sim 54$ nm ($trans$-$13,14$-diol). This trend in fiber diameters is also found qualitatively in the objects seen in the POMs.

### 3.3.5 Molecular packing arrangements from PXRD data

PXRD diffractograms of neat gelator powders and fast-cooled 10 wt % gels, both employing the liquids noted in Table 3.5, are compared in Figure 3.9. The lattice spacings ($d$, nm) calculated from the Bragg relationship are collected in Table 3.5, as well. Both a vapor diffusion technique with acetic acid as the good solvent and acetone as the anti-solvent and a slow evaporation technique with methanol and ethanol were attempted to grow single crystals suitable for X-ray diffraction. Unfortunately, these attempts were unsuccessful; difficulties in obtaining diffraction quality single crystals of gelators are common.$^{31}$ However, when a sufficient number of diffraction peaks were collected, cell constants of the neat gelators could be calculated.$^{70}$ for $9,12R$-diol (17 peaks), monoclinic packing ($a=46.8$ Å, $b=4.75$ Å, $c=13.5$ Å); for $trans$-$9,10$-diol (19 peaks), orthorhombic packing ($a=7.51$ Å, $b=48.1$ Å, $c=9.76$ Å); for $cis$-$9,10$-diol (23 peaks), monoclinic packing ($a=7.4$, $b=10.5$, $c=43.4$ Å); for $cis$-$13,14$-diol (23 peaks), orthorhombic packing ($a=52.3$, $b=4.8$, $c=25.7$ Å). Too few diffraction peaks were collected to index with a reasonable degree of confidence the molecular packing of $trans$-$13,14$-diol.
Figure 3.9 PXRD diffractograms at room temperature of (a) neat $9,12R$-dial powder (blue) and its fast-cooled 10 wt % nitrobenzene gel (red); (b) neat $trans-9,10$-dial powder (blue) and its fast-cooled 10 wt % nitrobenzene gel (red); (c) neat $trans-13,14$-dial powder (blue) and its fast-cooled 10 wt % nitrobenzene gel (red); (d) neat $cis-9,10$-dial powder (blue); (e) neat $cis-13,14$-dial powder (blue).
Table 3.5 Calculated lengths of a pair of extended or bent interacting gelator molecules ($2L$, Å)$^{[a]}$ and $d$-spacings (Å) from PXRD peaks (with $2θ < 10°$) of 9,12R-diol, trans-9,10-diol, trans-13,14-diol, cis-9,10-diol, and cis-13,14-diol in their neat powders and of 10 wt % 9,12R-diol, trans-9,10-diol and trans-13,14-diol in fast-cooled nitrobenzene gels.

<table>
<thead>
<tr>
<th>gelator</th>
<th>$2L$, Å</th>
<th>crystallization solvent$^{[b]}$</th>
<th>$d$ (powder), Å</th>
<th>$d$ (gel), Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>9,12R-diol</td>
<td>49.7</td>
<td>chloroform/diethyl ether mixture</td>
<td>46.8, 23.4, 15.4, 10.6, 6.7, 5.8, 4.7, 4.4, 4.2, 3.9, 3.7, 3.4, 3.1, 2.5, 2.3, 2.2</td>
<td>46.8, 15.6, 10.3, 5.8, 4.7, 4.4, 4.2, 3.9</td>
</tr>
<tr>
<td>trans-9,10-diol</td>
<td>49.2</td>
<td>95 % ethanol</td>
<td>48.1, 24.3, 16.0, 12.0, 9.6, 8.0, 6.8, 5.9, 4.8, 4.1, 3.6, 3.0, 2.9, 2.7, 2.5, 2.4, 2.3, 2.0</td>
<td>48.0, 17.2, 12.3, 8.3, 6.8, 4.9, 4.5, 4.2, 3.9, 3.6</td>
</tr>
<tr>
<td>trans-13,14-diol</td>
<td>59.5</td>
<td>95 % ethanol</td>
<td>58.6, 19.2, 14.5, 8.2, 4.6, 3.9, 3.7</td>
<td>57.9, 28.1, 18.8, 14.2, 8.1, 4.4, 3.9</td>
</tr>
<tr>
<td>cis-9,10-diol</td>
<td>44.8</td>
<td>95 % ethanol</td>
<td>43.6, 21.5, 14.2, 10.6, 8.5, 7.0, 6.0, 5.8, 5.2, 4.8, 4.7</td>
<td>/</td>
</tr>
<tr>
<td>cis-13,14-diol</td>
<td>53.9</td>
<td>95 % ethanol</td>
<td>52.4, 26.1, 17.3, 12.9, 10.7, 8.5, 7.3, 6.3, 5.0, 4.7, 4.6</td>
<td>/</td>
</tr>
</tbody>
</table>

$^{[a]}$ Extended (for trans) and bent conformations (for cis) of pairs of gelator molecules (including van der Waals radii of terminal atoms);$^{251}$ see Figure 3.11; geometry optimized by Gaussian using M06/6-31+G(d,p).$^{252}$ $2L$ is shorter than twice the calculated molecular length of single molecules (Figure 3.10) due to H-bonding interactions between terminal carboxylic acid groups. $^{[b]}$ Solvent from which the neat powders were precipitated.
The $d$-spacings of the peaks below 10° in $2\theta$ for $9,12R$-dil and trans-$9,10$-dil follow a progression ratio of 1:1/2:1/3:1/4, which is consistent with a lamellar organization.\textsuperscript{253} The $d$-spacings corresponding to the lowest peaks for trans-$13,14$-dil are 58.6, 19.2, and 14.5 Å, corresponding to ratios of 1:1/3:1/4. The absence of the 1/2 peak may be due to interference phenomena\textsuperscript{254} and to low signal-to-noise ratios in the diffractogram. We assume that the packing of neat trans-$13,14$-dil is lamellar as well. The $d$-spacings of the peaks below 10° in $2\theta$ for cis-$9,10$-dil and cis-$13,14$-dil are also consistent with lamellar organizations.

Geometry optimization by Gaussian using M06/6-31+G(d,p)\textsuperscript{252} was performed and the molecular length of each diol molecule was calculated (Figure 3.10). Except for the cis-diols, all of the lamellae identified from the PXRD study seem to be in bilayers because the thicknesses are approximately equal to the calculated lengths of a pair of extended, interacting molecules (Figure 3.11 and Table 3.5). In the case of $9,12R$-dil, which is in a monoclinic packing arrangement, the long axis may be tilted with respect to the layer plane. A similar bilayered packing arrangement has been reported for racemic D-$12$HSA, for which a single crystal structure is available.\textsuperscript{255} Because the 2\theta values of the diffraction peaks are the same for neat $9,12R$-dil and its SAFiN in nitrobenzene, as are those of trans-$13,14$-dil, molecules in solid and gel fibers have the same packing arrangement.\textsuperscript{70,238} However, the diffractograms of neat trans-$9,10$-dil and its nitrobenzene gel do not have the same 2\theta values, and the diffraction peaks of the gel could not be indexed. Regardless, the $d$-spacing of the peak with the lowest 2\theta value for the nitrobenzene gel of trans-$9,10$-dil does correspond to the calculated length of a pair of interacting extended molecules.

Due to the potential competition between inter- and intra-molecular H-bonding interactions, geometry optimization of the cis-diols results in bent and extended conformations.
(Figure 3.10). Although the calculated layer thicknesses of both cis-diols are less than twice the calculated extended molecular lengths (Table 3.5), they are nearly twice the calculated lengths of the bent conformations shown in Figure 3.11. We suspect that the presence or absence of intra-molecular H-bonding is an important factor in determining molecule conformation and packing within the assemblies. As shown by the Newman projections in Figure 3.11, the trans-diols can pack in extended conformations, regardless of whether inter- or intra-molecular H-bonding interactions (or a combination of the two) is dominant, while intra-molecular H-bonding forces the cis-diol isomers into bent conformations. If, as we suspect, molecular packing arrangements of the gelators within their fibers are strongly dependent upon conformations conducive to the formation of extended inter-molecular H-bonding networks along the alkyl chains, the observed greater gelating efficiencies of the trans-diols than their cis-isomers can be attributed to their propensities to undergo inter- or intra-molecular H-bonding interactions.
Figure 3.10 Molecular structures of the gelators and their calculated molecular lengths (including van der Waals radii of terminal atoms) after geometry optimization by Gaussian using M06/6-31+G(d,p) visualizing by Avogadro: (a) **9,12R-diol**, 25.5 Å; (b) **trans-9,10-diol**, 25.3 Å; (c) **trans-13,14-diol**, 30.8 Å; (d) **cis-9,10-diol** (extended), 25.5 Å; (e) **cis-13,14-diol** (extended), 30.5 Å; (f) **cis-9,10-diol** (bent), 23.0 Å; (g) **cis-13,14-diol** (bent), 27.5 Å.
Figure 3.11 Proposed interacting arrangements of pairs of gelator molecules in their assemblies, from geometry optimization by Gaussian using M06/6-31+G(d,p)\textsuperscript{[38]} and visualized by Avogadro.\textsuperscript{[39]} (a) 9,12\textit{R}-diol; (b) \textit{trans}-9,10-diol; (c) \textit{trans}-13,14-diol; (d) \textit{cis}-9,10-diol; (e) \textit{cis}-13,14-diol. Only one enantiomer or diastereomer is shown.

The calculated packing arrangements in Figure 3.11, although only for pairs of molecules, indicate crudely what bilayer packing might entail. As noted in Table 3.1, the \textit{trans}-forms of the racemic 9,10-diols and 13,14-diols favor fiber formation, while those of the corresponding \textit{cis}-diols do not. Previously, it was found that DL-\textit{erythro}-dihydrosphingosine forms needle-like crystals from 62.5 \% methanol in water solutions, while DL-\textit{threo}-dihydrosphingosine yields platelets;\textsuperscript{256} dihydrosphingosine consists of an octadecyl chain in which the head group contains one amino and two hydroxyl groups. Those results and the energy-minimized models suggest
that divergent orientations of the two-hydroxyl groups profoundly influence both the modes of inter-molecular interactions and the packing arrangements. However, deeper insights into why the trans- and cis-diols in our study lead to very different gelation behaviors cannot be discerned from calculations on pairs of molecules alone. The packing models shown in Figures 3.12, 3.13 and 3.14, are based on allowing units in Figure 3.11, including their enantiomers, to interact while maximizing H-bonding interactions along the chains. For both the trans- and cis-diols, the presence of inter-molecular H-bonding interactions is predicted. In the trans-diols, two inter-molecular hydroxyl H-bonds per molecule can be made along the axis orthogonal to the long molecular axis (promoting stabilization of fibrillar structures). However, the cis-diols are able to utilize only one hydroxyl group per molecule to construct a secondary H-bonding network that is limited to pairs of molecules. The other two hydroxyl groups appear to contribute to intra-molecular H-bonding interactions. These models, although simple, may explain why the trans-diols are able to effect gelation and the cis-diols are not. The actual aggregates are much more complex; our calculations may not include a sufficient number of molecules to discern other factors responsible for the gelation differences and the role of the liquid in the critical steps leading to aggregation and nucleation are not considered.
Figure 3.12 Possible cis-9,10-diol and trans-9,10-diol packing modes. Inter-molecular H-bond interactions are noted in the green rectangles. Packing of molecules is shown in a top view (2D) projection.

Figure 3.13 Proposed dense packing arrangements of six geometry optimized (by Gaussian using M06/6-31+G(d,p)) cis-9,10-diol or trans-9,10-diol molecules visualized by Avogadro. The packing arrangement of molecules is shown in a side view projection. Inter-molecular H-bond interactions are noted in green boxes. Hydrogen atoms of C-H bonds are not shown to make the H-bond clearer.
Figure 3.14 Proposed dense packing arrangements of six geometry-optimized (by Gaussian using M06/6-31+G(d,p))\textsuperscript{252} \textit{cis-9,10-diol} or \textit{trans-9,10-diol} molecules visualized by Avogadro.\textsuperscript{257} The packing arrangement of molecules is shown in a top view projection. Intermolecular H-bond interactions are noted in green boxes.

3.3.6 \textit{H-bonding interaction assignments from FT-IR}

FT-IR was used to probe the type of H-bonding within the neat solid (Figure 3.16 c) and SAFiN phases (Figures 3.15 and 3.16 a, b) of the gelators. The peaks at 1700 cm$^{-1}$ are ascribed to cyclic dimers of carboxylic acid head groups.\textsuperscript{75} In the nitrobenzene gels of \textit{trans-9,10-diol} and \textit{trans-13,14-diol}, this region was obscured even after empirical subtraction of peaks from the
liquid portion. Regardless, the data indicate that the carboxylic acid head groups in the solid and gel states prefer to exist as inter-molecular cyclic dimers. The FT-IR spectra of both the solid and gel phases of $9,12$-$R$-dil (consisting of a 9:1 ratio of diastereomers) is the only gelator of the ones examined here that also displays a weak shoulder at $\sim 1720$ cm$^{-1}$, attributable to acyclic dimers of the carboxylic acid groups. However, fibers (instead of platelets, found when acyclic dimers predominate) are still present in the AFM and POM images of the gels (Figures 3.7 and 3.8).

Figure 3.15 FT-IR spectra of (a) gels of 5 wt % $9,12$-$R$-dil (blue), D-12HSA (black) in nitrobenzene and neat nitrobenzene (red); (b) gels of 5 wt % $trans$-$9,10$-dil (black) and $trans$-$13,14$-dil (red) in nitrobenzene without subtraction of the liquids.
Figure 3.16 FT-IR spectra of (a) nitrobenzene gels with 5 wt % 9,12\textit{R}-diol (black) and D-12HSA (red); (b) nitrobenzene gel with 5 wt % \textit{trans}-9,10-diol (red) and \textit{trans}-13,14-diol (black); (c) neat solid 9,12\textit{R}-diol, D-12HSA, \textit{cis}-13,14-diol, \textit{cis}-9,10-diol, \textit{trans}-9,10-diol, and \textit{trans}-13,14-diol (from top to bottom). The peaks from nitrobenzene in the gel spectra have been subtracted empirically.

In both the solid and gel states of all gelators, there is no evidence for free hydroxyl groups: only peaks at 3150-3400 cm\textsuperscript{-1} and none at \textasciitilde 3600 cm\textsuperscript{-1} could be detected.\textsuperscript{114} There is no discernible frequency difference between the broad OH stretching bands in the spectra of neat D-12HSA and 9,12\textit{R}-diol or their nitrobenzene gels. However, these vibrational bands are
composed of contributions from gelator molecules in different H-bonded environments. In the neat solid state of D-12HSA, the band at ~3296 cm$^{-1}$ is stronger than that at ~3235 cm$^{-1}$; the opposite band intensity contributions are found in the solid spectra of 9,12R-diol. The relative difference in the contributions implies that the H-bonding in the 9,12R-diol solid state is stronger than that of D-12HSA. Based on FT-IR spectra, the same conclusion is reached for the comparative hydroxyl H-bonding strengths in the nitrobenzene gels of 9,12R-diol and D-12HSA. The similarities between the frequencies of the OH stretching (as well as the similarities in the PXRD diffraction patterns) (Figure 3.16 and Table 3.5) strongly suggest that the molecular packing within a SAFiN and the corresponding neat gelator are very similar.

PXRD results for the solid assemblies of 9,12R-diol demonstrate that the hydroxyl groups are incapable of interacting intra-molecularly because the molecules are in extended conformations. The two hydroxyl groups will form a seven-membered ring, which is entropically unfavorable, via intra-molecular H-bonding. Thus, the intra-molecular H-bonding is instable and inter-molecular H-bonding plays the dominant role. Therefore, the FT-IR data are interpreted on the basis of inter-molecular hydroxyl H-bonding interactions. Such H-bonding may be responsible for the SAFiN network of 9,12R-diol being more robust than those of D-12HSA in the same liquid at equal gelator concentrations: stronger inter-molecular hydroxyl H-bonding interactions between 9,12R-diol molecules would increase the energy required to melt or mechanically break the SAFiN network.

At least in their neat solids states, the frequencies of both of the non-gelating cis-diols, cis-9,10-diol and cis-13,14-diol, are much lower (~3250 cm$^{-1}$) than those of the trans-isomers. The lower frequencies are attributed to stronger intra-molecular H-bonding, as indicated by the packing model discussed in Figure 3.12, where the prediction is that the trans-diols are more
involved in inter-molecular H-bonding. Our hypothesis is that stronger (intra-molecular) H-bonding interactions impede the aggregation modes that lead to SAFiNs, but help nucleation and growth of 3D solids that lead to precipitate).  

Intra-molecular interactions are possible in assemblies of trans-9,10-diol and, if present, they would reduce inter-molecular H-bonding interactions and impede the formation of SAFiNs. For both neat trans-9,10-diol and its gels, the frequency at maximum intensity of the OH stretch is higher than those of D-12HSA and 9,12R-diol; we suggest that inter-molecular H-bonding interactions in the trans-9,10-diol solid and gel states are weaker. The models suggested by the combination of FT-IR and PXRD data would explain why the trans-9,10-diol gels are weaker than those of D-12HSA and 9,12R-diol in the same liquid at equal gelator concentrations and have thicker fibers in the nitrobenzene gels (Figures 3.7 and 3.8).

3.3.7 Gelation and Hansen Space

Besides interactions between gelator molecules, liquid-diol structural interactions must also be considered when discussing the nucleation and growth processes leading to fibers. In that regard, attempts to correlate the \( E_T(30) \) scale and systems involving 9,12R-diol, trans-9,10-diol, and trans-13,14-diol were unsuccessful (Figure 3.17). The inability of \( E_T(30) \) to predict the formation of gels within the diol gelators implies that bulk polarity is an insufficient criterion to judge when a gel will or will not be formed; specific liquid-gelator interactions at the molecular level must be considered as well.
Table 3.6 HSPs (MPa$^{0.5}$) of liquids examined and appearances of 5 wt% 9,12R-diol, trans-9,10-diol and trans-13,14-diol in various liquids after preparation by the fast-cooling process.$^\text{[a]}$

<table>
<thead>
<tr>
<th>liquid</th>
<th>$\delta_p$ $^{[a]}$</th>
<th>$\delta_h$ $^{[a]}$</th>
<th>$\delta_d$ $^{[a]}$</th>
<th>$\delta$</th>
<th>9,12R-diol</th>
<th>trans-9,10-diol</th>
<th>trans-13,14-diol</th>
</tr>
</thead>
<tbody>
<tr>
<td>dimethyl sulfoxide (DMSO)</td>
<td>16.4</td>
<td>10.2</td>
<td>18.4</td>
<td>26.7</td>
<td>S</td>
<td>P</td>
<td>P</td>
</tr>
<tr>
<td>dimethylformamide (DMF)</td>
<td>13.7</td>
<td>11.3</td>
<td>17.4</td>
<td>24.9</td>
<td>S</td>
<td>P</td>
<td>S</td>
</tr>
<tr>
<td>acetone (ACT)</td>
<td>10.4</td>
<td>7.0</td>
<td>15.5</td>
<td>19.9</td>
<td>P</td>
<td>P</td>
<td>P</td>
</tr>
<tr>
<td>toluene (TOL)</td>
<td>1.4</td>
<td>2.0</td>
<td>18.0</td>
<td>18.2</td>
<td>G</td>
<td>G</td>
<td>P</td>
</tr>
<tr>
<td>CCl$_4$ (CTC)</td>
<td>0.0</td>
<td>0.6</td>
<td>17.8</td>
<td>17.8</td>
<td>G</td>
<td>P</td>
<td>P</td>
</tr>
<tr>
<td>ethyl acetate (EAC)</td>
<td>5.3</td>
<td>7.2</td>
<td>15.8</td>
<td>18.2</td>
<td>P</td>
<td>P</td>
<td>P</td>
</tr>
<tr>
<td>CH$_2$Cl$_2$ (DCM)</td>
<td>6.3</td>
<td>6.1</td>
<td>18.2</td>
<td>20.2</td>
<td>G</td>
<td>P</td>
<td>P</td>
</tr>
<tr>
<td>CHCl$_3$ (CHF)</td>
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<td>5.7</td>
<td>17.8</td>
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<td>G</td>
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<td>ethanol (EOH)</td>
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<td>15.8</td>
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<td>S</td>
<td>S</td>
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<tr>
<td>1-octanol (OOH)</td>
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<td>11.9</td>
<td>17.0</td>
<td>21.0</td>
<td>S</td>
<td>G</td>
<td>P</td>
</tr>
<tr>
<td>acetonitrile (ATN)</td>
<td>18</td>
<td>6.1</td>
<td>15.3</td>
<td>24.4</td>
<td>P</td>
<td>P</td>
<td>P</td>
</tr>
<tr>
<td>chlorobenzene (CHB)</td>
<td>4.3</td>
<td>2.0</td>
<td>19.0</td>
<td>19.6</td>
<td>G</td>
<td>G</td>
<td>G</td>
</tr>
<tr>
<td>Liquid</td>
<td>$\delta_p$ $^a$</td>
<td>$\delta_h$ $^a$</td>
<td>$\delta_d$ $^a$</td>
<td>$\delta$</td>
<td>9,12$R$-dol</td>
<td>trans-9,10-diol</td>
<td>trans-13,14-diol</td>
</tr>
<tr>
<td>------------------------------</td>
<td>-----------------</td>
<td>-----------------</td>
<td>-----------------</td>
<td>----------</td>
<td>--------------</td>
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<td>-----------------</td>
</tr>
<tr>
<td>nitrobenzene (NTB)</td>
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<td>4.1</td>
<td>20.0</td>
<td>22.2</td>
<td>G</td>
<td>G</td>
<td>G</td>
</tr>
<tr>
<td>benzonitrile (BZN)</td>
<td>9.0</td>
<td>3.3</td>
<td>17.4</td>
<td>19.9</td>
<td>G</td>
<td>G</td>
<td>G</td>
</tr>
<tr>
<td>$n$-butylbenzene (BBN)</td>
<td>0.1</td>
<td>1.1</td>
<td>17.4</td>
<td>17.4</td>
<td>G</td>
<td>G</td>
<td>G</td>
</tr>
<tr>
<td>$p$-xylene (PXL)</td>
<td>1.0</td>
<td>3.1</td>
<td>17.6</td>
<td>17.9</td>
<td>G</td>
<td>P</td>
<td>G</td>
</tr>
<tr>
<td>$o$-xylene (OXL)</td>
<td>1.0</td>
<td>3.1</td>
<td>17.8</td>
<td>18.1</td>
<td>G</td>
<td>G</td>
<td>G</td>
</tr>
<tr>
<td>$m$-xylene (MXL)</td>
<td>1.0</td>
<td>3.1</td>
<td>17.4</td>
<td>17.7</td>
<td>G</td>
<td>G</td>
<td>G</td>
</tr>
<tr>
<td>octane (OCT)</td>
<td>0.0</td>
<td>0.0</td>
<td>15.5</td>
<td>15.5</td>
<td>P</td>
<td>P</td>
<td>P</td>
</tr>
<tr>
<td>dodecane (DOD)</td>
<td>0.0</td>
<td>0.0</td>
<td>16.0</td>
<td>16.0</td>
<td>P</td>
<td>P</td>
<td>P</td>
</tr>
<tr>
<td>decane (DCN)</td>
<td>0.0</td>
<td>0.0</td>
<td>15.7</td>
<td>15.7</td>
<td>P</td>
<td>P</td>
<td>P</td>
</tr>
<tr>
<td>hexanes (HXN)</td>
<td>0.0</td>
<td>0.0</td>
<td>14.4</td>
<td>14.4</td>
<td>P</td>
<td>P</td>
<td>P</td>
</tr>
<tr>
<td>methyl salicylate (MS)</td>
<td>8.0</td>
<td>12.3</td>
<td>16.0</td>
<td>21.7</td>
<td>G</td>
<td>P</td>
<td>G</td>
</tr>
<tr>
<td>hexamethylphosphoramide (HMP)</td>
<td>8.6</td>
<td>11.3</td>
<td>18.5</td>
<td>23.3</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>$N,N$-dimethylacetamide (NDM)</td>
<td>11.5</td>
<td>10.2</td>
<td>16.8</td>
<td>22.8</td>
<td>S</td>
<td>G</td>
<td>G</td>
</tr>
<tr>
<td>methyl-2-pyrroldone (MP)</td>
<td>12.3</td>
<td>7.2</td>
<td>18.0</td>
<td>23.0</td>
<td>S</td>
<td>G</td>
<td>G</td>
</tr>
</tbody>
</table>

$^a$ HSPs for the neat liquids were taken from the literature.\textsuperscript{86}
Figure 3.17 $E_T(30)$ values of the studied liquids on the gelation behaviors of 9,12R-diol, trans-9,10-diol, and trans-13,14-diol. Gels (●), precipitates (■), solutions (▲). Some points are offset horizontally to make them distinguishable.

Thus, our efforts turned to possible correlations between gelation properties and HSPs (Table 3.6).\textsuperscript{73,75,76} The construction of concentric solvent spheres here, using the three parameters as axes, is based upon data with more than 20 liquids covering a wide range of polarities. Hansen Space can provide an initial hypothesis on the selection of neat solvents for gelation studies.\textsuperscript{75} However, attempts to generate concentric spheres in this way from 9,12R-diol systems were unsuccessful, probably because the points are localized in a small portion of each of the gel and precipitate spheres (Figure 3.18). In this case, the concentric sphere approach provides neither a good representation of the range of liquids that the gelator is (and is not) able to gelate nor the locations of the sphere centers. Also, there are only 3 and 4 solution data points for trans-9,10-diol and trans-13,14-diol, respectively; therefore, it is not possible to build creditable solution
spheres for them either, and it is not known whether their centers match those of the gel spheres.

Figure 3.18 Hansen Space using the concentric spheres fitting method for 9,12R-diol in 5 wt % samples prepared by the fast-cooling process. Soluble sphere (blue), gel sphere (green), and precipitated sphere (red). Note that the data are plotted as $2\delta_d$ as recommended by Hansen. See Table 3.6 for abbreviations.

For these reasons, the ‘discrete-spheres’ approach was adopted (Figures 3.19, 3.20 and 3.21). The group-contribution method, presumably a significantly better measure of the true sphere center for each gelator, was also used to calculate the HSPs of the gelators (Table 3.7). However, as described in Section 1.1.6, the group-contribution method does not distinguish
among stereo and positional isomers, although some isomers are known to be much better or worse gelators than others. The effects of this limitation are demonstrated by the very different gelation behaviors of the positional isomers, \textit{trans-9,10-diol}, \textit{cis-9,10-diol}, and \textit{9,12R-diol}, whose HSPs are calculated to be the same according to the group-contribution method; for this reason, the HSPs from the experimental data and from the group-contribution method are quite different. Both the empirically and group-calculated HSPs should be used judiciously; each has its limitations. Based upon the empirically calculated HSPs, $\delta_p$ of \textit{trans-9,10-diol} is larger than that of \textit{9,12R-diol} or \textit{trans-13,14-diol}. This observation implies (as expected) that the $\alpha$-diol with a shorter alkyl chain is more polar than the $\alpha$-diol with a longer chain or the $\gamma$-diol.

Table 3.7 Individual HSPs (MPa$^{0.5}$) for gelators from the ‘discrete-sphere-fitting’ approach to the experimental data and from the group-contribution method.

<table>
<thead>
<tr>
<th>gelator</th>
<th>discrete-sphere-fitting</th>
<th>group-contribution method</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\delta_p$</td>
<td>$\delta_h$</td>
</tr>
<tr>
<td>9,12R-diol</td>
<td>2.4</td>
<td>4.7</td>
</tr>
<tr>
<td>\textit{trans-9,10-diol}</td>
<td>6.1</td>
<td>4.9</td>
</tr>
<tr>
<td>\textit{trans-13,14-diol}</td>
<td>4.3</td>
<td>3.2</td>
</tr>
</tbody>
</table>
Figure 3.19 Hansen Space using the discrete-spheres-fitting method for 9,12R-diol in samples prepared by the fast-cooling process. Solution sphere (blue), gel sphere (green), and precipitates sphere (red). The acronyms for the different liquids are defined in Table 3.1. Note that the data are plotted as $2\delta_d$ as recommended by Hansen. See Table 3.6 for abbreviations.
Figure 3.20 Hansen Space using the discrete spheres fitting method for *trans-9,10-diol* in 5 wt % samples prepared by the fast-cooling process. Solution points (blue points), gel sphere (blue sphere), and precipitates sphere (green sphere). Note that the data are plotted as $2\delta_d$ as recommended by Hansen.\textsuperscript{86} See Table 3.6 for abbreviations.
Figure 3.21 Hansen Space using the discrete spheres fitting method for \textit{trans-13,14-diol} in 5 wt \% samples prepared by the fast-cooling process. Solution points (blue points), gel sphere (blue sphere), and precipitates sphere (green sphere). Note that the data are plotted as $2\delta_d$ as recommended by Hansen.\textsuperscript{86} See Table 3.6 for abbreviations.

As shown from the discrete-spheres-fitting approach (Figure 3.19), the solution sphere of \textit{9,12R-diol} is well separated from the gel and precipitate spheres. Only the gel and precipitate spheres were plotted for \textit{trans-9,10-diol} and \textit{trans-13,14-diol}. Although only liquids whose HSPs are inside the gel sphere should form a gel, there is a significant overlap between the gel and precipitate spheres for the three diols. Because both the gelation and precipitation processes involve aggregation, the overlap of their spheres can be reconciled more easily if the precipitated objects inside the intersection region are needle-like (i.e., similar in form to the fibers of the
SAFiNs). The precipitated mixtures containing 5 wt % 9,12R-diol in ethyl acetate, decane, or dodecane are points inside the intersection region of the gelation and precipitate spheres, while those in acetone, octane, hexane or acetonitrile lie outside of the intersection region. POM images of these precipitates (Figure 3.22a) in ethyl acetate show spherulitic objects. Although dodecane and decane are not gelated, the 9,12R-diol aggregates are rod-like. It was not possible to record the shapes of the precipitates from trans-9,10-diol and trans-13,14-diol in some of the liquids with boiling points much lower than the melting points of the gelators. Mixtures at 5 wt % concentrations had to be heated to temperatures near the melting points of these gelators in order to dissolve them completely. Regardless, in all these intersection cases investigated for all three diols (Figure 3.23), elongated objects are present. However, the interaction between the objects must be too weak to form a SAFiN capable of immobilizing macroscopically the liquid components. Equally important, there are no apparent elongated objects in the precipitated mixtures whose data points lie outside the intersection region (Figures 3.22 and 3.23). Therefore, Hansen Space can provide a qualitative prediction of in which liquids one of the gelators examined here will or will not form elongated objects.
Figure 3.22 POMs of fast-cooled mixtures: 5 wt % 9,12R-diol in ethyl acetate (a) and in acetone (b); 5 wt % trans-9,10-diol in p-xylene (c) and in methyl salicylate (d); 5 wt % trans-13,14-diol in decane (e) and in DMSO (f).

Figure 3.23 POMs of fast-cooled 5 wt % 9,12R-diol in dodecane (a), decane (b), octane (d), hexane (e), and acetonitrile (f) and of 5 wt % trans-13,14-diol in 1-octanol (c).
Correlations between HSPs of the liquids and the CGCs of 9,12R-diol are shown in Figure 3.24. Although the CGCs decrease roughly with an increase in $\delta_p$, $\delta_h$, and overall $\delta$ of the gelated liquids (indicating that the effectiveness of this gelator is enhanced as polar and H-bonding interactions increase), there is no clear correlation between the CGCs and the dispersive component, $\delta_d$. A similar trend between increasing values of $\delta_p$, $\delta_h$, and overall $\delta$ of the gelated liquids and decreasing CGC values was found for trans-9,10-diol (Figure 3.25). However, the CGCs of trans-13,14-diol gels increase with increasing $\delta_p$, $\delta_h$, and overall $\delta$ of the gelated liquids (Figure 3.26); the gelation efficiency decreases in liquids with more polar and H-bonding interactions. We hypothesize that in liquids with more polar and H-bonding interactions, the enhanced interaction between the gelator and the liquid causes a higher driving force for solvation than for aggregation, which, in turn, leads to less effective gelating ability.
Figure 3.24 CGCs of 9,12R-diol after preparation by the fast-cooling process in organic liquids as a function of (a) $\delta_p$, (b) $\delta_h$, (c) $\delta_d$, and (d) overall $\delta$ in Hansen Space.
Figure 3.25 CGCs of trans-9,10-diol in organic liquids after preparation by the fast-cooling process as a function of (a) $\delta_p$, (b) $\delta_h$, (c) $\delta_d$, and (d) overall $\delta$ in Hansen Space.

Figure 3.26 CGCs of trans-13,14-diol in organic liquids after preparation by the fast-cooling process as a function of (a) $\delta_p$, (b) $\delta_h$, (c) $\delta_d$, and (d) overall $\delta$ in Hansen Space.
3.4 Conclusions

Quantitative correlations between structural features of hydroxylated derivatives of long-chain, naturally-occurring fatty acids and their efficiency of their gelation have been demonstrated. The results lead to the conclusions that diol stereochemistry, the number of carbon atoms separating the two hydroxyl groups, and the length of the alkanoic chains are the most important structural parameters controlling efficiency of gel formation for this class of gelators. The $\gamma$-diol, 9,12R-diol, in which the two hydroxyl groups are separated by two methylene units along the chain, is found to form thermally more stable and mechanically stronger gels than those of D-12HSA, except in low polarity liquids like alkanes. Due to the extended conformation of 9,12R-diol in its SAFiNs, inter-molecular H-bonding is more extensive than with the mono-hydroxyl gelator, D-12HSA.

Fiber formation by $\alpha$-diols is more complicated by the stereochemical relationship between the two hydroxyl groups; their proximity allows the possibility of both inter- and intramolecular H-bonding, even when the alkyl chains are fully extended. However, our modeling studies indicate that inter-molecular H-bonding networks are more favored by the trans-diols than by the cis-diols. The latter can aggregate in motifs with more intra-molecular H-bonding interactions and less extensive inter-molecular H-bonding networks. We hypothesize that intra-molecular H-bonding interactions enhance the probability of growth of 3D crystallites (i.e., leading to precipitates). The dependence of diol stereochemistry on the ability of aggregates to grow into fibrillar objects observed here begs further investigation in order to ascertain the degree of generality. It will require results from gelation tests that employ enantio-pure compounds. Although fiber formation is favored by the trans-diols, the presence of intra-
molecular H-bonding interactions and the lower overall strength of those interactions result in lower gelator efficiencies for the γ-diol or even the mono-ol, D-12HSA.

In addition, elongating the alkyl chain length of the gelators (without disturbing the carboxylic dimer head-group interactions) leads to an improvement in the physical properties of the gels. Thus, trans-13,14-diol is a more efficient gelator than trans-9,10-diol. Increasing the number of methylene units leads to the greater London dispersion interactions within the fully formed SAFiNs, and greater driving force for aggregation. Elongation of the alkyl chain is also considered to be responsible for the greater gelating efficiency of trans-13,14-diol than that of D-12HSA based on the physical properties of the corresponding gels, despite the presence of intra-molecular H-bonding interactions in trans-13,14-diol. Also, the relationships between the gelation behaviors of the diols and their HSPs indicate that polar and H-bonding interactions between the gelator molecules and the liquid components are important. Those interactions must be manifested during the transformations of the sol phases to their gels or precipitates (i.e., during the nucleation and growth stages of the gelator aggregates) as well as after the gels or precipitates are formed.

The comparisons and correlations here have focused on gelators with substituent hydroxyl groups, long flexible chains, and carboxylic acid head groups. They are easily synthesized from naturally occurring molecules. The results demonstrate how the efficiency of gelation can be modulated by very small structural changes. These results also suggest how other structural modifications may be exploited to create very efficient gelators from other naturally occurring molecules based upon the observed relationships between hydroxyl group interactions and the modes of self-assembly in a wide range of liquids. Clearly, similar studies in which
different functional groups at different positions are appended to long alkyl chains of these and other naturally occurring molecules would yield additional insights and interesting gelators.
4 MECHANO-RESPONSIVE, THERMAL-REVERSIBLE, LUMINESCENT ORGANOGELS DERIVED FROM A LONG-CHAIN, NATURALLY-OCCURRING FATTY ACID

4.1 Introduction

As mentioned in Chapter 1, the reversible formation of SAFiNs can lead to significant changes in physical properties of the materials. Specifically, in some organogels that contain a luminogen, the formation of SAFiNs has provided attractive routes for the construction of AIE materials.\(^\text{204,205}\) However, few studies involve fatty acid gelators with luminogen groups to achieve and control the AIE activity of gels.

10-Oxooctadecanoic acid (10-KSA), a mono-keto derivative of stearic acid (SA), has been reported to be a more efficient gelator than SA as a result of its added ability to initiate inter-molecular keto-keto dipolar interactions along the polymethylene chain.\(^\text{261}\) Here, an even better gelator with an \(\alpha\)-diketo group along the polymethylene backbone of SA, 9,10-dioxooctadecanoic acid (DODA), is reported. In addition, the gelating ability of the methyl ester of DODA, 9,10-dioxooctadecanoic acid methyl ester (DODE), has been used to assess the influence of the loss of the terminal H-bonding site on gelator efficiency. Our rationale for introducing an \(\alpha\)-diketo group is based on two principal considerations: (1) the second keto group (N. B., 10-KSA) produces an additional dipole-dipole interaction; (2) because the \(\alpha\)-diketo group fluoresces and phosphoresces in solution at room temperature, it affords a tool to design AIE materials and to explore subtle changes in the DODA environment as the sols are transformed into gels (and vice versa).\(^\text{262}\) The information gleaned cannot be duplicated by any of the other analogues of the SA family produced to date.

Surprisingly, some DODA-based gels also exhibit reversible mechano-responsive
properties, a characteristic rare in molecular gels with crystalline SAFiNs.\textsuperscript{64} DODA is the simplest gelator, of which we are aware, that exhibits reversible changes in emission wavelength and mechanical strength induced both thermally and mechanically. As such, it is a very attractive model for gaining insights into the design requirement for constructing other mechano-responsive, thermal-reversible luminescent soft materials. The work described in this chapter has been published in Zhang \textit{et al.}\textsuperscript{263}

\begin{center}
\textbf{Scheme 4.1} Structures of gelators derived from SA and OA.
\end{center}
4.2 Experimental Section

4.2.1 Materials

Methyl oleate (Hormel Institute, >99 %), acetic anhydride (Fisher Scientific, certified), potassium permanganate (Fisher Scientific, certified), sulfuric acid (Mallinckrodt Chemical, 95\%-98 %), acetic acid (glacial, Fisher Scientific, certified ACS), sodium bisulfate (Fisher Scientific, certified), sodium bicarbonate (Sigma Aldrich, >99.5 %), sodium chloride (Sigma Aldrich, >99 %), and sodium sulfate (anhydrous, Fisher Scientific, certified) were used as received. All solvents and other chemicals used for syntheses and gelation studies are listed in Chapter 2.

4.2.2 Instrumentation and sample preparation

4.2.2.1 TEM

The TEM images were obtained on an EM400 transmission electron microscope (Phillips Research Laboratories) at 120 kV. The samples were prepared by three different methods. First, one drop of 0.5 wt % sols was directly placed on blank copper grids (600 mesh, Electron Microscopy Science). Second, the 5 wt % gels were dispersed on the surface of an immiscible liquid, water, and the grid was used to pick up the aggregates. The last method was to spin cast the 5 wt % hot sol on a Si wafer by a WS-650MZ-23NPDB spin coater (Laurell Technologies Corporation). Spin rates from 1000 to 3000 rotations per minute (rpm) were used. A thin layer of carbon (tens of nanometers) was deposited onto the spin-cast film. The thickness of the carbon layer was measured by a spectroscopic ellipsometer (M-2000 series, by J.A. Woollam Co.). A poly(acrylic acid) (PAA) aqueous solution was then drop-cast on top of the carbon-coated film and heated overnight at 55 °C. The dried PAA flake came off the substrate spontaneously or with
little prying, taking along the spin-cast film underneath. The delaminated film was floated on water for ca. 3 h (until PAA was completely dissolved), and then picked up with a blank TEM copper grid.

4.2.2.2 Single crystal X-ray diffraction

Single crystal X-ray diffraction data were collected at 137 K using an Oxford Cryosystems 700 Cryostream and a Bruker APEX II Duo diffractometer equipped with an APEX II CCD detector (Bruker-AXS) and Mo Kα radiation (0.71073 Å). A single crystal of DODA was grown by slow evaporation of a solution in dichloromethane at room temperature. Cell refinement and reduction of the diffraction data were conducted by the SAINT program (Bruker-AXS). The structure was solved by direct methods and refined using SHELXS-97. Non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were placed in calculated positions and refined using a riding model. The molecular graphic was generated by X-SEED. CCDC deposition number 1440666 contains the supplementary crystallographic data for the single crystal structure. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

4.2.2.3 Absorption, emission, and excitation

UV-Vis absorption spectra were obtained on a Varian UV-visible (Cary 300 Bio) spectrophotometer in 1×1cm quartz cuvettes. Steady-state excitation and emission spectra and emission spectra for kinetic measurements were recorded on a Photon Technology International Fluorometer (SYS 2459) with Felix 32 software for data analysis, a 150 W high-pressure xenon lamp, a Quantumwest Peltier temperature controller, and an Omega temperature probe. Emission spectra were recorded in the front-face mode at an angle of ∼45° with respect to the incident beam in flame-sealed, flattened glass capillaries (Vitro Dynamics) for solution samples (4 mm
thick) and gel samples (0.4 mm thick) with and without degassing (5 freeze (liquid nitrogen)-
pump (0.12 torr)-thaw cycles). The gel samples for kinetic measurements were heated to their sol
phase in a boiling water bath and then transferred rapidly to a decane bath in the sample cell of
the fluorimeter that had been equilibrated at a preset temperature below $T_g$. The emission
intensities at 458 nm ($\lambda_{ex}$ 400 nm) were recorded immediately as a function of time at a rate of 2
data points per second. The neat solid samples of DODA—the solidified melt (prepared by
submerging the sealed capillaries of the hot melt in an ice-water bath) and DODA powder—were
flame-sealed in 0.4 mm thick capillaries without degassing.

4.2.2.4 DLS and SLS

DLS and SLS studies were carried out on a LS Instruments 3D LS spectrometer. 3D cross
correlation technology was used to eliminate the contributions of multiple scattering. DODA was
firstly dissolved in dichloromethane and the solution was passed 3 times through a 200 nm
polytetrafluoroethylene syringe filter into a 10 mm glass tube. The solvent was evaporated under
a gentle stream of nitrogen flush and the solid, covered loosely with a layer of Parafilm®, was
further dried in a vacuum oven (20 mmHg) for 1 h. Carbon tetrachloride was passed 3 times
through a 200 nm polytetrafluoroethylene syringe filter into the glass tube to form a mixture at a
given concentration. The measurements were conducted after incubating a hot sol (heated to 60
°C) at a given temperature (55 ºC or 25 ºC) for 1h. The viscosities of carbon tetrachloride at 55
°C and 25 ºC are 0.612 cP and 0.901 cP, respectively. The refractive indexes of carbon
tetrachloride at 55 ºC and 25 ºC are 1.44 and 1.46, respectively.

4.2.2.5 Viscoelastic recovery studies

Rheo-mechanical experiments were performed on an Anton Paar-Physica MCR 302
strain-controlled rheometer using Peltier temperature-controlled parallel plates (25 mm diameter)
at a gap of 0.5 mm. Data were collected using Rheoplus/32 Service V3.10 software. Samples were heated between the rheometer plates to 80 °C (a temperature at which solution/sols were formed), cooled to 0 °C (at 20 °C /min), equilibrated at 0 °C for 5 min, warmed to 20 °C, and then incubated in place for 20 min to reform the gels before commencing data collection. A constant frequency (1Hz) and a constant oscillatory shear strain which was sufficient to destroy the gel structure (100 %) were applied to the sample for 2 min followed by a very small, constant oscillatory shear strain in the linear viscoelastic region. Both $G'$ and $G''$ were recorded as a function of time. This protocol was repeated several times on each sample.

4.2.3 Syntheses

**DODE** was synthesized from methyl oleate by oxidation with potassium permanganate (Scheme 4.2).

![Scheme 4.2 Synthesis of DODE.](image)

A solution of methyl oleate (2.028 g, 6.500 mmol) in 18 mL of acetic anhydride was stirred for 72 h under a nitrogen atmosphere at room temperature. The solution was then cooled to -3 °C in an ice-salt bath. Potassium permanganate (4.54 g) was slowly added to the reaction system under nitrogen. The reaction temperature was kept below 0 °C. After further reaction for 2 h, an ice-cold mixture of 20 mL of saturated aqueous NaCl solution and 20 mL of aqueous saturated NaHSO$_3$ solution was added to the reaction mixture followed by the addition of 20 mL
of ethyl acetate and 10 mL of hexane. After stirring for 5 min, the organic layer was separated and washed once with an ice-cold mixture of 20 mL of saturated aqueous NaCl solution and 20 mL of aqueous saturated NaHSO₃ solution, 4 times with 30 mL of an aqueous saturated NaHCO₃ solution, and then twice with 30 mL of deionized water. After drying with Na₂SO₄ and filtering, the liquid was reduced to 1.06 g of a yellow solid at 50 °C (20 mmHg) on a rotary evaporator. It was recrystallized twice from 2 mL of methanol to yield 873 mg (40 %) of DODE (98 % purity by GC-MS analysis: m/z = 326.7) as yellow crystalline needles, mp 53.4-53.9 °C (lit.²⁶⁷ 50 °C).

IR (neat solid, cm⁻¹): 2918 (C-H stretching), 1739 (COOCH₃, C=O stretching), 1713 (α-diketone,²⁶⁸ C=O stretching).¹H-NMR (CDCl₃, 400 MHz) chemical shifts (ppm): 3.66 (s, 3H, -OCH₃), 2.70-2.74 (t, 4H, -CH₂C(=O)C(=O)-CH₂-, J = 8 Hz), 2.28-2.32 (t, 2H, CH₂-COOH, J = 8 Hz), 1.55-1.61 (m, 6H, -CH₂CH₂C(=O)C(=O)CH₂CH₂- and -CH₂-CH₂-COOH), 1.27-1.31 (m, 16H, CH₂-CH₂), 0.86-0.89 (t, 3H, CH₃, J = 6 Hz).¹³C-NMR (CDCl₃, 100 MHz) chemical shifts (ppm): 200 (2C, -C(=O)), 174 (1C, -COOCH₃), 51 (1C, -OCH₃), 22-36 (14C, -CH₂-), 14 (1C, CH₃). MS (m/z): calculated for C₁₉H₃₄O₄ [M]⁺: 326.25; found: 326.7 [M]⁺, 295 [M-OCH₃]⁺, 185 [C₁₀H₁₇O₃]⁺. Elemental analysis (%) calculated for C₁₉H₃₄O₄: C, 69.90; H, 10.50; N, 0.00; found: C, 69.91; H, 10.69; N, 0.06.

**DODA** was synthesized by hydrolysis of DODE under acidic conditions (Scheme 4.3).

![Scheme 4.3 Synthesis of DODA.](image)

**DODE** (700 mg, 2.13 mmol) was dissolved in a mixture of 11 mL of 4 % concentrated sulfuric acid in acetic acid and refluxed for 1.5 h. 6 mL of the solvent was removed by
distillation at 1 atm, and the concentrate was cooled and diluted with 11 mL of water. After vacuum filtration and washing of the solid with methanol (3 × 5 mL), 398 mg of a golden solid was obtained. It was recrystallized from 5 mL of hexanes to yield 293 mg (44 %) of golden needles, mp 84.1-84.8 °C (lit:266 85.0–85.5 °C). IR (neat solid, cm⁻¹): 2600-3500 (broad, COOH), 2918 (C-H stretching), 1712 (α-diketone,268 C=O stretching), and 1701 (COOH, C=O stretching). ¹H-NMR (CDCl₃, 400 MHz) chemical shifts (ppm): 2.70-2.74 (t, 4H, -CH₂C(=O)C(=O)-CH₂-, J = 8 Hz), 2.33-2.37 (t, 2H, CH₂-COOH, J = 8 Hz), 1.54-1.65 (m, 6H, -CH₂CH₂C(=O)C(=O)CH₂CH₂- and -CH₂-CH₂-COOH), 1.26-1.36 (m, 16H, CH₂-CH₂), 0.86-0.89 (t, 3H, CH₃, J = 6 Hz). ¹³C-NMR (CDCl₃, 100 MHz) chemical shifts (ppm): 200 (2C, -C(=O)), 178 (1C, -COOCH₃), 22-36 (14C, -CH₂-), 14 (1C, CH₃). Elemental analysis (%) calculated for C₁₈H₃₂O₄: C, 69.19; H, 10.32; N, 0.00; found: C, 68.82; H, 10.58; N, 0.08.

4.3 Results and discussion

4.3.1 Gelation properties

The gelation abilities of 10-KSA have been studied extensively.¹¹⁰,²⁶¹ Here, the gelating properties of DODA and DODE are investigated in a wide range of liquids and compared with data using 10-KSA as the gelator (Table 4.1). The rheological properties of 5 wt % 10-KSA gels and 5 wt % DODA gels in silicone oil²⁶¹ are compared in Figure 4.1. The results are correlated with the molecular structures and inter-molecular interactions of the gelators.

In addition to liquids that 10-KSA was able to gelate (decane and silicone oil),²⁶¹ 5 wt % DODA was able to gelate carbon tetrachloride, 1-octanol, ethyl acetate, and some aromatic liquids. The superiority of DODA is clearly indicated by its wider range of liquids gelated. In addition, where direct comparisons were possible, the CGC of 10-KSA were higher than those of
**DODA** and the stability periods of the **DODA** gels were longer than those of **10-KSA**. A mechanically stronger **SAFiN** for the **DODA** gel is indicated by its lower loss tangent than that of the **10-KSA** gel (Figure 4.1 and Table 4.2). This conclusion is reinforced by the observation that the yield strain was significantly higher for the **DODA** than for the **10-KSA** gel in silicone oil. However, the thermal stabilities of the 5 wt % **DODA** gels are lower than those of 5 wt % **10-KSA** gels in both decane and silicone oil; the latter melt at higher temperatures. Regardless, the additional dipole-dipole interactions gained by the presence of a second keto group clearly improve most of the physical properties of the gels.

**Table 4.1** Appearances, $T_g$ values ($^\circ$C) of gels with 5 wt % gelator [in brackets], and CGCs (wt %) in different liquids.[a]

<table>
<thead>
<tr>
<th>liquid</th>
<th><strong>DODE</strong></th>
<th><strong>DODA</strong></th>
<th><strong>10-KSA</strong>[b]</th>
</tr>
</thead>
<tbody>
<tr>
<td>toluene</td>
<td>S</td>
<td>OG [35-36], 1.7$\pm$0.1[c]</td>
<td>PG</td>
</tr>
<tr>
<td>benzonitrile</td>
<td>S</td>
<td>OG [32-34], 2.9$\pm$0.1[c]</td>
<td>/</td>
</tr>
<tr>
<td>chlorobenzene</td>
<td>S</td>
<td>OG [33-35], 2.8$\pm$0.1[c]</td>
<td>/</td>
</tr>
<tr>
<td>hexylbenzene</td>
<td>S</td>
<td>OG [44-47], 1.0$\pm$0.05[c]</td>
<td>/</td>
</tr>
<tr>
<td>nitrobenzene</td>
<td>S</td>
<td>OG [34-36], 3.2$\pm$0.1[c]</td>
<td>/</td>
</tr>
<tr>
<td>CCl₄</td>
<td>S</td>
<td>OG [40-43], 1.4$\pm$0.2[d]</td>
<td>Sus</td>
</tr>
<tr>
<td>1-octanol</td>
<td>S[d]</td>
<td>OG [39-42], 1.9$\pm$0.1[c]</td>
<td>PG</td>
</tr>
<tr>
<td>ethyl acetate</td>
<td>S</td>
<td>OG [30-31], 1.9$\pm$0.1[c]</td>
<td>/</td>
</tr>
</tbody>
</table>
Table 4.1 (cont.)

<table>
<thead>
<tr>
<th>liquid</th>
<th>DODE</th>
<th>DODA</th>
<th>10-KSA[^b]</th>
</tr>
</thead>
<tbody>
<tr>
<td>decane</td>
<td>P</td>
<td>OG [46-48], 0.7±0.05[^d]</td>
<td>OG [65-69], 3.6[^f]</td>
</tr>
<tr>
<td>hexanes</td>
<td>S</td>
<td>P</td>
<td>WG</td>
</tr>
<tr>
<td>silicone oil</td>
<td>WG</td>
<td>OG [54-56], 1.4±0.1[^e]</td>
<td>OG [77-78], 1.6[^f]</td>
</tr>
<tr>
<td>DMSO</td>
<td>Sus</td>
<td>Sus</td>
<td>Sus</td>
</tr>
<tr>
<td>DMF</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>acetone</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>acetonitrile</td>
<td>S</td>
<td>Sus</td>
<td>P</td>
</tr>
<tr>
<td>CHCl₃</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>CH₂Cl₂</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>methanol</td>
<td>S</td>
<td>P</td>
<td>S</td>
</tr>
<tr>
<td>ethanol</td>
<td>P</td>
<td>P</td>
<td>S</td>
</tr>
<tr>
<td>water</td>
<td>I[^e]</td>
<td>I</td>
<td>I</td>
</tr>
</tbody>
</table>

[^a] OG = opaque gel, CG = clear gel, WG = weak gel, S = solution, P = precipitate, I = insoluble, Sus = suspension, PG = partial gel; see Chapter 2 for details.  
[^b] From ref 261.  
[^c] Phase separation after 24h.  
[^d] Phase separation after one week.  
[^e] No detectable phase separation after > 6 months.  
[^f] Phase separation after 3 days.  

The methyl ester of DODA, DODE, was much more soluble than DODA in most of the liquids examined. The lack of H-bonding among the head groups of DODE is the likely reason...
for this difference: one of the very important inter-molecular interactions has been eliminated upon esterification of the carboxylic acid head group of DODA. Inter-molecular dipole-dipole interactions between α-diketo groups of DODE alone appear to be too weak to drive the formation of fibers in the liquids examined. An analogous example of this phenomenon is found in the aggregation of docosanoic acid where its CGC in vegetable oil increases upon methylation.106

Figure 4.1 Log-log plots of strain sweeps (a,c) and angular frequency sweeps (b,d) for gels of 5 wt %. DODA (▲,△) and 10KSA (●,○) in silicone oil (a,b); DODA in silicone oil (▲,△), 1-octanol (■,□) and benzonitrile (★,☆) (c,d). G’ are closed symbols and G” are open symbols.
Table 4.2 $G'$, $G''$, and loss tangent (at 0.01 % strain), and yield strains (i.e., crossover points) of gels with 5 wt % gelator.

<table>
<thead>
<tr>
<th>gel</th>
<th>$G''$ (Pa)</th>
<th>$G'$ (Pa)</th>
<th>loss tangent</th>
<th>yield strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10-KSA/silicone oil</td>
<td>1600±500[a]</td>
<td>3800±1300[a]</td>
<td>0.43±0.02[a]</td>
<td>1.8[a]</td>
</tr>
<tr>
<td>DODA/silicone oil</td>
<td>25000±2300</td>
<td>120000±16000</td>
<td>0.21±0.02</td>
<td>19</td>
</tr>
<tr>
<td>DODA/1-octanol</td>
<td>400±60</td>
<td>1400±200</td>
<td>0.28±0.05</td>
<td>15</td>
</tr>
<tr>
<td>DODA/benzonitrile</td>
<td>1400±550</td>
<td>7000±4000</td>
<td>0.25±0.08</td>
<td>5</td>
</tr>
</tbody>
</table>

[a] From ref 261.

4.3.2 Morphologies from POMs

The morphologies of gels consisting of 5 wt % DODA in 1-octanol, prepared by incubation of the sol phase at different temperatures below $T_g$, were investigated by POM (Figure 4.2). The SAfIN structures of the gels formed by incubation at 0 °C consisted of small bundles of fibrillar objects. They became longer and thicker as the incubation temperature was increased to 25 °C. When incubated at 30 °C, the SAfINs consisted of both fibers and platelets, and, at 35 °C, platelets were even more prevalent but phase separation was observed. Platelets were also found for the neat DODA powder that was crystallized from dichloromethane. Temperature-induced morphological transitions of gels have been observed in other systems as well (for example, in silicone oil gels of dialkyl ureas\(^269\)), where spherulitic objects were observed when the gels were prepared by incubation at lower temperatures or by fast-cooling rates, and elongated fibers were seen in gels prepared by incubation at higher temperatures or by slow-cooling rates.\(^50,269\) Higher incubation temperatures slow nucleation and growth, and can
alter the relationship between their rates, leading to different packing motifs within the SAFiNs. Thus, it appears that lower incubation temperatures, where the thermodynamic driving force for phase separation is greater, favor less discriminate aggregation processes and fibers rather than platelets. The morphological transition, from fibers to platelets, has consequences also for the emission spectra found from DODA (vide infra).

Figure 4.2 POMs of samples of 5 wt % DODA in 1-octanol after incubating the sol phase at (a) 0 °C, (b) 5 °C, (c) 10 °C, (d) 15 °C, (e) 20 °C, (f) 25 °C, (g) 30 °C, and (h) 35 °C.

In an attempt to confirm the change in morphology at a smaller length scale, gels of 5 wt % DODA in 1-octanol and in CCl₄ that had been incubated at 0 °C were examined by AFM. However, interaction between the AFM tip and the sample was stronger than that between the glass substrate and the sample; as a result, no images with real features of the sample surface could be obtained. TEM was then used to probe the morphology of a 5 wt % DODA xerogel in CCl₄ that had been incubated at 0 °C. The first two sample preparation methods, adding a dilute sol on a copper grid and picking up the dispersed gel layer by the grid, provided very thick sample layers and no clear morphology information was obtained. However, the spin-cast film was thin enough to be imaged by TEM. On the micrometer length scale, fiber-like objects were
observed (Figure 4.3a). However, within seconds, crystalline objects were destroyed by the electron beam (Figures 4.3b and 4.3c). In order to confirm the change in morphology on the nanometer length scale, an electron beam with higher energy was used. Although the objects could not be captured clearly (Figure 4.3d), the material is highly crystalline as indicated by the interference pattern in Figure 4.3e. As before, the interference pattern disappeared after the imaging due to damage of the crystalline objects by the electron beam. Although using TEM to probe the morphology change at a smaller length scale was unsuccessful, the interference pattern indicated that the growth of a single crystal of DODA might be feasible.

**Figure 4.3** TEM images (a, b, c, and d) and interference pattern (e) at 20 °C of a spin-casted film from a 5 wt % hot sol of DODA in carbon tetrachloride. Images were taken at the same spot over a time interval of few seconds (a, b, and c).
4.3.3 Single crystal structure and molecular packing arrangements

Difficulties in obtaining diffraction quality single crystals of gelators, especially long-chain fatty acids, are common.\textsuperscript{31} Few studies have reported crystal structures of long-chain fatty acids that are efficient gelators. One involves racemic 12-hydroxystearic acid.\textsuperscript{255}

In order to obtain a single crystal of DODA for X-ray structural investigation, several attempts were made. A vapor diffusion technique was used with acetic acid as the good solvent and methanol as the anti-solvent. A slow evaporation technique was also tried with dichloromethane, chloroform, and mixtures of octane and chloroform and toluene and chloroform. Among these, slowing evaporation from dichloromethane led to crystals most suitable for an X-ray structural investigation. Details of the crystallographic measurements and refinement are summarized in Table 4.3. DODA crystallizes in the monoclinic space group \( P2_1/c \), with one molecule in each asymmetric unit. The polymethylene chain of DODA adopts an \textit{all-transoid} conformation and the \( \alpha \)-diketo group is in an \textit{anti}-conformation; the dihedral angle between the two carbonyl groups (\( \phi, \angle O(3)=C(9)\cdots C(10)=O(4) \)) is 179.8(0.2)° (Figure 4.4a). A pair of inversion-related molecules forms a cyclic O-H\cdots O H-bonded dimer between carboxylic acid groups; \( \angle O(1)-H(1)\cdots O(2) = 172(3)° \) at a O(1)\cdots O(2) distance of 2.662(0.002) Å (Figure 4.4b). The molecules pack in a bilayered lamellar arrangement without interdigitation. Also, pairs of molecules aggregate along the polymethylene chain through inter-molecular, attractive dipole-dipole interactions between carbonyl groups in head-to-tail orientations at an angle of 58.75(0.16)° (Figure 4.4c). The distance between C9\cdots O4 (2.902 Å), being much shorter than the sum of the van der Waals radii of carbon and oxygen (3.2 Å) atoms,\textsuperscript{270} also supports the attractive nature of the dipole-dipole interaction between the two carbonyl groups. The angle
between the two inter-molecular dipoles leads to a 2D sheet-like packing arrangement and platelets.

**Table 4.3** Summary of crystallographic data and refinement for DODA crystallized from dichloromethane.

<table>
<thead>
<tr>
<th>formula</th>
<th>C_{18}H_{32}O_{4}</th>
<th>V, Å³</th>
<th>1736.0(15)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(M_r), g/mol</td>
<td>312.44</td>
<td>Z 4</td>
<td></td>
</tr>
<tr>
<td>wavelength, Å</td>
<td>0.71073</td>
<td>(T), K</td>
<td>173 K</td>
</tr>
<tr>
<td>crystal system</td>
<td>monoclinic</td>
<td>(\rho_{\text{calc}}, \text{g/cm}^3)</td>
<td>1.195</td>
</tr>
<tr>
<td>space group</td>
<td>P2_1/C</td>
<td>F(000)</td>
<td>688.0</td>
</tr>
<tr>
<td>crystal dimensions, mm³</td>
<td>1.22 × 0.68 × 0.05</td>
<td>reflections collected</td>
<td>11957</td>
</tr>
<tr>
<td>(a), Å</td>
<td>49.45(0.02)</td>
<td>unique reflections</td>
<td>3029</td>
</tr>
<tr>
<td>(b), Å</td>
<td>6.841(0.03)</td>
<td>reflections with (I &gt; 2\sigma(I))</td>
<td>2514</td>
</tr>
<tr>
<td>(c), Å</td>
<td>5.133(0.03)</td>
<td>(R_{int})</td>
<td>0.0321</td>
</tr>
<tr>
<td>(\alpha),°</td>
<td>90.00</td>
<td>(R_1, wR_2 [I &gt; 2\sigma(I)])</td>
<td>0.0547, 0.1548</td>
</tr>
<tr>
<td>(\beta),°</td>
<td>90.170(6)</td>
<td>goof</td>
<td>1.095</td>
</tr>
<tr>
<td>(\gamma),°</td>
<td>90.00</td>
<td>(\mu \text{ MoK} \alpha, \text{mm}^{-1})</td>
<td>0.079</td>
</tr>
</tbody>
</table>
Figure 4.4 Representations of the crystal structure of DODA. (a) a thermal ellipsoid plot of a single molecule (50 % probability level); (b) a 2D packing diagram viewed perpendicular to the polymethylene chains; the red dashed lines indicate the positions of H-bonds; (c) a 2D packing diagram viewed along the axis of the polymethylene chains; the blue dashed lines indicate dipole-dipole interactions.

PXRD diffractograms of neat DODA powder, and of 10 wt % gels in silicone oil and 1-octanol have been compared as well (Figure 4.5). The 2θ values of the diffraction peaks of the SAFiNs in both 1-octanol and silicone oil match well those of the neat gelator; the packing arrangements appear to be the same or very similar. However, the paucity of diffraction peaks collected for the SAFiNs, especially in silicone oil, limits the strength of this conclusion.
Figure 4.5 PXRD diffractograms of neat DODA powder (red), and its 10 wt % gels in 1-octanol (blue) and in silicone oil (black). The curves are offset along the Y-axis for the sake of clarity.

4.3.4 Photophysical properties of DODA in its solution/sol, solid and gel states

The absorption spectra of a 6.0×10⁻³ mol/L DODA sol in dry THF at room temperature showed a band from an α-diketo based n-π* transition centered near 425 nm (molar absorption coefficient = 20 M⁻¹ cm⁻¹) and another band centered near 271 nm (molar absorption coefficient = 50 M⁻¹ cm⁻¹) (Figure 4.6).²⁷¹
When excited at 425 nm, both aerated and the degassed solutions of DODA in dry THF displayed a fluorescence band with the maximum intensity at 481 nm and a shoulder at ~510 nm (Figure 4.7). The shape of the emission spectra remained the same when the solutions were excited at 410, 425, and 440 nm, which suggests only one species fluoresced when excitation was at these three wavelengths. In addition, the degassed sample exhibited an emission peak at 548 nm. The phosphorescence maximum from 2,3-octanedione in hexanes is reported to be at 548 nm.\textsuperscript{262} Based on the structural similarity of DODA and 2,3-octanedione, the emission peak observed for the solution of DODA at 548 nm is attributed to phosphorescence. Also, as temperature was decreased from 45 to -15 °C, the relative intensity of the peak at 548 nm (with respect to the peak at 481 nm) increased dramatically for the degassed sample, but there was no change in the intensity at 548 nm for the aerated sample. The singlet and triplet lifetimes of
Biacetyl in de-aerated benzene at 27 °C are 12.3 nsec\textsuperscript{272} and 0.5 msec\textsuperscript{273} respectively. The longer triplet lifetime allows it to be quenched selectively in an aerated sample. The selective quench in the aerated sample also marks the ~548 nm shoulder in the emission spectrum of DODA as phosphorescence.

![Figure 4.7](image)

**Figure 4.7** Spectra of 6.0×10\textsuperscript{-3} mol/L (0.2 wt %) DODA in dry THF: (a) aerated excitation (\(\lambda_{ex}\) 481 nm) and emission (\(\lambda_{ex}\) 425 nm) spectra at -15 °C (red), 0 °C (black), and 45 °C (blue); (b) degassed excitation and emission spectra at -15 °C (red), 0 °C (black), and 45 °C (blue). The direction of the vertical arrow in (b) indicates increasing temperature.
Figure 4.8 Excitation (a) and emission (b) spectra of a gel of 5 wt % DODA in 1-octanol at 25 °C (black, $\lambda_{em}$ 458 nm, $\lambda_{ex}$ 400 nm), a 5 wt % sol of DODA in 1-octanol at 45 °C (blue, $\lambda_{em}$ 481 nm, $\lambda_{ex}$ 425 nm), and melt-solidified DODA at 25 °C (red, $\lambda_{em}$ 458 nm, $\lambda_{ex}$ 400 nm). Excitation (c) and emission (d) spectra of a gel of 5 wt % DODA in CCl$_4$ at 25 °C (black, $\lambda_{em}$ 458 nm, $\lambda_{ex}$ 400 nm) and a 5 wt % sol of DODA in CCl$_4$ at 45 °C (blue, $\lambda_{em}$ 481 nm, $\lambda_{ex}$ 425 nm). All of the samples were aerated.
Figure 4.9 Excitation and emission spectra ($\lambda_{em}$ 458 nm, $\lambda_{ex}$ 402 nm) at 25 °C of neat DODA powder recrystallized from dichloromethane (blue) and melt-solidified DODA obtained by placing the melt directly in an ice-bath (black) or a liquid nitrogen bath (red). All of the samples were aerated.

The emission and excitation spectra of melt-solidified DODA, and a gel of 5 wt % DODA in 1-octanol at 25 °C, and sol at 45 °C were then compared (Figures 4.8a,b). The cooling process employed to create the gels from their sol phases was simulated in the solidification process for the solidified melt of DODA. The shapes and positions of the emission and excitation spectra of a 5 wt % sol of DODA in 1-octanol at 45 °C match those of the solution of DODA in THF. However, although the shapes of the excitation and emission peaks of 1-octanol gel and the solidified-melt of DODA are very similar, they were blue shifted by ~25 nm from the excitation
and emission peaks of the 1-octanol sol at 45 °C. A similar blue shift of the excitation and emission peaks was also observed for a gel of 5 wt % DODA in CCl₄ at 25 °C compared to its sol at 45 °C (Figures 4.8c,d). In addition, the positions of the emission and excitation spectral bands of the solidified-melt of DODA are identical to those of the crystallized DODA powder. However, the relative intensities between the peaks are different (Figure 4.9), indicating that the gel and the solidified-melt of DODA may have a different packing arrangement from that of the crystallized DODA.

In that regard, there is no significant difference at angles below 20° in the powder X-ray diffractograms of the crystallized and the melt-solidified DODA (Figure 4.10), although some differences were observed at angles above 20°; there may be small packing differences within the layers. Due to the limited number of diffraction peaks observed in the PXRD of the 1-octanol gel at higher angles, it is unclear whether the packing arrangement within its SAFiN is different from that of the two neat solids. Regardless, the similarity in emission and excitation spectra indicates that the morphology of the solidified-melt DODA and the SAFiN of the 1-octanol gel are similar, but may differ from that of the crystallized DODA, as indicated also by the POMs. However, the PXRD patterns suggest that the fast-cooled gel also exhibits similar bilayered, extended packing arrangements and hence similar anti-conformations for the α-diketo group.
Figure 4.10 Powder X-ray diffractograms at 25 °C of neat DODA powder recrystallized from dichloromethane (black) and powder diffractogram of melt-solidified DODA obtained by placing the melt directly in an ice-bath (red).

The position of the $n-\pi^*$ absorption band of an $\alpha$-diketo group is known to depend on the dihedral angle between the carbonyl groups. The absorption band is known to be progressively blue-shifted as the dihedral angle increases from 0° to 90° and then to be red shifted as the dihedral angle increases further, from 90° to 180° (Figure 4.11a). In principle, the excitation energy and the dihedral angle of the $\alpha$-diketo group of DODA in the 1-octanol sol should follow the same trend. On this basis, the inter-carbonyl dihedral angle for DODA in the sol is in the range of 155-180°. However, the excitation wavelength maximum of the DODA gel in 1-octanol, with an anti-conformation of the $\alpha$-diketo group, is much lower (i.e., blue-shifted) than expected. The shift is probably a consequence of restricted motions within the excited states.
when the DODA molecules are aggregated within their SAFIns and, perhaps, additional ground state stabilization induced by inter-molecular dipolar interactions in the ground states.

Figure 4.11 Dependence of the excitation maxima (a) and the emission maxima (b) on the inter-carbonyl dihedral angle of a series of $\alpha$-diketo containing molecules at 25 °C in aerated solution (black; taken from ref 271); an aerated gel of 5 wt % DODA in 1-octanol at 25 °C (red); and an aerated 5 wt % sol of DODA in 1-octanol at 45 °C (green). The range of multiple excitation maxima of the aerated 5 wt % sol of DODA in 1-octanol is indicated by the curve between the two green triangles.

In support of this explanation, there is no clear correlation between the transition energy associated with the fluorescence and the dihedral angles of $\alpha$-diketo groups (Figure 4.11b). In addition, there is no mirror image relationship between the absorption and fluorescence spectra of such molecules. The explanation advanced for this observation is that flexible $\alpha$-diketo groups relax to planar conformations before emitting. Therefore, the blue shift of the DODA emission peaks from the solution/sol state to the gel state cannot be rationalized solely on the basis of changes in dihedral angles; as mentioned above, it appears to be aggregation-induced. Upon gel formation, rotation of the $\alpha$-diketo groups is more restricted, and the $\alpha$-diketo inter-molecular
dipole-dipole interactions (as noted from the single crystal structure) become available, resulting in enhancement of emission intensity and increased transition energies.\textsuperscript{211}

In addition, the shape of the emission and excitation spectra differ significantly when the DODA gel in 1-octanol was formed by incubating its sol phase at 0 °C and 30 °C (Figure 4.12). Both gels exhibit an aggregation induced blue shift in their emission spectra. However, the relative intensities of the peaks at 489 nm and 458 nm are different. When the sol was incubated at 0 °C, both the shape of the emission and excitation spectra were similar to those of melt-solidified DODA, while the spectra of the gel from incubation at 30 °C were like that of the crystallized powder. As noted above, the morphology of the SAFiNs of a gel of 5 wt % DODA in 1-octanol change from fibers to platelets as the incubation temperature is increased. The difference in relative intensities of the emission peaks appears to be related to the different morphologies (i.e., the different molecular packing arrangements) of the emitting species.

\textbf{Figure 4.12} Excitation (a) and emission (b) spectra at 25 °C of the aerated gels of 5 wt % DODA in 1-octanol after incubating the sols at 0 °C (black, $\lambda_{em}$ 458 nm, $\lambda_{ex}$ 400 nm), 30 °C (red, $\lambda_{em}$ 458 nm, $\lambda_{ex}$ 400 nm), and 45 °C (blue, $\lambda_{em}$ 481 nm, $\lambda_{ex}$ 425 nm).
4.3.5 Kinetic studies of thermally formed gels by fluorescence measurements.

As mentioned in Section 1.1.4, the kinetics of nucleation and growth of 0D and 1D objects and their further assembly into 3D networks is another important aspect of gelation. Unfortunately, the rapid formation of most molecular gels made it difficult to follow. However, the transformation of sols of DODA in 1-octanol to their gels occurs on time scales of a few minutes to hours at different incubation temperatures. Furthermore, the spectral changes in the emission of DODA offer a convenient and fast tool to assess the degree of aggregation. Here, Avrami\textsuperscript{50,61,62} (Equation 1.1) and Dickinson theories\textsuperscript{63} (Equation 1.2) are applied to gain insights into the formation of SAFiNs of DODA in 1-octanol.

As mentioned above, the emission peaks of a sample of 5 wt % DODA in 1-octanol undergo a blue shift as the sol is transformed to the gel state. Here, the intensity of the new fluorescence peak at 458 nm, which appears when the gel starts to form, has been used to monitor the nucleation of gelator molecules and the degree of their growth at different temperatures in samples incubated at 0, 5, 10, 15, 20, 25, 30 and 35 °C, a series of temperatures below \( T_g \) (Figure 4.13).

At all of these incubation temperatures, the intensity of the 458 nm emission peak increased with time and eventually reached a plateau value (Figure 4.13). Consistent with less driving force for phase separation as temperature approaches \( T_g \), the rate of gel formation (i.e., \( K \)) decreased at higher temperatures. Avrami plots for samples incubated at different temperatures are shown in Figure 4.14 and the parameters are summarized in Table 4.4. Avrami exponents near 2 imply either an instantaneous nucleation to platelet-type (2D) objects or a heterogeneous nucleation to rod-like (1D) objects.\textsuperscript{56,61,62} The fibrous objects in the POMs for SAFiNs constructed below 30 °C are consistent with heterogeneous nucleation to 1D objects;
above 30 °C, the presence of platelets indicates instantaneous nucleation to 2D objects. The fractal dimensions $D_f$, 1.0 to 1.5 at all of the incubation temperatures examined for the DODA gels in 1-octanol (Figure 4.15 and Table 4.4), imply fiber-like SAfNs.\textsuperscript{63,274} However, the platelets (observed with some fibers) in the POMs from experiments with incubation temperatures $>30$ °C predict higher fractal dimensions than the values calculated. We suggest that different aggregation processes control the kinetics at different stages of the aggregation, nucleation, and growth into 3D networks.

Figure 4.13 Plots of emission intensity ($\lambda_{ex}$ 400 nm, $\lambda_{em}$ 458 nm) versus time for an aerated sample of 5 wt % DODA in 1-octanol: incubated at (a) 0, 5, 10, 15, 20, and 25 °C or at (b) 30 and 35 °C.
Figure 4.14 Avrami plots (according to equation 1.1) of emission intensities ($\lambda_{ex}$ 402 nm, $\lambda_{em}$ 458 nm) of aerated gels of 5 wt % DODA in 1-octanol formed upon incubating sols at 0 (a), 5 (b), 10 (c), 15 (d), 20 (e), 25 (f), 30 (g), and 35 °C (h). The sample incubated at 35 °C is not a gel.
Figure 4.15 Dickinson plots (according to equation 1.2) of emission intensity ($\lambda_{\text{ex}}$ 402 nm, $\lambda_{\text{em}}$ 458 nm) of aerated gels of 5 wt % DODA in 1-octanol formed by incubating sols at 0 (a), 5 (b), 10 (c), 15 (d), 20 (e), 25 (f), 30 (g), and 35 °C (h). The sample incubated at 35 °C is not a gel.
Table 4.4 Summary of $K$ and $n$ values from the Avrami equation and $D_f$ values from the Dickinson equation based on analyses of data from gelation of aerated sols of 5 wt % DODA in 1-octanol incubated at different temperatures.[a]

<table>
<thead>
<tr>
<th>$T$, °C</th>
<th>$n$</th>
<th>$K \times 10^3$, s$^{-2}$[b]</th>
<th>$R_{Avrami}^2$[c]</th>
<th>$D_f$</th>
<th>$R_{Dickinson}^2$[c]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.23/2.30</td>
<td>6.82/6.70</td>
<td>0.98/0.98</td>
<td>1.0/1.0</td>
<td>0.99/0.98</td>
</tr>
<tr>
<td>5</td>
<td>2.13/2.16</td>
<td>7.81/7.64</td>
<td>0.98/0.97</td>
<td>1.0/1.1</td>
<td>0.99/0.99</td>
</tr>
<tr>
<td>10</td>
<td>1.75/1.70</td>
<td>6.07/6.16</td>
<td>0.98/0.99</td>
<td>1.1/1.1</td>
<td>0.99/0.99</td>
</tr>
<tr>
<td>15</td>
<td>1.72/1.75</td>
<td>1.34/1.31</td>
<td>0.99/0.98</td>
<td>1.2/1.1</td>
<td>0.99/0.98</td>
</tr>
<tr>
<td>20</td>
<td>1.76/1.78</td>
<td>1.98/2.02</td>
<td>0.99/0.99</td>
<td>1.2/1.2</td>
<td>0.99/0.99</td>
</tr>
<tr>
<td>25</td>
<td>1.73/1.77</td>
<td>6.84/6.78</td>
<td>0.99/0.99</td>
<td>1.4/1.3</td>
<td>0.99/0.99</td>
</tr>
<tr>
<td>30</td>
<td>2.2</td>
<td>$1.37 \times 10^{-3}$</td>
<td>0.99</td>
<td>1.1</td>
<td>0.98</td>
</tr>
<tr>
<td>35</td>
<td>1.7</td>
<td>$1.60 \times 10^{-4}$</td>
<td>0.99</td>
<td>1.3</td>
<td>0.97</td>
</tr>
</tbody>
</table>

[a] Data from two kinetic experiments are reported at each incubation temperature except at 30 and 35 °C. [b] The units of $K$ are $t^n$, because the exponential factor must be dimensionless. Here, an approximate integer of $n = 2$ is used. [c] $R^2$ is the square of the correlation coefficient.

### 4.3.6 DLS and SLS study of DODA mixtures

The formation of gels of 5 wt % DODA in 1-octanol has been monitored by fluorescence. However, the change in shape and size of the aggregates at the early stage of gel formation is still unclear. DLS and SLS offer the possibility to monitor the change in shape and size of the
objects starting at an early stage of aggregation and nucleation. The hydrodynamic radius ($R_h$) of the objects can be determined by dynamic light scattering. Then, using the scattered intensity $I_s(q)$ measured at different scattering angles $\theta$, a Guinier plot can be constructed to determine the radius of gyration ($R_g$). The shape of the objects can be extracted from the relationship between $R_g$ and $R_h$.

In the Guinier equations 4.1 and 4.2, $\theta$ is the scattering angle, $n$ is the refractive index of the liquid, $q$ is the scattering vector for vertically polarized light and $\lambda$ is the wavelength of the light source. $I_s$ is the scattered intensity and $I_i$ is the light intensity. However, a Guinier plot has certain conditions that should be satisfied in order for their interpretation in terms of particle size and shape to be valid. One is that $qR_g < 1$. If the object has a large gyration radius, only very low scattering angles can satisfy the condition of $qR_g < 1$.

$$q = \frac{4\pi n \sin(\frac{\theta}{2})}{\lambda}$$ (4.1)

$$\ln I_s(q) = \ln I_i - \frac{q^2 \times R_g^2}{3}$$ (4.2)

Because of the high viscosity of 1-octanol, CCl$_4$ was used as the liquid in DLS and SLS studies. Preliminary tests on sols of 1, 3, and 5 wt % DODA in CCl$_4$ at 55°C were carried out to estimate the size of the objects at different concentrations. Figure 4.16 shows the intensity correlation function ($g^2(s)$) of aggregates in sols of 1, 3, and 5 wt % DODA in CCl$_4$ at 55 °C and 90 ° scattering angles. The DLS data curves are fitted well to the simulation curves, including the intercepts and the entire slopes. The average hydrodynamic radii of the objects in sols of 5, 3, and 1 wt % DODA in CCl$_4$ at 55°C are 1350, 600, and 230 nm, respectively (Table 4.5). Rough estimates of $R_g$ based on a cylinder model and a sphere model were calculated (equations 4.3 and 4.4; Table 4.5). One assumption made in the estimate based on the cylinder model is that the
radius is 1/10 of the length of the cylinder. Both estimates indicate that even 1 wt % is too high a concentration to measure in this way the radii of gyration of the objects at 55 °C. Although DODA does not form a gel in CCl₄ at concentrations lower than 1 wt %, it does form 1D objects that are important to understand the formation of the 3D SAFiN gel networks.

\[
\text{Cylinder model: } \quad Rg^2 = \frac{R^2}{2} + \frac{h^2}{12} \quad (4.3)
\]

\[
\text{Sphere model: } \quad Rg^2 = 0.6R^2 \quad (4.4)
\]

![Figure 4.16](image-url) Variation of intensity correlation functions of aggregates in sols of 5 (blue), 3 (red), and 1 (green) wt % DODA in CCl₄ at 55 °C and 90 ° scattering angle. Black curves are the fits to the scattering data.
Table 4.5 Hydrodynamic radii of aggregates in sols of 5, 3, and 1 wt % DODA in CCl₄ at 55 °C and 90 ° scattering angle.

<table>
<thead>
<tr>
<th></th>
<th>5 wt %</th>
<th>3 wt %</th>
<th>1 wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rₜ, nm</td>
<td>1283±607</td>
<td>557±158</td>
<td>236±107</td>
</tr>
<tr>
<td></td>
<td>1355±654</td>
<td>643±304</td>
<td>221±95</td>
</tr>
<tr>
<td></td>
<td>1385±671</td>
<td>672±319</td>
<td>247±117</td>
</tr>
<tr>
<td>estimated Rₜ (cylinder), nm</td>
<td>400</td>
<td>178</td>
<td>68</td>
</tr>
<tr>
<td>scattering angles that satisfy the qRₜ &lt; 1 condition (cylinder), °</td>
<td>&lt; 10</td>
<td>&lt; 20</td>
<td>&lt; 60</td>
</tr>
<tr>
<td>estimated Rₜ (sphere), nm</td>
<td>1046</td>
<td>465</td>
<td>178</td>
</tr>
<tr>
<td>scattering angles that satisfy the qRₜ &lt; 1 condition (sphere), °</td>
<td>&lt; 10</td>
<td>&lt; 9</td>
<td>&lt; 20</td>
</tr>
</tbody>
</table>

[a] Averages of three runs for each concentration.

A 0.05 wt % sol of DODA in CCl₄ was then used for dynamic and static light scattering study at 55 °C. Figure 4.17 shows the intensity correlation function (g²(s)) of aggregates of this sample at 90 ° scattering angle. The distributions of Rₜ of the objects at different scattering angles are shown in Figure 4.18, and they yield very similar values of Rₜ, 100 ± 20 nm. A rough estimate of the Rₜ based on a sphere model (equation 4.2) was calculated to be 77 nm. Thus, it appears that the data collected below 70 ° can be used to plot a Guinier regression (Figure 4.18). From the slope of the linear Guinier plot, Rₜ is calculated to be 115 nm. The relationship between
$R_g$ and $R_h$ suggests that the objects in the sol of 0.05 wt % DODA in CCl$_4$ at 55°C are sphere-like objects with radii \( \sim 110 \) nm.

**Figure 4.17** Variation of intensity correlation functions of aggregates in a sol of 0.05 wt % DODA in CCl$_4$ at 55 °C at different scattering angles: 20° (blue), 30° (red), 40° (green), 50° (pink), 60° (purple), and 70° (orange). Black curves are the fits to the scattering data.

**Figure 4.18** (a) Hydrodynamic radii distributions of aggregates in a 0.05 wt % sol of DODA in CCl$_4$ at 55 °C measured at different scattering angles and (b) a Guinier plot in static light scattering of the data in (a).
Figure 4.19a shows the intensity correlation function \( g^2(s) \) of aggregates in a sol of 0.05 wt % DODA in CCl\(_4\) at 25 °C at different scattering angles. The simulation curves fit well the DLS curves, including the intercept and the entire slopes. The scattering at angles above 50 ° are very dispersive. Two distributions of objects are indicated by the \( R_h \) at different scattering angles (Figure 4.19b). The averages of the first (1 %) and second (99 %) distributions are 40 ± 20 nm and 550 ± 120 nm, respectively. In addition, the intercepts of some of the correlation curves, much larger than 1, indicate the presence of micrometer scale aggregates in the sol, as well. Thus, a meaningful Guinier plot cannot be constructed for this sample.

**Figure 4.19** (a) Variation of intensity correlation functions of aggregates in sols of 0.05 wt % DODA in CCl\(_4\) at 25 °C at different scattering angles: 20° (blue), 30° (red), 40° (green), 50° (pink), 60° (purple), and 70° (orange). Black curves are the fits to the scattering data. (b) Hydrodynamic radii distributions of aggregates in a sol of 0.05 wt % DODA in CCl\(_4\) at 25 °C measured at different scattering angles.

A sample with 0.02 wt % DODA concentration in CCl\(_4\) was then examined at 55 °C and 25 °C (Figure 4.20). The scattering signals are very dispersive and the signal-to-noise is very poor. The count rate and the intercept of the correlation curves are relatively low as well. As a
result, attempts to fit the correlation curves failed. Although the attempt to define the shapes of aggregates in the 0.05 wt % sample at 25 °C was unsuccessful, it may be possible at a higher temperature, such as 35 °C.

Figure 4.20 Variation of intensity correlation functions at different scattering angles of aggregates in a sol of 0.02 wt % DODA in CCl₄ at 55 °C (a) and 25 °C (b).

4.3.7 Thixotropic properties: mechanical destruction and formation of SAFiNs

Interestingly, gels of 5 wt % DODA in 1-octanol, silicone oil, and benzonitrile are partially thixotropic: they recover some of their viscoelasticity after being transformed mechanically into their sol phases (i.e., $G'$ became less than $G''$). After the cessation of destructive strain, $G'$ again became higher than $G''$. The evolution of the recovery of the moduli were recorded (Figures 4.21, 4.22, and 4.23), and changes in the $G'$ values were used to follow the reformation of the SAFiNs. The data were fitted to a stretched exponential expression (eq 4.5)$^{150}$ in which $t$ is time after cessation of destructive strain and $\tau$ is the calculated recovery time constant. $G'_0$ is the value when the destructive strain ceased, $G'_t$ is an intermediate value at time
\[ G'_t = G'_\infty - (G'_\infty - G'_0) e^{-t/\tau} \] (4.5)

Figure 4.21 \( G' \) and \( G'' \) as a function of time and application of different strains to a gel of 5 wt \% DODA in 1-octanol at 20 °C. LVR: \( \gamma = 0.01 \% \), \( f = 1 \) Hz; destructive strain (DS): \( \gamma = 100 \% \), \( f = 1 \) Hz. Rotational strain was kept at 0 % for 1 s before changing from DS to LVR conditions. Data points were collected every 5 s after the cessation of destructive strain.
Figure 4.22 $G'$ and $G''$ as a function of time and application of different strains to a gel of 5 wt % DODA in silicone oil at 20 °C. LVR: $\gamma = 0.01 \%$, $f = 1$ Hz. DS: $\gamma = 100 \%$, $f = 1$ Hz. Rotational strain was kept at 0 % for 1 s before changing from DS to LVR conditions. Data points were collected every 2 s after the cessation of the destructive strain.
Figure 4.23 $G'$ and $G''$ as a function of time and application of different strains to a gel of 5 wt % DODA in benzonitrile at 20 ºC. LVR: $\gamma = 0.01 \%$, $f = 1$ Hz. DS: $\gamma = 100 \%$, $f = 1$ Hz. Rotational strain was kept at 0 % for 1 s before changing from DS to LVR conditions. Data points were collected every 2 s after the cessation of the destructive strain.

The recoveries were not complete. 36 % of the original $G'$ value was recovered after the initial application of the destructive strain to a gel of 5 wt % DODA in 1-octanol. Only 70 % of that value (i.e., ~21 % of the initial value) was recovered in the subsequent cycle and $G'$ increased to 60~64 % of the value after the first cycle in another 5 subsequent cycles (Figure 4.21 and Table 4.6). The best exponential fits of the $G'$ data indicate a recovery time of 3-4 s (Figure 4.24). Note that the recovery times reported here and for other gels are only approximations because the recovery of $G'$ was faster than the response time of our rheometer in most cases. Similarly, a gel of 5 wt % DODA in silicone oil and a gel of 5 wt % DODA in benzonitrile recovered only 34 % and 27 %, respectively, of their original $G'$ values. In
subsequent cycles, $G'$ increased to 40~60 % and 53~70 % of the value after the first cycle, respectively, but never to complete recovery although the recovery times were very rapid for both gels (~10 s for the silicone oil gel and ~2 s for the benzonitrile gel (Figures 4.25 and 4.26; Tables 4.7 and 4.8). Unfortunately, attempts to utilize the differences in emission intensities and wavelength maxima to probe the kinetics of isothermal reformation of the SAFiNs after the cessation of destructive strain were unsuccessful—the recovery process was more rapid than the response time of our fluorimeter.

**Figure 4.24** The best fit to a single exponential rise (lines; see equation 4.5) for the recovery data of $G'$ (dots) for a gel of 5 wt % DODA in 1-octanol at 20 °C after cessation of destructive strain and return to the LVR condition. (a) Data collected from the first four cycles. (b) Data collected from 4 cycles, starting from the 4th cycle.
Table 4.6 Thixotropic parameters related to gels of 5 wt % DODA in 1-octanol: recovery times (τ) and % of thixotropic recovery after different numbers of LVR-DS cycles.

<table>
<thead>
<tr>
<th>Cycle</th>
<th>τ (s)</th>
<th>% of thixotropic recovery[^a]</th>
</tr>
</thead>
<tbody>
<tr>
<td>first cycle</td>
<td>~4</td>
<td>~36 %</td>
</tr>
<tr>
<td>second cycle</td>
<td>~4</td>
<td>~70 %</td>
</tr>
<tr>
<td>third cycle</td>
<td>~4</td>
<td>~90 %</td>
</tr>
<tr>
<td>4th cycle</td>
<td>~4</td>
<td>~95 %</td>
</tr>
<tr>
<td>5th cycle</td>
<td>~4</td>
<td>~100 %</td>
</tr>
<tr>
<td>6th cycle</td>
<td>~3</td>
<td>~100 %</td>
</tr>
<tr>
<td>7th cycle</td>
<td>~3</td>
<td>~100 %</td>
</tr>
</tbody>
</table>

[^a]: Percentage recovery of $G'$ taking the value from the previous cycle as 100 %.

Figure 4.25 The best fit to a single exponential rise (lines; see equation 4.5) for the recovery data of $G'$ (dots) in a sample of 5 wt % DODA in silicone oil at 20 °C after cessation of destructive
strain and return to the LVR condition. (a) Data collected from the first four cycles. (b) Data collected from 4 cycles, starting from the 4\textsuperscript{th} cycle.

**Table 4.7** Thixotropic parameters related to gels of 5 wt % DODA in silicone oil: recovery times ($\tau$) and % of thixotropic recovery after different numbers of LVR-DS cycles.

<table>
<thead>
<tr>
<th></th>
<th>$\tau$ (s)</th>
<th>% of thixotropic recovery\textsuperscript{[a]}</th>
</tr>
</thead>
<tbody>
<tr>
<td>first cycle</td>
<td>~12</td>
<td>~34 %</td>
</tr>
<tr>
<td>second cycle</td>
<td>~8</td>
<td>~59 %</td>
</tr>
<tr>
<td>third cycle</td>
<td>~10</td>
<td>~78 %</td>
</tr>
<tr>
<td>4\textsuperscript{th} cycle</td>
<td>~12</td>
<td>~95 %</td>
</tr>
<tr>
<td>5\textsuperscript{th} cycle</td>
<td>~14</td>
<td>~98 %</td>
</tr>
<tr>
<td>6\textsuperscript{th} cycle</td>
<td>~18</td>
<td>~91 %</td>
</tr>
<tr>
<td>7\textsuperscript{th} cycle</td>
<td>~20</td>
<td>~93 %</td>
</tr>
</tbody>
</table>

\textsuperscript{[a]} Percentage recovery of $G'$ taking the value from the previous cycle as 100 %.
**Figure 4.26** The best fit to a single exponential rise (lines; see equation 4.5) for the recovery data of $G'$ (dots) in a sample of 5 wt % DODA in benzonitrile at 20 ºC after the cessation of destructive strain and return to the LVR condition. (a) Data collected from the first three cycles. (b) Data collected from 4 cycles, starting from the 3rd cycle.

**Table 4.8** Thixotropic parameters related to gels of 5 wt % DODA in benzonitrile: recovery times ($\tau$) and % of thixotropic recovery after different numbers of LVR-DS cycles.

<table>
<thead>
<tr>
<th>Cycle</th>
<th>$\tau$ (s)</th>
<th>% of thixotropic recovery$^{[a]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st cycle</td>
<td>~2</td>
<td>~27 %</td>
</tr>
<tr>
<td>2nd cycle</td>
<td>~2</td>
<td>~70 %</td>
</tr>
<tr>
<td>3rd cycle</td>
<td>~2</td>
<td>~97 %</td>
</tr>
<tr>
<td>4th cycle</td>
<td>~2</td>
<td>~95 %</td>
</tr>
<tr>
<td>5th cycle</td>
<td>~2</td>
<td>~90 %</td>
</tr>
<tr>
<td>6th cycle</td>
<td>~2</td>
<td>~96 %</td>
</tr>
<tr>
<td>7th cycle</td>
<td>~2</td>
<td>~95 %</td>
</tr>
</tbody>
</table>

$^{[a]}$ Percentage recovery of $G'$ taking the value from the previous cycle as 100 %.
The morphologies of these thixotropic gels before and after the destruction-recovery processes were investigated by POM. Based upon the POM images and PXRD diffractograms, the SAFiNs of these gels are crystalline; as mentioned, few gels with crystalline SAFiNs are thixotropic.64 Before the initial application of the destructive strain, the DODA gel SAFiNs consisted of bundles of fibrillar objects (Figure 4.27). After the destruction-recovery process, only some of the bundles remained. These observations and the very rapid recovery rates indicate that the application of destructive strain results in loss of contact between fiber bundles (retaining 1D objects), but not reversion to 0D objects (such as unassociated or small aggregates of DODA molecules).64 As discussed above, the PXRD diffractions of the single crystal and SAFiN structures of DODA imply that the extended α-diketo dipole-dipole interactions are prevalent in both, and are one of the dominating driving forces for SAFiN formation. We hypothesize that α-diketo dipole-dipole interactions at their junction zones are disrupted primarily, leaving 1D fiber bundles that are no longer in direct contact (Figure 4.28); contacts among the bundles are reestablished rapidly (albeit incompletely) after the cessation of the destructive strain.70 Although spherulites were not observed in the DODA gels, it has been hypothesized in a previous study that the destruction and reconnection between spherulites are crucial to the thixotropic behavior of gels with (R)-12-hydroxystearic acid (D-12HSA) as the gelator.70 In addition, the decreased number of bundles observed in the POMs after recovery is consistent with the lower values of the storage modulus. The re-establishment of inter-fiber connections may not be very efficient in DODA gels because α-diketo dipole-dipole interactions are weaker than H-bonding between hydroxyl groups that are available in assembles of D-12HSA and some of its derivatives, (where ~90 % recovery has been achieved).64,70,279
Figure 4.27 POMs at room temperature of gels consisting of 5 wt % DODA in 1-octanol (a,d), silicone oil (b,e), and benzonitrile (c,f) before (a,b,c) or after a destruction-recovery process (d,e,f).

Figure 4.28 Schematic representation of a possible mechanism for thermal- and mechano-destruction and reformation of SAFiN s in DODA gels.
4.4 Conclusions

A supramolecular gel system consisting of one of several liquids and a modified fatty acid with an $\alpha$-diketo functionality, DODA, has been developed. It exhibits reversible, hypsochromically-shifted emission and viscoelastic properties that can be modulated mechanically or thermally. Of special note is the thixotropic nature of many of the DODA gels; few molecular gels with crystalline SAFiNs are known to be thixotropic. DODA is found to form mechanically stronger gels, in a broader range of liquids, at lower CGCs and with longer lifetimes, than the analogous gelator with one carbonyl group, 10-KSA. The single crystal structure and PXRD results of the gels suggest an anti-conformation for the $\alpha$-diketo group and bilayered, extended packing arrangements of DODA molecules within their SAFiNs. This arrangement promotes inter-molecular, attractive, dipole-dipole interactions that are more extensive than with 10-KSA. Although fiber formation is favored for the $\alpha$-diketo derivative, the absence of H-bonding among the head groups of the corresponding methyl ester, DODE, results in very inefficient gelator efficiency. In fact, the importance of the head group interactions is clear from the fact that both DODA and 10-KSA are able to gel several liquids whereas DODE was unable to gelate any of the ones that were examined here.

In addition to the structural insights, the DODA gels demonstrated some interesting physical properties. For example, gelation of DODA could be induced by both the thermal and mechanical stimuli. We hypothesize that the destruction and reformation of the SAFiNs in DODA gels depend principally upon dipole-dipole interactions that are either inter-molecular (during thermally stimulated changes) or inter-fiber (during mechanical stimulated changes) in nature. Upon being heated (i.e., during thermal destruction), the networks of inter-molecular dipole-dipole interactions within the SAFiNs are lost and the DODA molecules dissociate into
0D objects. Upon being cooled, the DODA molecules within the solutions/sols aggregate through dipole-dipole and H-bonding interactions, thus reforming the SAFiNs. Concurrent with the thermal formation or destruction of the SAFiNs is a reversible ~25 nm shift in the emission maximum. That change has been exploited to probe the kinetics of the aggregation and de-aggregation processes. Also, changes in the temperature at which the solutions/sols are incubated (below the gel melting temperature) produce a gradual morphological change in and different formation modes for the SAFiNs that were detected in POMs and in the emission spectra.

In contrast to the thermal process, we hypothesize that the mechano-destruction of gels of DODA occurs principally through a loss of the α-diketo dipole-dipole interactions between fiber bundles in the SAFiNs. That is, destruction of the gels involves conversion of the 3D networks into 1D fibers or into bundles of aggregates that have lost contact with their neighbors; the very rapid reformation of the gels after the cessation of destructive shear occurs as the connectivities are reestablished.

In sum, the results reported here should aid in the design of subtly modified molecular gelators to create other mechano-responsive, thermal-reversible gels in which the emission can be modulated significantly. It offers a new approach to the construction of systems with aggregation-induced emission.\textsuperscript{211,212}
5 MECHANO-SWITCHABLE, LUMINESCENT GELS DERIVED FROM SALTS OF A LONG-CHAIN, FATTY-ACID GELATOR

5.1 Introduction

As discussed in Section 1.3, stimulus-responsive molecular gels, specifically mechano-responsive molecular gels, have attracted considerable attention for their numerous potential and realized applications. However, very few mechano-responsive molecular gels have crystalline SAFiN. Metallo-gels with reversible metal-ligand coordination are one of the most common classes of such crystalline molecular gels. However, most of the metallo-gelators have complicated ligand structures, and understanding the design principles to make new metallo-molecular gelators with simple ligand structures that can respond reversibly to mechanical stimuli remains a formidable challenge. In that regard, it would be useful to be able to compare the properties of gels made from several metallo-molecular gelators with simple ligand structures in which only the metal ion is changed. Here, we report such a study.

Metal salts of derivatives of long-chain, naturally-occurring fatty acids are one potential source of such gelators. Thus, the gelating properties of some metal salts of stearic acid (SA) and (R)-12-hydroxystearic acid (D-12HSA) have been explored previously and summarized in Section 1.2. Those studies demonstrate that the gelator efficiency depends dramatically on the nature of the metal-carboxylate interactions. In Chapter 4, we reported that gels of 9,10-dioxooctadecanoic acid (DODA), a gelator derived from OA with an α-diketo group, in 1-octanol, benzonitrile and silicone oil are thixotropic, but with only partial recovery of their viscoelastic properties. In addition, we found that some DODA-based gels exhibit emission spectra that are blue-shifted with respect to those of their sol phases by ~25 nm as a result of enhanced aggregation.
Here, five metal salts of DODA—calcium(II) 9,10-dioooctadecanoate (DODA-Ca), copper(II) 9,10-dioooctadecanoate (DODA-Cu), nickel(II) 9,10-dioooctadecanoate (DODA-Ni), and its monohydrate (DODA-Ni • H$_2$O), and zinc(II) 9,10-dioooctadecanoate (DODA-Zn)—have been investigated as metallo-gelators (Scheme 5.1). The gelation efficiency, as well as the mechano-response to destructive strain and the luminescent properties of the gels, can be modulated dramatically by the nature of the metal ions (i.e., how they influence the self-assembly of the gelators and, thus, their SAFiNs). Clearly, the morphologies and the molecular packing arrangements of these metallo-gelators are important factors in controlling the different gelation behaviors and thixotropic properties. Overall, the results provide a facile strategy for the design of luminescent materials with controllable mechano-responsiveness by modifying the metal ions within the fibrillar assemblies. The work described in this chapter has been published.\textsuperscript{284}

\textbf{Scheme 5.1} Structures of salts examined as metallo-gelators derived from DODA.

\begin{center}
\includegraphics[width=\textwidth]{Scheme_5.1.png}
\end{center}

\textbf{9,10-dioooctadecanoic acid metal salts}

DODA-M • x H$_2$O, M=Ca$^{2+}$, Cu$^{2+}$, Zn$^{2+}$, Ni$^{2+}$

x=0, DODA-Ca, DODA-Zn, DODA-Cu, DODA-Ni

x=1, DODA-Ni • H$_2$O
5.2 Experimental Section

5.2.1 Materials

DODA was prepared according to the procedure described in Chapter 4.\textsuperscript{263} Triethylamine (Alfa Aesar, 99 %), nickel(II) chloride hexahydrate (Alfa Aesar, 98 %), cupric chloride dihydrate (J. T. Baker Chemical, >99 %), zinc chloride (Fisher Scientific, 98.6 %), calcium chloride (Fisher Scientific, anhydrous, >96 %) were used as received. All solvents and other chemicals used for syntheses and gelation studies are listed in Chapter 2.

5.2.2 Instrumentation and sample preparation

5.2.2.1 Preparation of samples and their preliminary classification

Most of the samples used for gelation tests were prepared by the fast-cooling process as described in Chapter 2. The anhydrous sample of 5 wt % DODA-Ni in toluene was prepared as follows: DODA-Ni • H\textsubscript{2}O (6.5 mg) was placed in a glass capillary (4 mm i.d.); the capillary was purged with nitrogen and evacuated 3 times (20 mmHg) before being heated at 100-105 °C for 10 min under vacuum (20 mmHg); then, 130 mg toluene that had been dried according to a literature method\textsuperscript{236} was added to the capillary under a nitrogen atmosphere, and the tube was flame-sealed. The hot solution/sol was placed in an ice-water bath for 10 min and finally kept at room temperature for 1 h.

5.2.2.2 SAXS and WAXS

SAXS and WAXS experiments were carried out using a Xeuss 2.0 system at Xenocs headquarters in Sassenage, France. Measurements were performed using a Pilatus 300K detector at a sample-to-detector distance of 2451.3 mm. An exposure time of 1 min was first applied to
screen the samples, and 10 min were used thereafter to improve signal-to-noise ratios. SAXS data were collected using the ‘Very High Resolution’ mode to achieve a $q_{\text{min}} = 0.0025$ Å$^{-1}$ and $q_{\text{max}} = 0.17$ Å$^{-1}$ with a nominal $\Delta q$ resolution of 0.00029 Å$^{-1}$. Simultaneous WAXS measurements provided an increased $q$ range covering 1.0 to 3.0 Å$^{-1}$. The neat powder sample and the liquid sample used for the gel were flame-sealed in glass capillaries (W. Müller, Schönwalde, Germany) 1.5 mm optical thicknesses. The gel sample was prepared by flame-sealing a hot solution/sol in one of the glass capillaries and allowing it to cool to room temperature. The diffraction peaks of the gels were identified by subtracting empirically the diffractograms of the liquids from those of the gels. The gel diffraction intensities were then normalized using glassy carbon as a secondary standard.

Steady-state excitation, emission studies, and rheological measurements were conducted as described in Chapter 4. Other common instrumentation and general procedures are listed in Chapter 2.

5.2.3 Syntheses

The metal salts were synthesized from DODA, triethylamine, and a metal chloride—nickel(II) chloride hexahydrate, cupric chloride, zinc chloride, or calcium chloride (Scheme 5.2).
9,10-dioxooctadecanoic acid (DODA)

\[
\text{DODA-} \cdot \text{Ni} \cdot \text{H}_2\text{O} : \text{DODA} (303 \text{ mg, 0.97 mmol}) \text{ was dissolved in 3 mL of chloroform. Triethylamine (98 mg, 0.96 mmol) was dissolved in 0.5 mL of chloroform separately and it was added to the DODA solution dropwise. The mixture was stirred for 3 h. Nickel(II) chloride hexahydrate (115 mg, 0.48 mmol) was dissolved in 0.5 mL methanol and added dropwise. The mixture was further stirred overnight and the solvent was removed under a stream of nitrogen at room temperature. The residual solid was stirred sequentially in ethyl acetate (5 mL), water (5 mL), and methanol (2 × 5 mL) for 30 min each and then vacuum filtered to yield 206 mg (61 \%) of DODA-Ni \cdot \text{H}_2\text{O}, a green solid that did not melt below its decomposition temperature (139 °C, Figure 5.1). IR (\nu_{\text{max}}/ \text{cm}^{-1}): 2922, 2849 (\text{C-H stretching}), 1711 (\alpha\text{-diketone, } \text{C=O stretching}), 1558 (\text{COONi, C=O asymmetric stretching}), \text{ and } 1408 (\text{COONi, C=O symmetric stretching}). \text{ Elemental analysis (\%}) \text{ calculated for } \text{C}_{36}\text{H}_{64}\text{O}_9\text{Ni}: \text{ C, 61.81; H, 9.22; N, 0.00; found: C, 61.93; H, 9.23; N, 0.06.}
\]

9,10-dioxooctadecanoic acid metal salts
DODA-M \cdot x \text{H}_2\text{O}, M=\text{Ca}^{2+}, \text{Cu}^{2+}, \text{Zn}^{2+}, \text{Ni}^{2+}
x=0, \text{DODA-Ca, DODA-Zn, DODA-Cu}
x=1, \text{DODA-Ni-H}_2\text{O}

\text{Scheme 5.2 Syntheses of DODA-M \cdot xH}_2\text{O.}

\text{DODA-Ca: DODA} (367 mg, 1.18 mmol) \text{ was dissolved in 3 mL of chloroform. Triethylamine (125 mg, 1.23 mmol) was dissolved in 0.5 mL of chloroform separately and it was
added to the **DODA** solution dropwise. The mixture was stirred for 3 h. Calcium (II) chloride (67 mg, 0.60 mmol) was dissolved in 0.5 mL methanol and added dropwise. The mixture was further stirred overnight and the solvent was removed under a stream of nitrogen at room temperature. The residual solid was stirred sequentially in ethyl acetate (5 mL), water (5 mL), and methanol (2 × 5 mL) for 30 min each and then vacuum filtered to yield 138 mg (35 %) of **DODA-Ca**, a yellow solid that did not melt below its decomposition temperature (130 °C, Figure 5.1). IR (υ_{max}/ cm\(^{-1}\)): 2922, 2848 (C-H stretching), 1711 (α-diketone,\(^{268}\) C=O stretching), 1572 (COOCa, C=O asymmetric stretching), and 1436 (COOCa, C=O symmetric stretching). \(^1\)H NMR (DMSO-d\(_6\), 400 MHz) chemical shifts (ppm): 2.64-2.68 (t, 4H, -CH\(_2\)C(=O)C(=O)-CH\(_2\)-, J = 8 Hz), 2.04-2.08 (t, 2H, CH\(_2\)-COOH, J = 8 Hz), 1.40-1.46 (m, 6H, -CH\(_2\)CH\(_2\)C(=O)C(=O)CH\(_2\)CH\(_2\)- and -CH\(_2\)-CH\(_2\)-COOH), 1.10-1.30 (m, 16H, CH\(_2\)-CH\(_2\)), 0.82-0.85 (t, 3H, CH\(_3\), J = 6 Hz). Elemental analysis (%) calculated for C\(_{36}\)H\(_{62}\)O\(_8\)Ca: C, 65.22; H, 9.43; N, 0.00; found: C, 65.50; H, 9.07; N, 0.10.

**DODA-Zn**: **DODA** (300 mg, 0.96 mmol) was dissolved in 3 mL of chloroform. Triethylamine (102 mg, 1.00 mmol) was dissolved in 0.5 mL of chloroform separately and it was added to the **DODA** solution dropwise. The mixture was stirred for 3 h. Zinc(II) chloride (68 mg, 0.48 mmol) was dissolved in 0.5 mL methanol and added dropwise. The mixture was further stirred overnight and the solvent was removed under a stream of nitrogen at room temperature. The residual solid was stirred sequentially in ethyl acetate (5 mL), water (5 mL), and methanol (2 × 5 mL) for 30 min each and then vacuum filtered to yield 230 mg (69 %) of **DODA-Zn**, a pale yellow solid that did not melt below its decomposition temperature (134 °C, Figure 5.1). IR (υ_{max}/ cm\(^{-1}\)): 2919, 2848 (C-H stretching), 1711 (α-diketone,\(^{268}\) C=O stretching), 1544 (COOZn, C=O asymmetric stretching), and 1407 (COOZn, C=O symmetric stretching). \(^1\)H NMR (DMSO-
$d_6$, 400 MHz) chemical shifts (ppm): 2.65-2.67 (t, 4H, -CH$_2$C(=O)C(=O)-CH$_2$-, $J = 8$ Hz), 2.03–2.07 (t, 2H, CH$_2$-COOH, $J = 8$ Hz), 1.40-1.46 (m, 6H, -CH$_2$CH$_2$C(=O)C(=O)CH$_2$CH$_2$- and -CH$_2$-CH$_2$-COOH), 1.10-1.30 (m, 16H, CH$_3$-CH$_2$), 0.82-0.85 (t, 3H, CH$_3$, $J = 6$ Hz). Elemental analysis (%) calculated for C$_{36}$H$_{62}$O$_8$Zn: C, 62.82; H, 9.07; N, 0.00; found: C, 62.73; H, 9.27; N, 0.12.

**DODA-Cu**: DODA (322 mg, 1.03 mmol) was dissolved in 3 mL of chloroform. Triethylamine (107 mg, 1.05 mmol) was dissolved in 0.5 mL of chloroform separately and it was added to the DODA solution dropwise. The mixture was stirred for 3 h. Cupric chloride dihydrate (90 mg, 0.52 mmol) was dissolved in 0.5 mL methanol and added dropwise. The mixture was further stirred overnight and the solvent was removed under a stream of nitrogen at room temperature. The residual solid was stirred sequentially in ethyl acetate (5 mL), water (5 mL), and methanol (2 × 5 mL) for 30 min each and then vacuum filtered to yield 328 mg (48 %) of DODA-Cu, which did not melt below its decomposition temperature (125 °C, Figure 5.1). IR ($\nu_{\text{max}}$/ cm$^{-1}$): 2920, 2848 (C-H stretching), 1711 (α-diketone, C=O stretching), 1587 (COOCu, C=O asymmetric stretching), and 1414 (COOCu, C=O symmetric stretching). Elemental analysis (%) calculated for C$_{36}$H$_{62}$O$_8$Cu: C, 62.99; H, 9.10; N, 0.00; found: C, 62.85; H, 9.34; N, 0.14.

**5.2.4 Attempts to grow single crystals**

A variety of attempts to grow single crystals of DODA salts suitable for X-ray diffraction were made. Due to the low solubilities of the DODA salts in common solvents, slow evaporation and vapor diffusion methods were unsuccessful. Liquid diffusion methods were attempted as well. Thus, 0.008 mol/L solutions of each metal chloride (nickel(II) chloride hexahydrate, cupric chloride dihydrate, zinc chloride, and calcium chloride) were prepared in 1 mL of deionized
water, DMF, methanol, and ethanol, and each was placed in an NMR tube. Separately, DODA
(40 mg, 0.08 mmol) and triethylamine (13 mg, 0.10 mmol) were dissolved in 8 mL of methanol
or chloroform. After 30 min, 1 mL of the solution of deprotonated DODA was added carefully
with minimal disturbance to each NMR tube, so that a liquid-liquid interface was created on the
top of the solution of metal chloride. The mixtures precipitated at the interface, became
suspensions, or remained solutions after three weeks. Overall, these attempts were unsuccessful
although the crystal structure of DODA was successfully solved and the data are presented in
Chapter 4.263

5.3 Results and Discussion

5.3.1 Thermal stability of the salts

Before testing the gelating abilities of the salts, their thermal stabilities were evaluated by
TGA measurements (Figure 5.1). All of the DODA metal salts prepared started to decompose
between 125 and 140 °C (Figure 5.1). Thus, all of the DODA-M • xH₂O were heated no higher
than 120 °C during gelation studies. There was an additional weight loss (2.61 wt %) for DODA-
Ni • H₂O at 70-100 °C that is consistent with the expected weight loss (2.60 wt %) for a
monohydrate. This amount of water was also consistent with the results from the elemental
analysis.
**Figure 5.1** Weight loss as a function of temperature by TGA for DODA-M • xH₂O neat solids.

### 5.3.2 Gelation behavior and physical properties.

The gelation properties of samples with 5 wt % of each DODA salt in a wide variety of organic liquids are summarized in Table 5.1. The metal salts tend to have a stronger driving force for aggregation than the parent acid, and most of them have lower solubilities in most of the liquids examined.²⁶³ DODA-Ca and DODA-Zn are inefficient gelators: DODA-Ca did not dissolve in any of the liquids tested and DODA-Zn formed 3D objects that precipitated without
forming SAFiNs even at 1 wt % concentrations. In contrast, DODA-Cu and DODA-Ni • H₂O formed gels in a similar range of liquids as DODA. For example, DODA-Cu gelated carbon tetrachloride and aromatic liquids. DODA-Ni • H₂O formed gels with a wide range of organic liquids, including aromatic liquids, long-chain alcohols, ethyl acetate, and alkanes. However, after removing the one water molecule of hydration, the anhydrous DODA-Ni was no longer able to gelate liquids such as toluene, CCl₄, or decane (Figure 5.2). Thus, the water molecule in the nickel salt complex plays an important role in the formation of its SAFiNs.

Table 5.1 Appearances, Tₙ values (°C) of gels with 5 wt % gelator [in brackets], and CGCs (wt %) in different liquids.[a][b]

<table>
<thead>
<tr>
<th>liquid</th>
<th>DODA-Zn</th>
<th>DODA-Ca</th>
<th>DODA-Ni • H₂O[c]</th>
<th>DODA-Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHCl₃</td>
<td>P</td>
<td>I</td>
<td>I</td>
<td>P</td>
</tr>
<tr>
<td>CCl₄</td>
<td>Sus</td>
<td>I</td>
<td>S</td>
<td>TG [68-70], 0.8±0.1</td>
</tr>
<tr>
<td>toluene</td>
<td>Sus</td>
<td>I</td>
<td>CG [42-44], &lt; 1.4</td>
<td>TG [60-62], 1.2±0.2</td>
</tr>
<tr>
<td>benzonitrile</td>
<td>P</td>
<td>I</td>
<td>CG [50-52], &lt; 1.8</td>
<td>OG [52-55], 1.3±0.2</td>
</tr>
<tr>
<td>chlorobenzene</td>
<td>Sus</td>
<td>I</td>
<td>S</td>
<td>OG [55-57], 1.4±0.2</td>
</tr>
<tr>
<td>nitrobenzene</td>
<td>Sus</td>
<td>P</td>
<td>CG [42-45], &lt; 3.0</td>
<td>OG [66-69], 1.5±0.1</td>
</tr>
<tr>
<td>1-octanol</td>
<td>Sus</td>
<td>P</td>
<td>OG [46-48], &lt; 2.0</td>
<td>Sus</td>
</tr>
<tr>
<td>ethanol</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>P</td>
</tr>
<tr>
<td>ethyl acetate</td>
<td>P</td>
<td>I</td>
<td>OG [52-54], &lt; 2.0</td>
<td>P</td>
</tr>
<tr>
<td>decane</td>
<td>I</td>
<td>I</td>
<td>OG [81-83], &lt; 1.5</td>
<td>I</td>
</tr>
</tbody>
</table>
Table 5.1 (cont.)

<table>
<thead>
<tr>
<th>liquid</th>
<th>DODA-Zn</th>
<th>DODA-Ca</th>
<th>DODA-Ni • H₂O[c]</th>
<th>DODA-Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetonitrile</td>
<td>I</td>
<td>I</td>
<td>I</td>
<td>P</td>
</tr>
<tr>
<td>water</td>
<td>I</td>
<td>I</td>
<td>I</td>
<td>I</td>
</tr>
</tbody>
</table>

[a] OG = opaque gel, CG = clear gel, TG = translucent gel, S = solution, P = precipitate, I = insoluble, Sus = suspension; see Chapter 2 for details. [b] Gels formed over periods of a few hours to a few days depending on the gelator concentrations when they were below 5 wt %; the appearances of the samples during the CGC tests were recorded 5 days after their preparation. [c] Data for DODA-Ni are not included in the table; they are described in the text.

Figure 5.2 Appearance of a mixture of (a) 5 wt % DODA-Ni • H₂O in toluene and (b) 5 wt % DODA-Ni in dry toluene.
Figure 5.3 Log-log plots of strain sweeps (a, frequency = 1Hz) and angular frequency sweeps (b, strain = 0.01 %) for gels of 5 wt % DODA (■,□), DODA-Cu (▲,△), and DODA-Ni • H₂O (●,○) in benzonitrile. G’ are closed symbols and G’’ are open symbols.

Table 5.2 G’, G’’, loss tangent (at 0.01 % strain), and yield strains of gels with 5 wt % gelator in benzonitrile.

<table>
<thead>
<tr>
<th>gel</th>
<th>G’’ (Pa)</th>
<th>G’ (Pa)</th>
<th>loss tangent</th>
<th>yield strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DODA[a]</td>
<td>930±160[a]</td>
<td>6800±370[a]</td>
<td>0.14±0.03[a]</td>
<td>5[a]</td>
</tr>
<tr>
<td>DODA-Cu</td>
<td>290±40</td>
<td>2900±50</td>
<td>0.10±0.02</td>
<td>25</td>
</tr>
<tr>
<td>DODA-Ni • H₂O</td>
<td>30±10</td>
<td>700±30</td>
<td>0.04±0.01</td>
<td>28</td>
</tr>
</tbody>
</table>

[a] From ref 263.

The CGCs of the DODA-Cu and DODA-Ni • H₂O gels were lower and the gel melting temperatures were higher than those of DODA in the same liquids. Also, the yield strains during the strain sweeps were significantly higher for gels of 5 wt % DODA-Cu and DODA-Ni • H₂O in benzonitrile than for the gels of 5 wt % DODA in benzonitrile (Figure 5.3 and Table...
5.2), and the loss tangent values of DODA-Cu and DODA-Ni • H$_2$O gels were much lower than that of the corresponding DODA gel (Figure 5.3 and Table 5.2). These observations indicate that gels made from the salts are mechanically stronger than the DODA gels; the metal-ligand interactions gained by adding copper(II) or nickel(II) cations clearly improve the physical properties of the gels.

Overall, the change of the carboxylic acid head group into a carboxylate with a metal cation greatly reduces the solubility of DODA and aids its aggregation. However, whether SAFiNs form is dependent on the specific metal cation. In hard and soft (Lewis) acid and base (HSAB) theory, Ca$^{2+}$ is a “hard” acid, while Ni$^{2+}$, Cu$^{2+}$, and Zn$^{2+}$ are borderline acids, but softer than Ca$^{2+}$. Thus, DODA-Ca is expected to have more ionic character at its head group than the other salts. Also, according to Allred-Rochow electronegativity values, $\chi$Ca$^{2+}$ (1.04) is much lower than $\chi$Cu$^{2+}$ (1.75), $\chi$Ni$^{2+}$ (1.75), and $\chi$Zn$^{2+}$ (1.66), and the difference between $\chi$O$^{2-}$ and $\chi$Ca$^{2+}$ is much larger than that for Ni$^{2+}$, Cu$^{2+}$ and Zn$^{2+}$. Based upon these considerations, the stronger electrostatic forces and larger ionic character between a carboxylate and a metal ion appear to decrease its ability to be solvated efficiently by most of the organic liquids tested. Thus, the propensity of the calcium salt to form gels is limited. Working in concert, perhaps, with the electrostatic arguments are the differences in molecular packing arrangements imposed by the metal ions (vide infra).

5.3.3 Viscoelastic recovery studies

As reported in Chapter 4, gels of 5 wt % DODA in benzonitrile are thixotropic; $\sim$30 % of the original $G'$ value was recovered after the cessation of destructive strain (i.e., after return to conditions in the LVR). Here, 5 wt % DODA-Cu and DODA-Ni • H$_2$O gels in benzonitrile
also regained some or all of their viscoelasticity after being transformed into their sol phases by destructive strain. The evolution of $G'$ and $G''$, after applying a 100 % strain to the gels, was recorded (Figure 5.4). A gel of 5 wt % DODA-Ni • H$_2$O in benzonitrile fully recovered its original $G'$ value after the cessation of destructive strain; the recovery was reproducible during each of the 6 subsequent cycles and the recovery was very rapid. The evolution of the complex viscosity ($\eta^*$) of the gel of 5 wt % DODA-Ni • H$_2$O in benzonitrile, after applying a 100 % strain to the gel, also suggests the thixotropic nature of the gels (Figure 5.5). $\eta^*$ of the gel decreased upon application of destructive strain. After the cessation of destructive strain, the complex viscosity of the sample increased to the original value immediately. The recovery time, $\tau$, was calculated to be less than 3 s based on qualitative fits of the $G'$ data measured during the recovery periods to an exponential function (Equation 4.5, Figure 5.6). However, the recovery times reported are only approximations because very few points could be collected in the rising regions due to recovery being faster than the response time of our rheometer. A movie showing the destruction of a larger sample of this gel by vigorous mechanical stirring and then its recovery is presented in ref 279. The sample flowed when stirred and became a gel again within 30 s after the cessation of stirring (Figure 5.7).
Figure 5.4 $G'$ and $G''$ as a function of time and application of different strains to samples in benzonitrile of (a) 5 wt % DODA-Ni • H$_2$O and (b) a 5 wt % DODA-Cu at 20 ºC. LVR: $\gamma = 0.01$ %, $f = 1$ Hz; DS: $\gamma = 100$ %, $f = 1$ Hz. Rotational strain was kept at 0 % for 1 s before changing from DS to LVR conditions. Data points were collected every 1 s (DODA-Ni • H$_2$O) or 5 s (DODA-Cu) after the cessation of destructive strain.

Figure 5.5 Complex viscosity ($\eta^*$) as a function of time and application of different strains to samples in benzonitrile of 5 wt % DODA-Ni • H$_2$O at 20 ºC. LVR: $\gamma = 0.01$ %, $f = 1$ Hz; DS: $\gamma = $
100 \%, f = 1 \text{ Hz}. \text{ Rotational strain was kept at 0 \% for 1 s before changing from DS to LVR conditions. Data points were collected every 1 s after the cessation of destructive strain.}

\textbf{Figure 5.6} The best fit to a single exponential rise (blue line)\textsuperscript{150,281} for the recovery data of \(G'\) (dots; data averaged from 6 cycles, starting from the first cycle) for a gel of 5 wt \% DODA-Ni • H\textsubscript{2}O in benzonitrile at 20 ºC after cessation of destructive strain and return to the LVR condition.
Figure 5.7 Appearances of samples of 5 wt % DODA-Ni • H₂O in benzonitrile: (a) gel formed by cooling from the sol phase; (b) within 5 s after cessation of vigorous mechanical stirring by a submerged stir bar; and (c) 30 s after the cessation of stirring.

However, only ~20 % of the original $G'$ value was recovered after the initial application of destructive strain to a gel of 5 wt % DODA-Cu in benzonitrile. In the subsequent 5 cycles, $G'$ increased to ~50 % of the value after the first cycle. The best exponential fit of the $G'$ recovery data indicate a recovery time of less than 10 s for each cycle (Figure 5.8 and Table 5.3).\textsuperscript{150}

Figure 5.8 The best fit to a single exponential rise (blue lines)\textsuperscript{150,281} for the recovery data of $G'$ (dots) for a gel of 5 wt % DODA-Cu in benzonitrile at 20 °C after cessation of destructive strain
and return to the LVR condition. (a) Data collected from the first cycle. (b) Data averaged from 6 cycles, starting from the second cycle.

Although both gels of DODA-Cu and DODA-Ni • H₂O in benzonitrile are thixotropic, the viscoelasticities of the reformed networks are very different. The full recovery of viscoelasticity of the DODA-Ni • H₂O gel indicates that its mechanical properties from thermal formation are very similar to those of the mechanically reformed gel. However, similar to DODA gels in benzonitrile, the reformed network of the DODA-Cu gel is very weak. The low recovery percentage and the higher loss tangent value (Tables 5.2 and 5.3) of the reformed gel than those of the thermally formed gel suggest that the former gel is mechanically weaker. We speculate that the difference in the mechanical properties of the reformed gels is related to the different morphologies of the fibrillar objects and the interactions between them in their SAFiNs during the destruction-recovery process. This hypothesis will be examined further in the discussion of proposed models for molecular packing of the salts (vide infra).

Table 5.3 Thixotropic parameters related to gels of 5 wt % DODA-Cu and DODA-Ni • H₂O gels in benzonitrile: recovery times (τ), % of thixotropic recovery, and loss tangent after different numbers of LVR-DS cycles.

<table>
<thead>
<tr>
<th></th>
<th>τ (s)</th>
<th>% of thixotropic recovery[a]</th>
<th>loss tangent</th>
</tr>
</thead>
<tbody>
<tr>
<td>DODA-Ni • H₂O</td>
<td>&lt; 3</td>
<td>~100 %</td>
<td>0.04±0.03</td>
</tr>
<tr>
<td>average of all</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cycles</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DODA-Cu 1st cycle</td>
<td>&lt; 10</td>
<td>~20 %</td>
<td>0.13±0.03</td>
</tr>
<tr>
<td>DODA-Cu average of 6 cycles starting from the 2nd cycle</td>
<td>&lt; 5</td>
<td>~10 %</td>
<td>0.14±0.03</td>
</tr>
</tbody>
</table>

[a] Percentage recovery of G' taking the initial G' as 100 %.
5.3.4 Photophysical properties

The emission and excitation spectra of a gel of 5 wt % DODA-Ni • H₂O in 1-octanol at 25 °C and the corresponding sol at 80 °C (a temperature above the Tᵩ) were compared with those of a gel of 5 wt % DODA in 1-octanol at 25 °C and its sol at 45 °C (Figure 5.9). The similarities between the emission and excitation spectra observed for both the DODA-Ni • H₂O sol and the DODA sol suggest that the conformations of the α-diketo groups and the morph of the solute in the two sols are similar. An aggregation-induced ~25 nm blue shift in both the emission and excitation spectra from the DODA sol state to the gel state has been noted in Chapter 4. However, a similar shift in the emission and excitation spectra was not found between the DODA-Ni • H₂O sol and gel states (Figure 5.9). Only the intensity of the emission of the sol decreased with increasing temperature (Figure 5.10) due to the greater conformational flexibility of the long alkyl chains and the consequent increase in the rates of non-radiative relaxation modes available to the α-diketo groups. Also, there is no clear aggregation-induced shift in the emission and excitation spectra of the DODA-Cu gel state (Figure 5.11). The similarity in the emission and excitation spectra of these sol and the gel states (i.e., the absence of aggregation-induced changes in wavelength maxima in the emission and excitation spectra) suggests that the coordination of carboxylate groups of DODA with metal cations limits the α-diketo inter-molecular dipole-dipole interactions even when the gelator molecules are within their SAFiNs.
Figure 5.9 Emission (a) and excitation (b) spectra in 1-octanol of an aerated gel of 5 wt % DODA-Ni • H₂O at 25 °C (red, λₑₘ 481 nm, λₑₓ 425 nm), an aerated sol of 5 wt % DODA-Ni • H₂O at 80 °C (blue, λₑₘ 481 nm, λₑₓ 425 nm), an aerated gel of 5 wt % DODA at 25 °C (black, λₑₘ 458 nm, λₑₓ 400 nm), and an aerated sol of 5 wt % DODA at 45 °C (green, λₑₘ 481 nm, λₑₓ 425 nm).

Figure 5.10 Excitation (λₑₘ 481 nm) and emission spectra (λₑₓ 425 nm) of (a) an aerated gel of 5 wt % DODA-Cu in CCl₄ at 25 °C (black) and its sol at 70 °C (red); (b) an aerated gel of 5 wt % DODA-Ni • H₂O in 1-octanol at 25 °C (red) and its sol at 80 °C (red).
Figure 5.11 Normalized (a) emission and (b) excitation spectra of an aerated gel of 5 wt% DODA-Cu in CCl₄ at 25 °C (red, λₑₗ 481 nm, λₑₓ 425 nm), its sol at 70 °C (blue, λₑₗ 481 nm, λₑₓ 425 nm), an aerated gel of 5 wt% DODA in CCl₄ at 25 °C (black, λₑₗ 458 nm, λₑₓ 400 nm), and its sol at 45 °C (green, λₑₗ 481 nm, λₑₓ 425 nm).

5.3.5 Morphology studies at the micron range distance scale

In benzonitrile, 5 wt% DODA-Ni • H₂O and 5 wt% DODA-Cu form a translucent gel and a clear gel, respectively, whereas 5 wt% DODA forms an opaque gel at the same concentration. Unless there are contributions to the appearances from index of refraction matching, aggregates in clear gels are smaller than those in opaque gels. No distinctive features of the SAFiNs were observed in DODA-Cu and DODA-Ni • H₂O gels by POM, while fibrillar objects on a 50 um length scale were observed in the gel of DODA in benzonitrile. The absence of clear features indicates that the aggregates in DODA-Cu and DODA-Ni • H₂O gels are much smaller than those in the DODA gel (assuming that the SAFiN and liquid are not index of refraction matched).
Gels of 5 wt% DODA-Cu and DODA-Ni • H₂O in benzonitrile were then examined by AFM. However, interaction between the AFM tip and the sample was stronger than that between the glass substrate and the sample; as a result, no images with creditable features of the sample surface could be obtained. Many efforts have been made to optimize parameters used in AFM measurements, as described in Chapter 3, including tip selection, hydrophobic modification of the tips, and optimizations of setpoint, gain, and scan rate.

However, no real features of the sample surface could be obtained for either DODA-Cu gel or DODA-Ni • H₂O gel due to their low elasticities (\(G'\) of DODA-Cu ~2000 Pa and \(G'\) of DODA-Ni • H₂O ~700 Pa). The most common problem was that the tip became trapped in the sample after a soft-approach. As benzonitrile started to evaporate, the stickiness of the sample decreased and the tip began to image the surface of the sample. Figure 5.12 shows the AFM image recorded for DODA-Cu gel one hour after exposing the sample to air. The quality of the image is still very low with several artifacts (stripes and noise) even when being recorded using a very low gain value (~ 0.1) and a very slow scanning rate (~ 0.1Hz). The wet samples during the evaporation process are still too sticky to be imaged by AFM. In addition, the image recorded cannot reflect the morphology of the whole sample due to its inhomogeneous nature during the evaporation process. Thus, although the xerogel networks may or may not resemble those in the actual gels, AFM images were recorded for dried dilute sols (0.5 wt%) of DODA-Cu and DODA-Ni • H₂O in benzonitrile (Figure 5.13). The DODA-Cu sample exhibited clear, untwisted fibrillar features. The fibers were bundled and the diameters of the fibers ranged from 15 nm to 65 nm. Instead of fibers, sphere-like particles with 135±40 nm diameters were observed for the DODA-Ni • H₂O sample.
Figure 5.12 AFM image at room temperature of a gel of 5 wt % DODA-Cu in benzonitrile with 30×30 μm scanning area. The image was recorded 1h after the sample was prepared in an open system.
Figure 5.13 AFM images at room temperature of (a and b) a dried sol of 0.5 wt % DODA-Ni • H₂O in benzonitrile with (a) 5×5 μm and (b) 1×1 μm scanning areas; (c and d) a dried sol of 0.5 wt % DODA-Cu in benzonitrile with (c) 5×5 μm and (d) 1×1 μm scanning areas.
Figure 5.14 SAXS data for a gel of 5 wt % DODA-Ni • H₂O in benzonitrile. (a) Log-log plot of SAXS intensity as a function of $q$. The solid line is the theoretical curve for fractal polycore with block radius 20 Å, shell thickness 3.2 Å, fractal dimension 2.9, correlation length 375 Å, and block polydispersity 0.07. (b) A Kratky plot of data in the low $q$ region (0.0025-0.01 Å⁻¹) showing two limiting slopes for the low $q$ data points and one for the higher $q$ points.

In order to probe the morphology of the actual gel without removing the liquid at different distance scales, a SAXS experiment was conducted on the gel of 5 wt % DODA-Ni • H₂O in benzonitrile. A log-log plot of the SAXS data is presented in Figure 5.14a. The curve was fitted well to a fractal polycore model,²⁸⁸,²⁸⁹ which is consistent with a fractal, sphere-like morphology. The Porod exponent, calculated from the high $q$ region is 2.3 (Figure 5.15), is indicative of a branched gelator network.²⁹⁰,²⁹¹ The scattering profile exhibits a power law decay of the slope near -4 in the low $q$ range, which is typical of interfacial scattering by the grains.²⁹² From the slope change observed in a Kratky plot in the low $q$ range (Figure 5.14b),²⁹³,²⁹⁴ the DODA-Ni • H₂O gel consists of nanostructured aggregates with characteristic diameters in the 110-130 nm range.²⁹³ The range of diameters is a result of our uncertainty about which data points to include within the lower $q$ region to generate the straight line segment in Figure 5.14b.
and, perhaps the intrinsic dispersity of the objects. Regardless of which extreme value is chosen, it is within the range observed in the xerogel by AFM. Thus, the morphologies of the gel and xerogel for DODA-Ni • H$_2$O in benzonitrile appear to be the same or very similar.\(^a\)

**Figure 5.15** Porod plot of SAXS data in the high $q$ region (0.019-0.052 Å$^{-1}$) for a gel of 5 wt % DODA-Ni • H$_2$O in benzonitrile.

### 5.3.6 Molecular structures and packing arrangement

In the absence of single crystal structures for the metal salts, a combination of FT-IR and PXRD was used to gain information about the molecular structure and packing arrangements of the DODA salts in their SAFiNs. FT-IR spectra were recorded to probe the type of coordination

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\(^a\) The SAXS and WAXS of the corresponding DODA-Cu gel were not recorded due to our limited access to the Xenocs instrument.
between the carboxylate groups and metal ions within the neat solids (Figure 5.16) and the SAFiNs of the gelators in benzonitrile (Figures 5.17 and 5.18). A carboxylate group can coordinate to a metal ion in monodentate, bidentate or bridge-type arrangements. For all of the samples, a characteristic peak of an \(\alpha\)-diketo group was present at 1710 cm\(^{-1}\). Based upon the spectra of a wide range of compounds of known structure, some interesting empirical relationships have been established:\(^{295,296}\) a separation between the asymmetric and symmetric stretching bands of a carboxylate group between 150 (ionic value, 164-171 cm\(^{-1}\)) and 200 cm\(^{-1}\) indicates bridging; virtually all carboxylate complexes with a separation <150 cm\(^{-1}\) are chelating. On this basis, DODA-Ca, DODA-Cu and DODA-Ni • H\(_2\)O appear to have bridging carboxylate groups, while DODA-Zn may have chelating carboxylate groups (Table 5.4). Also, because the IR spectra of the benzonitrile gels of DODA-Cu and DODA-Ni • H\(_2\)O show asymmetric and symmetric stretching of the carboxylate groups like those of their neat salts, the coordination (bridging bidentate) of the gelators in their gel and neat states appear to be the same or very similar. The nearly identical appearances of the other parts of the FT-IR spectra of the gels (after empirical subtraction of the benzonitrile peaks) and the neat solids are less definitive but still suggestive of similar molecular packing arrangements within the two phases.
Figure 5.16 Vertically offset FT-IR spectra: (a) neat solids of DODA-Ca (red, I), DODA-Ni • H₂O (blue, II), DODA-Zn (pink, III), and DODA-Cu (black, IV).

Table 5.4 Wavenumbers of symmetrical and asymmetrical stretching bands of carboxylate groups, and the assigned major coordination modes (see main text) from FT-IR spectra of neat DODA salts and 5 wt % gels in benzonitrile.

<table>
<thead>
<tr>
<th></th>
<th>υ&lt;sub&gt;asym&lt;/sub&gt; OCO</th>
<th>υ&lt;sub&gt;sym&lt;/sub&gt; OCO</th>
<th>separation</th>
<th>coordination type</th>
</tr>
</thead>
<tbody>
<tr>
<td>DODA-Ca (neat)</td>
<td>1572 cm⁻¹</td>
<td>1409 cm⁻¹</td>
<td>163 cm⁻¹</td>
<td>Bridging</td>
</tr>
<tr>
<td>DODA-Zn (neat)</td>
<td>1544 cm⁻¹</td>
<td>1407 cm⁻¹</td>
<td>137 cm⁻¹</td>
<td>Chelating</td>
</tr>
<tr>
<td>DODA-Cu (neat)</td>
<td>1587 cm⁻¹</td>
<td>1414 cm⁻¹</td>
<td>173 cm⁻¹</td>
<td>bridging</td>
</tr>
<tr>
<td>DODA-Cu (gel)</td>
<td>1588 cm⁻¹</td>
<td>1415 cm⁻¹</td>
<td>173 cm⁻¹</td>
<td>Bridging</td>
</tr>
<tr>
<td>DODA-Ni•H₂O (neat)</td>
<td>1560 cm⁻¹</td>
<td>1410 cm⁻¹</td>
<td>150 cm⁻¹</td>
<td>Bridging</td>
</tr>
<tr>
<td>DODA-Ni•H₂O (gel)</td>
<td>1562 cm⁻¹</td>
<td>1412 cm⁻¹</td>
<td>150 cm⁻¹</td>
<td>Bridging</td>
</tr>
</tbody>
</table>
Figure 5.17 FT-IR spectra of (a) gels of 5 wt % DODA-Cu (black) in benzonitrile without empirical subtraction of the benzonitrile peaks and neat benzonitrile (red); (b) gels of 5 wt % DODA-Ni • H₂O (black) in benzonitrile without empirical subtraction of the benzonitrile peaks and neat benzonitrile (red).
Figure 5.18 Vertically offset FT-IR spectra: gels of 5 wt % DODA-Cu (black) and DODA-Ni • H$_2$O (red) in benzonitrile. The peaks from benzonitrile in the gel spectra have been subtracted empirically.

Molecular packing arrangements of the gelators in their neat solid states were studied further by PXRD (Figure 5.19). It was possible to calculate cell constants of the neat gelators through indexing of at least 15 diffraction peaks for each neat gelator, except for DODA-Ni • H$_2$O where only 7 peaks were available (Table 5.5). The indexed cell constants and the spacings ($d$, nm), calculated from the Bragg relationship, are collected in Table 5.5. Except for DODA-Ni • H$_2$O, the metal salts have $d$-spacings of peaks below 10° in 2θ following a progression ratio which is consistent with a lamellar organization (i.e., 1:1/2:1/3:1/4). The longest $d$-spacings of DODA-Ca (53.8 Å) and DODA-Zn (51.9 Å) are near the length of two extended DODA molecules with transoid $\alpha$-diketo groups, 50.6 Å (as reported in Chapter 4), and twice the van der Waals radius of a calcium(II) (ca. 1.26 Å) or a zinc(II) (ca. 0.74 Å) ion. Note, however, that the longest $d$-spacings of DODA-Ni • H$_2$O (46.9 Å) and DODA-Cu (47.4 Å)
Å), the two most efficient gelators, are much shorter than the calculated extended lengths, and are even shorter than the lengths of two DODA molecules alone. Molecular packing within the SAFiNs of DODA-Ca and DODA-Zn appears to be less interdigitated or involve DODA chains that are either less tilted or with fewer gauche bends than in DODA-Cu.

![Graph showing PXRD diffractograms](image)

**Figure 5.19** Vertically offset PXRD diffractograms of neat DODA-Ca (red, I), DODA-Zn (black, II), DODA-Cu (blue, III), and DODA-Ni • H₂O (green, IV), all crystallized from methanol. Inset: Magnified diffraction intensities as a function of d-spacings (nm) calculated from the Bragg relationship in the 14–59 nm region.
Table 5.5 Calculated lengths of extended gelator molecules ($L$), longest $d$-spacings, $d$-spacings ratios, and indexed crystallography data from PXRD peaks of neat DODA-Ni • H$_2$O, DODA-Cu, DODA-Zn, and DODA-Ca.

<table>
<thead>
<tr>
<th>gelator</th>
<th>crystal system</th>
<th>space group</th>
<th>unit cell dimensions, Å and degrees</th>
<th>longest spacing, Å</th>
<th>$L$, Å</th>
<th>$d$ spacing ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>DODA-Ca</td>
<td>orthorhombic</td>
<td>Pmma</td>
<td>23.1, 26.2, 53.1; 90, 90, 90</td>
<td>53.8</td>
<td>53.1</td>
<td>1:1/2:1/3:1/4:1/5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DODA-Zn</td>
<td>tetragonal</td>
<td>P4/n</td>
<td>18.9, 18.0, 52.0; 90, 90, 90</td>
<td>51.9</td>
<td>52.3</td>
<td>1:1/2:1/3:1/4:1/5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DODA-Cu</td>
<td>monoclinic</td>
<td>Pc</td>
<td>26.3, 48.0, 10.7; 90, 96, 90</td>
<td>47.4</td>
<td>52.4</td>
<td>1:1/2:1/3:1/4:1/5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DODA-Ni•H$_2$O</td>
<td>orthorhombic</td>
<td>Pnc2</td>
<td>49.0, 4.2, 26.1; 90, 90, 90</td>
<td>46.9</td>
<td>51.9</td>
<td>no progression</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>ratio identified</td>
</tr>
</tbody>
</table>

PXRD diffractograms of the neat powder and of 10 wt % gels in benzonitrile have been compared (Figure 5.20). The $2\theta$ values of the diffraction peaks of the SAFiNs match well those of the neat gelator for both DODA-Cu and DODA-Ni • H$_2$O. WAXS profiles of neat DODA-Ni • H$_2$O powder and of a 5 wt % gel in benzonitrile have been compared, as well (Figure 5.21). The $q$ value ($1.51$ Å$^{-1}$) of the main Bragg reflection peak of the SAFiNs matches well that of the neat gelator.$^1$ The packing arrangements of the gelator molecules in both the gel and neat powder states appear to be the same or very similar for both DODA-Cu and DODA-Ni • H$_2$O. However, the paucity of diffraction peaks collected for the DODA-Ni • H$_2$O SAFiNs makes this conclusion only tentative.
Figure 5.20 (a) PXRD diffractograms of: (a) neat DODA-Cu powder (I) and a gel of 10 wt % DODA-Cu in benzonitrile (II); and (b) neat DODA-Ni • H₂O powder (I) and a gel of 10 wt % DODA-Ni • H₂O in benzonitrile. The curves are offset along the linear Y-axis for the sake of clarity. The small negative peaks in panels a(II) and b(II) at ca. 17° are due to the imprecision in the empirical subtraction.

Figure 5.21 WAXS intensity as a function of q for neat DODA-Ni • H₂O powder (red, I) and a gel of 5 wt % DODA-Ni • H₂O in benzonitrile (black, II).
5.3.7 Models for molecular packing in the SAFiNs

As discussed above, the low solubility of DODA-Ca and its inefficient gelation behavior in organic liquids are thought to be related to the ionic character and strong electrostatic forces of its carboxylate-metal center. In addition, although packing within the neat solid and SAFiN of either DODA-Cu or DODA-Ni • H₂O is the same, the molecular packing arrangements between them are somewhat different. Based on comparisons with FT-IR literature values for salts of known structure and the FT-IR results for the metal salts examined here, as well as the powder X-ray diffraction data, possible molecular packing models for DODA-Cu and DODA-Ni • H₂O in their gel states and DODA-Zn in its suspension state have been produced (Figures 5.22 and 5.24).

Figure 5.22 Schematic representation of the proposed molecular packing arrangement for neat DODA-Zn.
Zinc(II), with no ligand field stabilization, typically forms tetrahedral complexes with ligands. A model consistent with this mode of complexation and the experimental data for DODA-Zn is presented in Figure 5.22. An analogous packing arrangement has been reported for crystals of zinc(II) cyanoacetate. No significant interaction is proposed between the metal-carboxylate centers. In addition, the large distance between the carbonyl carbon atoms on adjacent chains and the orientation of the carbonyl groups appear to limit the inter-molecular dipole-dipole interaction between the α-diketo groups of DODA-Zn. The limited propensity of this gelator to form SAFiNs may be attributed to the lack of a strong driving force for 1D growth from secondary interactions along the polymethylene chains.

Molecular packing models with pseudo-square-planar coordination are proposed for DODA-Cu and DODA-Ni • H₂O. They appear to be interacting pair-wise. Two copper ions in the DODA-Cu salt are coordinated in a pseudo-square-planar fashion to four carboxylate groups, with an additional weakly interacting axial ligand that is the carboxylate group from another dimeric species. In each dimeric species, two polymethylene chains are extended and the other two are in bent conformations (Figures 5.23 and 5.24). This model is based in part on the crystal structure of copper(II) decanoate, a molecule similar in structure to DODA-Cu. Copper(II) decanoate molecules are tilted with regard to the longest axis of the unit cell, and the longest d-spacing is shorter than the theoretical extended molecular length. A similar tilt may be present in the aggregates of DODA-Cu. In this model, the efficient gelating ability of DODA-Cu can be rationalized by the availability of metal ligand coordination interactions between dimeric species along the polymethylene chains (Figure 5.24). In addition, 1D fibers observed for copper(II) decanoate are consistent with the fiber-like morphology observed for DODA-Cu/benzonitrile xerogels.
Similarly, **DODA-Ni • H₂O** molecules are proposed to be packed as dimers consisting of two nickel ions coordinated in a pseudo-square-planar fashion to four carboxylate groups (Figures 5.23 and 5.24). In addition, each nickel ion is proposed to be coordinated weakly with one molecule of water. A similar packing arrangement has been reported for nickel(II) propanoate monohydrate.303 The nickel(II) propanoate molecules do not pack in layers, and there is no relationship between the longest \(d\) spacing and the calculated extended length of the molecule.303 In addition, the Bragg reflection peak at \(q = 1.51 \text{ Å}^{-1}\) in the WAXS profile of the **DODA-Ni • H₂O** gel corresponds to a distance of 4.1 Å. This distance is in excellent agreement with the shortest distance between the adjacent polymethylene chains (4.2 Å) in the crystal structure of nickel(II) propanoate monohydrate.303 It further supports the proposed packing arrangement of **DODA-Ni • H₂O** in its **SAFiNs**. The substantially better gelating ability of **DODA-Ni • H₂O** than that of anhydrous **DODA-Ni** seems to be related to the importance of inter-molecular H-bonding interactions between water and carboxylate groups and/or metal-water coordination interactions (Figure 5.24), although different solubility characteristics and a different molecular packing arrangement for the anhydrous salt may be important contributing factors.

**Figure 5.23** Schematic representation of the proposed dimeric molecular packing arrangement for neat **DODA-Cu** and **DODA-Ni • H₂O**. \(R\) represents a polymethylene chain.
The pseudo-square-planar coordination arrangements of both DODA-Cu and DODA-Ni • H₂O greatly increase the distance between carbon atoms of carbonyl groups on neighboring polymethylene chains within one dimeric species or between two dimeric species. Assuming that the packing of DOD-Cu is the same as in copper(II) decanoate, the shortest distance between the carbon atoms of carbonyl groups on neighboring chains (4.5 Å)³⁰⁰ of the same molecule will be C9 of the extended chain and C10 of the bent chain. Almost the same distance is calculated between the closest carbonyl carbon atoms on chains of neighboring molecules. The 4.5 Å of separation is larger than the sum of the length of a carbonyl bond and the van der Waals radii of a carbon atom with a sp² orbital (1.2 Å) and a carbonyl oxygen (3.2 Å).²⁷⁰ Thus, the carbonyl groups are expected to have very weak electronic interactions based upon this packing model. Similarly, the closest separation between carbonyl carbon atoms on neighboring chains for DODA-Ni • H₂O, based on the proposed packing arrangement, (4.4 Å) is too large for strong electronic interactions to occur. The resultant lack of interactions among α-diketo groups in the SAFiNs are consistent with the absence of aggregation-induced, blue-shifted emissions in the DODA-Cu and DODA-Ni • H₂O gels.
Figure 5.24 Schematic representation of proposed molecular packing arrangements and proposed mechanisms for mechano-destruction and reformation of SAFiNs in DODA-Cu and DODA-Ni • H₂O gels.

Thus, the emission characteristics, IR spectra and WAXS and PXRD data, when combined with single crystal structures of analogous molecules from the literature, support the proposed packing arrangements of DODA-Cu and DODA-Ni • H₂O in their SAFiNs.

Based on the proposed molecular packing arrangements, inter-molecular H-bonding and metal-ligand interactions are the dominant driving forces for formation of SAFiNs of DODA-Ni • H₂O and DODA-Cu, respectively. As discussed above, the recovery of viscoelasticity after the cessation of destructive strain was exceedingly rapid. The fast rates indicate that the 1D objects lose contact at the “junction zones” of their SAFiNs when subjected to destructive strain, but
they do not revert to 0D objects (such as isolated molecules or small aggregates).\textsuperscript{64,263} We hypothesize that some inter-molecular H-bonding or metal-ligand interactions, which join spherulitic objects (like those indicated in the DODA-Ni • H\textsubscript{2}O/benzonitrile xerogel by AFM and in the gel of 5 wt % DODA-Ni • H\textsubscript{2}O in benzonitrile by SAXS) or fibrillar objects (like those constituting the DODA-Cu/benzonitrile xerogel by AFM), are broken within the 3D networks, leaving disconnected 1D objects that can rejoin easily once the destructive strain ceases (Figure 5.24).\textsuperscript{70,178} The different degrees of recovery for DODA-Ni • H\textsubscript{2}O and DODA-Cu gels can be attributed to a combination of entropic factors (that do not allow all of the “junction zones” to be reformed), to the different morphologies of the objects constituting the gels before destruction (i.e., spherulites and fibers), or to different morphologies of the newly formed 3D networks. In that regard, and consistent with the much higher recovery rate for DODA-Ni • H\textsubscript{2}O than DODA-Cu gels, we have found circumstantial evidence from other systems\textsuperscript{33,64,70,128,181,263} that reconnection among spherulitic objects is more efficient than among fibrillar ones. Based solely on geometric considerations, the orientational requirements for spheres to interact effectively are less stringent than for linear objects.

5.4 Conclusions

We have characterized in detail a series of metallo-molecular gel systems consisting of metal salts of an $\alpha$-diketo derivative of a fatty acid, DODA, in a wide range of liquids. The mechano-responsive and luminescent properties of the gels can be modulated dramatically by the nature of the metal ion within fibrillar assemblies of the gel networks. Based upon analyses of the micro-morphology, nanostructure and molecular packing studies using SAXS, WAXS, PXRD, AFM, and FT-IR techniques, models for the molecular packing arrangements of the
gelators within their SAFiNs have been proposed. In addition, several of the gels display thixotropic behavior; relatively few examples of molecular gels with crystalline SAFiNs are known to be thixotropic.

The metal cations aid aggregation of DODA molecules. Thus, DODA-Cu and DODA-Ni • H₂O form mechanically stronger gels, at lower CGCs and with higher thermal stability, than does DODA at the same wt % concentrations and in the same liquids. The molecular packing models for the SAFiNs suggest that inter-molecular H-bonding interactions and metal-ligand interactions are the crucial driving forces for gel formation of DODA-Cu and DODA-Ni • H₂O, respectively. The better gelating ability in the metal salt gels can be attributed to the stronger H-bonding and metal-ligand interactions than the α-diketo dipole-dipole interactions and carboxylic acid head-group association that are available in assembles of DODA. Although aggregation is favored for metal salts, the gelation ability differs dramatically based upon the nature of the metal cations. More ionic metal carboxylate interactions, stronger electrostatic interactions, and the absence of an overriding driving force for one-dimensional growth along the polymethylene chains of DODA-Ca and DODA-Zn result in lower gelator efficiencies compared to DODA-Cu and DODA-Ni • H₂O.

In addition, the nature of the metal cation modulates other physical aspects of the gels, including their luminescent and thixotropic properties. We hypothesize that these differences depend principally upon variations in molecular packing arrangements of the gelators in their SAFiNs. One manifestation is that the metal cations increase the closest distance between carbon atoms on neighboring polymethylene chains, thus limiting α-diketo inter-molecular and inter-chain dipole-dipole interactions. As a consequence, the emission and excitation spectra do not change their overall appearances upon passing from their sol-to-gel phases. The rapid
reformation of SAFiNs (i.e., the gel phases) after the cessation of destructive strain is hypothesized to occur through reestablishment of inter-fiber or inter-spherulite connections. The different degrees of recovery of the viscoelastic properties depend acutely on the different abilities of ‘junction zones’ between the fibers or spherulitic objects to reestablish strong contacts.

Overall, the results provide a facile approach to the design of mechano-responsive, luminescent metallo-materials by modifying the molecular packing arrangements within the fiber assemblies. Clearly, similar studies in which very small structural changes, different from the ones explored here, and with other luminescent molecules are needed in order to refine further the models presented.
6 GELATING ABILITIES AND STRUCTURES OF AMMONIUM SALTS OF A LONG-CHAIN AND UNSATURATED FATTY ACID

6.1 Introduction

Thus far, the gelating properties have been investigated for different series of molecular gelators in which minor additions and deletions of functional groups have been introduced on long-chain, naturally-occurring fatty acids.

In this Chapter, ricinelaicid acid (D-REA) and in the presence of group stoichiometric amounts of \( n \)-alkylamines or alkane-\( \alpha,\omega \)-diamines are investigated as molecular gelators. The \textit{cis}-double bond of the naturally-occurring isomer of D-REA, ricinoleic acid (D-RA), forces a structural bend along the octadecenyl chain that precludes easy crystallization, and increases the fluidity of cell membranes in which it is incorporated.\textsuperscript{304} D-RA has a melting temperature of 5 \(^\circ\)C,\textsuperscript{234} and is, thus, an inefficient gelator. The melting point of D-REA is ca. 51 \(^\circ\)C, and we find that it is a much more efficient gelator because it is able to adopt a linear and extended conformation. To date, only vegetable oil gels of D-REA appear to have been examined and without delving into the specific structure-property correlations of gelation mentioned in Chapter 1.\textsuperscript{117} A systematic study of D-REA in various of liquids is presented here.

Previous work with metal salts of fatty acids has included the sodium salt of (R)-12-hydroxystearic acid (D-12HSA) (see Chapter 1) and 9,10-dioxooctadecanoic acid (DODA) (see Chapter 5). In addition, the gelating abilities of ammonium carbamate salts derived from D-12HSA have been explored.\textsuperscript{70} Interestingly, some of these salts can form gels in an even broader range of liquids than their parent acids, while others were unable to form gels in any of the liquids examined. The electrostatic interactions of the charged centers of salts at the carboxylate head groups can introduce additional driving forces for aggregation and can significantly modify
the molecular packing of gelator molecules within their SAFiNs in different ways. By creating ammonium carboxylate head group interactions with various amines, as is done here, it is possible to modulate the electrostatic interactions incrementally, and thus, the packing arrangements within the SAFiNs of the gels. Formation of these ammonium salts opens opportunities to explore the influence of H-bonding interactions, London dispersive interactions, and, especially, electrostatic interactions on the self-assembly of fatty acid-derived gelators.

Scheme 6.1 Structures of gelators derived from D-RA.
6.2 Experimental Section

6.2.1 Materials

Ricinoleic acid (D-RA, 89 %; Wako Chemical Co.) and diphenyl disulfide (>98 %; Technical Chemical Laboratories) were used as received. All solvents and other chemicals used for syntheses and gelation studies are listed in Chapter 2.

6.2.2 Syntheses

REA was synthesized by the diphenyl disulfide initiated photoisomerization of D-RA (Scheme 6.2).

**Scheme 6.2 Synthesis of D-REA.**

D-RA (1.621 g, 4.350 mmol) and diphenyl disulfide (mp 58.9-59.8 °C, 33 mg, 2.0 mmol) were dissolved in 40 mL of 1:19 (v:v) ethyl acetate:hexane in a pyrex test tube at 30 °C. Nitrogen was bubbled through the solution with stirring for 1h, the tube was capped, and the solution was stirred and irradiated for 3.5 h in a 45 ºC water bath 2 cm from a Hanovia 450-W medium-pressure mercury lamp. The coupling constant between the CH=CH protons in $^1$H-NMR was used to monitor qualitatively the progress of the reaction from aliquots removed at different times. After irradiation, the solution was poured onto ice and vacuum filtered. The solid was recrystallized twice from 3 mL of hexane to yield 0.476 g (29.4 %) of D-REA, mp 48.4-49.6 °C (lit:\textsuperscript{305} 51.0–51.5 °C). IR (υ max/ cm\textsuperscript{-1}): 3232 (broad, O-H stretching), 1691 (COOH, C=O
stretching) and 960 (trans C=CH out of plane bending). $^1$H-NMR (CDCl$_3$, 400 MHz) chemical shifts (ppm): 5.49-5.57 (dt, 1H, CH=CH, J =14.96 Hz, 7.23 Hz), 5.38-5.44 (dt, 1H, CH=CH, J=14.96 Hz, 7.23 Hz), 3.58-3.62 (m, 1H, CH-OH), 2.33-2.34 (t, 2H, CH$_2$-COOH, J = 7.5 Hz), 2.20-2.23 (m, 2H, -OH-CH-CH$_2$-CH=CH), 2.04-2.06 (m, 2H, CH=CH-CH$_2$-CH$_2$), 1.47 (m, 2H, -OH-CH-CH$_2$-CH$_2$), 1.29-1.32 (m, 18H, CH$_2$-CH$_2$), 0.87- 0.90 (t, 3H, CH$_3$, J = 6.6 Hz). Elemental analysis (%) calculated for C$_{18}$H$_{34}$O$_3$: C, 72.44; H, 11.48; N, 0.00; found: C, 72.27; H, 11.72; N, 0.10.

Ammonium ricinelaidates were synthesized in one step by mixing solutions of D-REA and amines in stoichiometric amounts (Schemes 6.3 and 6.4).

\[ \text{OH} \quad \text{CH=CH-CH$_2$-CH=CH} \quad \text{OH} + \quad \text{H}_2\text{N} \quad \text{C}_1 \quad \text{O} \quad \text{NH} \quad \text{H}_n \quad \text{n=2, 8, 16} \]

\[ \text{OH} \quad \text{CH=CH-CH$_2$-CH=CH} \quad \text{OH} \quad \text{O}^- \text{H}_3\text{N} \quad \text{C}_1 \quad \text{O} \quad \text{NH} \quad \text{H}_n \quad \text{n=2, 8, 16} \]

\n
\text{Scheme 6.3 Synthesis of alkylammonium ricinelaidates.}
**Scheme 6.4** Synthesis of alkane-α,ω-diammonium ricinelaidates.

**C4REA**: D-REA (306 mg, 1.03 mmol) was dissolved in 5 mL of ethyl acetate. 1-Butylamine (75 mg, 1.0 mmol) was dissolved in 1 mL of ethyl acetate separately and then added to the D-REA ethyl acetate solution dropwise with stirring. The mixture was stirred at room temperature for 24 h. A white precipitate was isolated by vacuum filtration and then washed three times with cold ethyl acetate to yield 234 mg (57 %) of C4REA, mp 57.0-58.9 °C. IR (ν_max/ cm⁻¹): 1583 (COO⁻, C=O stretching) and 960 (trans C=CH out of plane bending). ¹H-NMR (CDCl₃, 400 MHz) chemical shifts (ppm): 5.46-5.56 (m, H, CH=CH), 5.33-5.44 (m, H, CH=CH), 5.50-5.65 (s, NH₃⁺, broad), 3.55-3.59 (m, H, CH-OH), 2.74-2.78 (t, 2H, CH₂-COOH), 2.17-2.26 (m, 3H, -C(OH)H-CHH⁺-CH=CH and -CH₂NH₃⁺), 1.98-2.08 (m, 3H, -C(OH)H-CHH⁺-CH=CH-CH₂-), 1.28-1.46 (m, 24H, CH₂-CH₂), 0.84-0.87 (m, 6H, -CH₃). Elemental analysis (%) calculated for C₂₂H₄₇O₃N: C, 71.11; H, 12.21; N, 3.77; found: C, 70.96; H, 12.46; N, 3.76.
**C10REA**: D-REA (310 mg, 1.04 mmol) was dissolved in 5 mL of ethyl acetate. 1-Decylamine (164 mg, 1.05 mmol) was dissolved in 1 mL of ethyl acetate separately and then added to the D-REA ethyl acetate solution dropwise with stirring. The mixture was stirred at room temperature for 24 h. A white precipitate was isolated by vacuum filtration and then washed three times with cold ethyl acetate to yield 298 mg (62%) of C10REA, mp 64.0-65.7°C. IR (υ max/ cm⁻¹): 1568 (COO⁻, C=O stretching) and 960 (trans C=CH out of plane bending).

\[^1\text{H}\]-NMR (CDCl₃, 400 MHz) chemical shifts (ppm): 5.47-5.52 (m, H, CH=C₃H), 5.36-5.42 (m, H, CH=CH), 5.60-5.80 (s, NH₃⁺, broad), 3.55-3.57 (m, H, CH-OH), 2.69-2.72 (t, 2H, CH₂-COOH), 2.20-2.24 (m, 3H, -C(OH)H-CHH’-CH=CH and -CH₂NH₃⁺), 1.96-1.98 (m, 3H, -C(OH)H-CHH’-CH=CH-CH₂-), 1.46-1.49 (m, 2H, CH₂-C(OH)H), 1.33-1.42 (m, 4H, -CH₂-CH₂NH₃⁺, -CH₂-CH₂-COOH), 1.24-1.31 (m, 30H, C₈H₁₇), 0.84-0.87 (t, 6H, -CH₃). Elemental Analysis (%) calculated for C₂₈H₅₇O₃N: C, 73.79; H, 12.61; N, 3.07; found: C, 73.56; H, 12.93; N, 3.08.

**C18REA**: D-REA (125 mg, 0.419 mmol) was dissolved in 3 mL of ethyl acetate. 1-Octadecylamine (124 mg, 0.460 mmol) was dissolved in 1 mL of ethyl acetate separately and then added to the D-REA ethyl acetate solution dropwise with stirring. The mixture was stirred at room temperature for 24 h. A white precipitate was isolated by vacuum filtration and then washed three times with cold ethyl acetate to yield 196 mg (82%) of C18REA, mp 76.4-77.8°C. IR (υ max/ cm⁻¹): 1581 (COO⁻, C=O stretching) and 960 (trans C=CH out of plane bending).

\[^1\text{H}\]-NMR (CDCl₃, 400 MHz) chemical shifts (ppm): 5.49 (m, 1H, CH=CH), 5.40 (dt, 1H, CH=CH), 3.56 (m, 1H, CH-OH), 2.67-2.71 (s, NH₃⁺, broad and t, 2H, CH₂-COOH), 2.19-2.29 (m, 3H, -C(OH)H-CHH’-CH=CH and -CH₂NH₃⁺), 1.98-2.04 (m, 3H, -C(OH)H-CHH’-CH=CH-CH₂-), 1.58-1.61 (m, 2H, CH₂-C(OH)H), 1.23-1.42 (m, 46H, CH₂-CH₂), 0.87-0.90 (t, 6H, -CH₃).
Elemental analysis (%) calculated for C_{36}H_{73}O_{3}N: C, 76.13; H, 12.95; N, 2.47; found: C, 75.84; H, 13.22; N, 2.55.

12DREA: D-REA (220 mg, 0.738 mmol) was dissolved in 3 mL of ethyl acetate. Ethane-1,2-diamine (22 mg, 0.37 mmol) was dissolved in 1 mL of ethyl acetate separately and then added to the D-REA ethyl acetate solution dropwise with stirring. The mixture was stirred at room temperature for 24 h. A white precipitate was isolated by vacuum filtration and then washed three times with cold ethyl acetate to yield 168 mg (69 %) of 12DREA, mp 86.9-88.8 °C. IR (υ_{max} / cm\(^{-1}\)): 1511 (COO\(^{-}\), C=O stretching) and 960 (trans C=CH out of plane bending).

\(^1\)H-NMR (CDCl\(_3\), 400 MHz) chemical shifts (ppm): 5.47-5.54 (dt, 2H, CH=CH), 5.37-5.42 (dt, 2H, CH), 3.29-3.36 (s, NH\(^3^+\), broad), 3.53-3.58 (m, 2H, CH-OH), 2.92-3.00 (m, 4H, -CH\(_2\)NH\(^3^+\)), 2.18-2.24 (m, 6H, -C(OH)H-CHH\(^{'}\)-CH=CH and CH\(_2\)-COO), 1.97-2.07 (m, 6H, -CH\(_2\)-CH=CH and -C(OH)H-CHH\(^{'}\)-CH=CH), 1.24-1.59 (m, 40H, CH\(_2\)-CH\(_2\)), 0.87-0.90 (t, 6H, -CH\(_3\)). Elemental analysis (%) calculated for C\(_{38}\)H\(_{76}\)O\(_6\)N\(_2\): C, 69.47; H, 11.66; N, 4.26; found: C, 69.32; H, 11.66; N, 4.46.

14DREA: D-REA (173 mg, 0.580 mmol) was dissolved in 3 mL of ethyl acetate. Butane-1,4-diamine (28 mg, 0.31 mmol) was dissolved in 1 mL of ethyl acetate separately and then added to the D-REA ethyl acetate solution dropwise with stirring. The mixture was stirred at room temperature for 24 h. A white precipitate was isolated by vacuum filtration and then washed three times with cold ethyl acetate to yield 124 mg (62 %) of 14DREA, mp 73.9-75.6 °C. IR (υ_{max} / cm\(^{-1}\)): 1581 (COO\(^{-}\), C=O stretching) and 960 (trans C=CH out of plane bending).

\(^1\)H-NMR (CDCl\(_3\), 400 MHz) chemical shifts (ppm): 5.49-5.57 (dt, 2H, CH=CH), 5.38-5.44 (dt, 2H, CH=CH), 3.64-3.86 (s, NH\(^3^+\), broad), 3.58-3.62 (m, 2H, CH-OH), 2.77-2.80 (t, 4H, CH\(_2\)-COOH), 2.19-2.26 (m, 6H, -CH\(_2\)NH\(^3^+\), -C(OH)H-CHH\(^{'}\)-CH=CH), 1.99-2.09 (m, 6H, -CH\(_2\)-COOH), 2.19-2.26 (m, 6H, -CH\(_2\)NH\(^3^+\), -C(OH)H-CHH\(^{'}\)-CH=CH), 1.99-2.09 (m, 6H, -CH\(_2\)-COOH).
CH₂NH₃⁺, -C(OH)H-CHH’-CH=CH), 1.29-1.32 (m, 44H, CH₂-CH₂), 0.87-0.90 (t, 6H, -CH₃). Elemental analysis (%) calculated for C₄₀H₈₀O₆N₂: C, 70.13; H, 11.77; N, 4.09; found: C, 69.84; H, 12.00; N, 3.92.

18DREA: D-REA (158 mg, 0.530 mmol) was dissolved in 3 mL of ethyl acetate. Octane-1,8-diamine (38 mg, 0.26 mmol) was dissolved in 1 mL of ethyl acetate separately and then added to the D-REA ethyl acetate solution dropwise with stirring. The mixture was stirred at room temperature for 24 h. A white precipitate was isolated by vacuum filtration and then washed three times with cold ethyl acetate to yield 108 mg (57 %) of 18DREA, mp 87.8-89.2 °C. IR (υ max/cm⁻¹): 1579 (COO⁻, C=O stretching) and 960 (trans C=CH out of plane bending). 

¹H-NMR (CDCl₃, 400 MHz) chemical shifts (ppm): 5.49-5.57 (dt, 2H, CH=CH), 5.38-5.44 (dt, 2H, CH=CH), 3.68-3.98 (s, NH₃⁺, broad), 3.58-3.62 (m, 2H, CH-OH), 2.77-2.80 (t, 4H, CH₂-COOH), 2.19-2.26 (m, 6H, -CH₂NH₃⁺, -C(OH)H-CHH’-CH=CH), 1.99-2.07 (m, 6H, -CH₂CH₂NH₃⁺, -C(OH)H-CHH’-CH=CH), 1.29-1.32 (m, 52H, CH₂-CH₂), 0.87-0.90 (t, 6H, -CH₃). Elemental analysis (%) calculated for C₄₄H₈₈O₆N₂: C, 71.30; H, 11.97; N, 3.78; found: C, 70.92; H, 12.16; N, 3.84.

6.3 Results and discussion

6.3.1 Gelation properties

The gelation properties of 5 wt % D-12HSA, D-REA, and ammonium ricinelaïdates in a wide range of organic liquids, are summarized in Table 6.1.
Table 6.1 Appearances, \[^{[a]}\] $T_g$ values ($^\circ$C) of fast-cooled gels with 5 wt % gelator, \[^{[b]}\] and CGCs (wt % in brackets) in different liquids. \[^{[c]}\]

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<tr>
<th>liquid</th>
<th>D-12HSA</th>
<th>D-REA</th>
<th>C4REA</th>
<th>C10REA</th>
<th>C18REA</th>
<th>D12REA</th>
<th>D14REA</th>
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<td>S</td>
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<td>P</td>
<td>GP</td>
<td>P</td>
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<td>GP</td>
</tr>
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<td>toluene</td>
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<td>S</td>
<td>S</td>
<td>PG</td>
<td>[OG 39-41,]</td>
<td>[OG 55-56,]</td>
<td>[TG 43-45,]</td>
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<td>S</td>
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<td>[0.30(0.05)]</td>
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<td>S</td>
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<td>[OG 54-56,]</td>
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<td>[OG 35-37,]</td>
<td>[Sus]</td>
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<td>CCl₄</td>
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</table>

[^a] OG = opaque gel, CG = clear gel, TG = translucent gel, S = solution, P = precipitated, I = insoluble, Sus = suspension, GP = gelatinous precipitate; see Chapter 2 for details. [^b] Based on the falling ball method. [^c] Numbers in parentheses are the error limits of the CGCs based upon the concentration increments shown. [^d] From ref 9.
**D-REA** formed gels in relatively low polarity liquids, such as alkanes and silicone oil. The only molecular structural difference between **D-REA** and **D-RA** is the configuration of the C=C bond. Here, **D-REA** is less soluble in most liquids examined and it is a much more efficient gelator than **D-RA**. The lower solubility can be attributed to the fact that the chains of *trans*-acids can pack and crystallize more easily than can the *cis* acids. Also, the data in Table 6.1 indicate that **D-REA** is more soluble than **D-12HSA** in many high and low polarity liquids. Gelation occurs only when the forces driving aggregation and solubilization are balanced. As a result, **D-REA** forms gels at higher CGCs and with lower thermal stabilities than does **D-12HSA**.

$T_g$s of the gels of **D-REA** in octane are plotted as a function of gelator concentration in Figure 6.1. $T_g$ increases as the gelator concentration increases up to the “plateau” region (ca. 4 wt %), where the basic structures and interactions of the SAFiN network are reasonably well established. DSC thermograms of neat **D-REA** and the corresponding 5 wt % gels in octane and silicone oil are shown in Figure 6.2. The reversibility of the SAFiNs and the thermal stability of **D-REA** are demonstrated by the reproducibility of the thermograms in several heating and cooling cycles. Both melting temperatures and enthalpies of the neat gelators are higher than those of their corresponding gels after concentration normalization because efficient solvation of the gelator molecules in the liquid component of the gels decreases the energy required to melt the SAFiNs. The much higher enthalpy of the gel of **D-REA** in octane than in silicone oil may be related to the different morphs of their SAFiNs (*vide infra*). Regardless, the higher CGC value in silicone oil means that, at the same total gelator concentration, a smaller fraction will be a part of the SAFiN.
Figure 6.1 $T_g$s of gels of D-REA in octane by the falling-ball method as a function of the concentration of D-REA. Vertical bars refer to the temperature range when the ball first penetrated the gel surface and when the ball touched the bottom of the tube as it was being heated.
Figure 6.2 DSC thermograms of neat D-REA, and gels of 5 wt % D-REA in silicone oil, or octane.
Table 6.2 $T_m$ or $T_{gm}$ (°C) and $T_c$ or $T_{gc}$ (°C) for neat D-REA or its gels, respectively and corresponding enthalpies (J/g) of transitions of neat D-REA or its 5 wt % gels (see Section 2.2 for a description of the normalization procedure) from DSC thermograms.[a]

<table>
<thead>
<tr>
<th></th>
<th>Heating</th>
<th>Cooling</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_m$ or $T_{gm}$</td>
<td>$\Delta H$</td>
</tr>
<tr>
<td></td>
<td>$T_c$ or $T_{gc}$</td>
<td>$\Delta H$</td>
</tr>
<tr>
<td>Neat</td>
<td>46.0</td>
<td>171</td>
</tr>
<tr>
<td></td>
<td>43.0</td>
<td>144</td>
</tr>
<tr>
<td>silicone oil gel</td>
<td>34.1</td>
<td>141</td>
</tr>
<tr>
<td></td>
<td>30.5</td>
<td>141</td>
</tr>
<tr>
<td>octane gel</td>
<td>42.2</td>
<td>121</td>
</tr>
<tr>
<td></td>
<td>40.5</td>
<td>77.2</td>
</tr>
</tbody>
</table>

[a] Averages of data from second and third heating and cooling cycles.

Both alkylammonium and alkane-$\alpha, \omega$-diammonium ricinelaidates, with various chain lengths, can form gels in a much wider range of liquids than the parent acid, D-REA. The superior gelation efficiency of the salts suggests that the added electrostatic interactions and H-bonding interactions in the salts, as well as the greater London dispersion forces from the ammonium groups, may be aiding the gelating ability. However, the salts were unable to gelate octane, although D-REA could. It appears that the increased polarity of the ionic pair in the ammonium salts decreases their ability to be solvated efficiently by low polarity liquids such as alkanes.

Based upon the range of liquids gelated and the CGC values, the gelating abilities of the salts improve with increasing alkyl chain lengths (Table 6.1). Within a single liquid, the $T_g$ values of the gels also increase as the chain of the alkyl ammonium salt becomes longer as a
result of the greater London dispersion interactions, reduced solubility, and the different molecular packing arrangements within the SAFiNs (vide infra).

However, there is no clear trend in gelation abilities among the three alkane-α,ω-diammonium salts. 14DREA appears to be a slightly more efficient gelator than the other two. It can form gels at lower concentrations than 12DREA and 18DREA, although the $T_g$ values of these gels are very similar in each of the liquids for which direct comparisons are possible.

### 6.3.2 Rheological properties.

The rheological properties of D-12HSA gels and D-REA gels in octane are compared in Figure 6.3. In order to ensure that the total amount of gelator in the SAFiN networks is the same, rheological studies were conducted at 4.3 wt % for the gels of D-12HSA in octane and 5 wt % for the gels of D-REA in octane, respectively; this concentration difference compensates for the differences in the CGC values of the two gelators. As indicated by the resistance of the octane gels to breaking at high strains, those with D-REA gels in octane are more brittle than those with D-12HSA (Figure 6.3a). The loss tangent and yield strain values (Table 6.3) further indicate that the presence of a double bond in the proximity of the 12-hydroxyl group in the D-REA gelator weakens the mechanical strength of the corresponding octane gel. In addition, the lower thermal-stabilities and the higher CGC values of D-REA gels than those of D-12HSA gels reinforces the conclusion that increasing unsaturation leads to SAFiNs whose gels are less robust.
Figure 6.3 Log-log plots of angular frequency sweeps (a; strain = 0.01 %) and strain sweeps (a; f = 1 Hz) at 25 °C for gels of 4.3 wt % D-12HSA in octane (■, □) and gels of 5 wt % D-REA in octane (▲, △). $G'$ are closed symbols and $G''$ are open symbols.

Table 6.3 Loss tangent (at 0.01 % strain) and yield strains of gels of 4.3 wt % D-12HSA in octane and gels of 5 wt % D-REA in octane at 25 °C.

<table>
<thead>
<tr>
<th>gelator</th>
<th>loss tangent</th>
<th>yield strain(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-12HSA</td>
<td>0.06</td>
<td>5.2</td>
</tr>
<tr>
<td>D-REA</td>
<td>0.24</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Comparative rheological studies have been conducted on the ammonium gelators of D-REA in nitrobenzene, a liquid in which the salts from all of the mono- and di-amines are able to form gels. As before, the concentrations of the gelators have been compensated for differences in the CGC values. Based upon data in Figure 6.4, the mechanical strength is the highest for the gel derived from the alkylammonium ricinelaicidate with the longest alkyl chain. The yield strain and loss tangent values are collected in Tables 6.4 and 6.5. The thermal stabilities also increase
with increasing alkyl chain length; greater London dispersion interactions appear to be responsible for the improvement of the physical properties of the gels and the gelation efficiencies. Although the nitrobenzene gels of the three alkane-\(\alpha,\omega\)-diammonium ricinelaidates exhibit similar loss tangent values, the gel with 14DREA has the highest yield strain (Table 6.5 and Figure 6.5). Considering the similarity in CGCs, mechanical strength, and \(T_g\)s of 12DREA and 18DREA, there is no clear correlation between the length of the linker between two carboxylates in the alkane-\(\alpha,\omega\)-diammonium salts and their gelation efficiencies.

Table 6.4 Loss tangents (at 0.01 % strain) and yield strains of gels of C4REA, C10REA, and C18REA in nitrobenzene at 25 °C.

<table>
<thead>
<tr>
<th>gelator</th>
<th>Concentration (wt %)</th>
<th>loss tangent</th>
<th>yield strain(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C4REA</td>
<td>6.3</td>
<td>0.29</td>
<td>0.79</td>
</tr>
<tr>
<td>C10REA</td>
<td>6</td>
<td>0.12</td>
<td>3.29</td>
</tr>
<tr>
<td>C18REA</td>
<td>5</td>
<td>0.06</td>
<td>57.4</td>
</tr>
</tbody>
</table>

Figure 6.4 Log-log plots of strain sweeps (a, frequency = 1Hz) and angular frequency sweeps (b, strain = 0.01 %) for gels of 6.3 wt % C4REA (■, □), 6 wt % C10REA (▲, △), and 5 wt % C18REA (●, ○) in nitrobenzene. G’ are closed symbols and G” are open symbols.
Figure 6.5 Log-log plots of strain sweeps (a, frequency = 1Hz) and angular frequency sweeps (b, strain = 0.01 %) for gels of 5 wt % 12DREA (■,□), 4.5 wt % 14DREA (▲,△), and 6.2 wt % 18DREA (●,○) in nitrobenzene. $G'$ are closed symbols and $G''$ are open symbols.

Table 6.5 Loss tangents (at 0.01 % strain) and yield strains of gels of 12DREA, 14DREA, and 18DREA in nitrobenzene at 25 °C.

<table>
<thead>
<tr>
<th>gelator</th>
<th>concentration (5 wt %)</th>
<th>loss tangent</th>
<th>yield strain(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12DREA</td>
<td>5</td>
<td>0.18</td>
<td>0.79</td>
</tr>
<tr>
<td>14DREA</td>
<td>4.5</td>
<td>0.17</td>
<td>35.6</td>
</tr>
<tr>
<td>18DREA</td>
<td>6.2</td>
<td>0.17</td>
<td>0.17</td>
</tr>
</tbody>
</table>

6.3.3 Morphologies from POM measurements.

Optical micrographs of 5 wt % fast-cooled gels of D-REA in silicone oil and in octane show different morphologies at the micron distance scales (Figure 6.6a,c). Also, the
microstructures of the fast- and slow-cooled gels are different in both octane and silicone oil (Figure 6.6a-d). In octane, the objects are spherulitic (fast-cooled) and rod-like (slow-cooled). In silicone oil, although the difference is less obvious, the objects from slow-cooling the sols are more fibrous. In order to investigate further the differences in the microstructures caused by the cooling protocols, gels of 5 wt % D-REA in octane were prepared by incubating their sols at several temperatures below $T_g$ (Figure 6.6e-h): the SAFiN structures from incubation at 0 °C are spherulitic and those at 30 °C are long fibers. As noted in other studies, 50,269,306 small fibers usually become longer and thicker as the incubation temperature is increased (and the driving force for phase separation is decreased), in addition to possible changes in the overall shapes. The observations here indicate that the relative rate of growth of branched fibers from a nucleation center is faster than that of growth of unbranched objects at 0 °C. With increasing incubation temperature, the relative rate of growth of branched fibers from a nucleation center becomes slower, and leads at 30 °C to long fibrous objects.

![Figure 6.6 POMs at 25 °C of gels of 5 wt % D-REA in (a) silicone oil after fast-cooling, (b) silicone oil after slow-cooling, (c) octane after fast-cooling and (d) octane after slow-cooling.](image)
and of gels of 5 wt % D-REA in octane after incubating at (e) 0 °C, (f) 10 °C, (g) 25 °C and (h) 30 °C.

The morphology of the SAFiNs in 5 wt % gels in nitrobenzene consists of spherulitic aggregates (C18REA) or long, fibrillar objects (C4REA and C10REA) (Figure 6.7). The thicker and larger fibrillary objects in the gels of C4REA and C10REA are consistent with weaker intermolecular interactions (i.e., London dispersion interactions) in their SAFiNs. POMs of 5 wt % gels of the diammonium salts in nitrobenzene consist of fibrillar objects whose diameters were 2-6 μm (12DREA) and 4-11 μm (14DREA) or spherulites (18DREA) (Figure 6.8).

Figure 6.7 POMs of fast-cooled gels consisting of 5 wt % gelator in nitrobenzene: C4REA (a); C10REA (b); and C18REA (c).

Figure 6.8 POMs of fast-cooled gels consisting of 5 wt % gelator in nitrobenzene: 12DREA (a); 14DREA (b); and 18DREA (c).
6.3.4 Molecular packing arrangements from PXRD data.

PXRD diffractograms of D-REA in its neat and fast-cooled 10 wt% in silicone oil and in octane gel states were recorded in order to probe the molecular packing arrangements at shorter distance scales of neat and (Figure 6.9). PXRD diffractograms of the neat ammonium ricinelaidsates and their 5 wt% fast-cooled gels in nitrobenzene were obtained as well (Figures 6.10 and 6.11). When a sufficient number of diffraction peaks were available, cell constants and Bragg spacings (d) of the neat gelators were calculated (Tables 6.6 and 6.7).\textsuperscript{9,20}

The d-spacings of the peaks below $10^\circ$ in $2\theta$ for D-REA and C18REA follow a progression ratio of 1:1/2:1/3:1/4, which is consistent with lamellar organizations.\textsuperscript{253} The longest d-spacings of D-REA (46.2 Å) and C18REA (49.9 Å) are near the lengths of the calculated extended molecules (47.2 Å, and 51.0 Å, respectively) including the van der Waals radii of the terminal hydrogens. Both D-REA and C18REA may pack in similar non-interdigitated bilayered arrangements (Figure 6.12a, b). However the longest d-spacings of C10REA (47.8 Å) and C4REA (49.6 Å) are much longer than the calculated extended molecular lengths. For that reason, we conjecture that these molecules may be arranged pairwise, with the long axes of neighboring molecules either antiparallel (Figure 6.12c) or parallel (Figure 6.12d). Of the two, the longest d-spacing of C10REA (47.8 Å) is more consistent with the calculated length of an antiparallel pair of molecules (46.5 Å),\textsuperscript{31} while the longest d-spacing of C4REA (49.6 Å) is more consistent with the calculated length of a parallel pair of molecules (49.6 Å).

Because the $2\theta$ values of the diffraction peaks of neat D-REA and in its SAFiN in octane are the same, they have the same packing arrangement.\textsuperscript{70,238} The relationship is not as clear for the silicone oil gel of D-REA because the peaks in its diffractogram are not very well defined and indicate a lower degree of crystallinity than in the octane gel. Also, the POMs of gels of D-
REA in silicone oil and in octane are clearly different (Figure 6.6). The POMs and PXRD data for these gels demonstrate that molecular packing arrangements in the two SAFiNs are different, and those differences are manifested in the better mechanical and thermal properties of the silicone oil gel. Although the diffraction patterns of the neat powder and nitrobenzene gel of C18REA are similar, those of C4REA and C10REA are not, and the diffraction peaks of these gels could not be indexed. Regardless, the $d$-spacings of the peaks with the lowest $2\theta$ value for these gels still match well the calculated extended molecular lengths from the proposed packing models in Figure 6.12.

Similarly, the $2\theta$ values of the diffraction peaks of the SAFiNs and the neat gelators match well for all three alkane-$\alpha,\omega$-diammonium salts (Figure 6.11); very similar packing arrangements are present in the SAFiNs and the neat powders. The longest $d$ spacings of 12DREA (1:1/2:1/3:1/4) and 14DREA (1:1/3:1/4:1/5) follow regressions that are consistent with lamellar packing arrangements; the absence of the 1/2 peak for 14DREA may be a consequence of interference phenomena or to the poor signal-to-noise of the diffractogram. Because the thicknesses of the layers are much less than the calculated extended molecular lengths (Figure 6.13 and Table 6.6), the molecules may be in bent conformations or their long axes may be tilted with respect to the layer planes. There is no identifiable regression for 18DREA, and its packing arrangement remains uncertain.
Figure 6.9 PXRD diffractograms of neat D-REA powder (blue), and its fast-cooled 10 wt % gels in octane (red) and in silicone oil (black).
Figure 6.10 PXRD diffractograms of neat powders (black) and 5 wt % nitrobenzene gels (red):

(a) C4REA; (b) C10REA; (c) C18REA.
Figure 6.11 PXRD diffractograms of neat powder (black) and 5 wt % fast-cooled nitrobenzene gels (red): (a) 12DREA; (b) 14DREA; (c) 18DREA.
Figure 6.12 Proposed packing arrangements of pairs of (a) D-REA; (b) C18REA; (c) C10REA; (d) C4REA molecules and their calculated lengths (including van der Waals radii of terminal atoms)\textsuperscript{251} after geometry optimization by MM2 and visualized by Avogadro.\textsuperscript{257}
Figure 6.13 Proposed packing arrangements of pairs of (a) 12DREA; (b) 14DREA; (c) 18DREA molecules and their calculated lengths (including van der Waals radii of terminal atoms)\cite{251} after geometry optimization by MM2 and visualized by Avogadro.\cite{257}
<table>
<thead>
<tr>
<th>Gelator</th>
<th>Crystal System</th>
<th>Space Group</th>
<th>Unit Cell</th>
<th>$d$ (Powder), Å</th>
<th>$d$ (Gel), Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-REA</td>
<td>orthorhombic</td>
<td>AMM2</td>
<td>9.6, 46.2, 7.3</td>
<td>23.6</td>
<td>46.2, 23.3, 15.3, 11.5, 8.6, 6.9, 5.8</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>octane gel: 46.2, 5.8, 4.8</td>
</tr>
<tr>
<td>C18REA</td>
<td>orthorhombic</td>
<td>P2₁2₁2</td>
<td>10.9, 16.9, 49.8</td>
<td>51.0</td>
<td>49.9, 25.0, 16.4, 7.02, 6.11</td>
</tr>
<tr>
<td>C10REA</td>
<td>tetrahedral</td>
<td>P422</td>
<td>20.6, 20.6, 46.9</td>
<td>40.6</td>
<td>47.8, 19.8, 14.7, 12.5, 9.8, 8.6, 7.3, 6.6, 6.2</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>47.3, 31.5, 18.0, 15.4, 0.9</td>
</tr>
<tr>
<td>C4REA</td>
<td>orthorhombic</td>
<td>Pmma</td>
<td>11.1, 9.1, 46.5</td>
<td>33.0</td>
<td>49.6, 23.4, 15.8, 10.9, 7.8, 6.8, 6.3, 5.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>50.0, 14.4, 9.7, 8.2</td>
</tr>
<tr>
<td>12DREA</td>
<td>monoclinic</td>
<td>C2</td>
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<td>54.7</td>
<td>44.4, 14.7, 11.1, 8.4, 7.0</td>
</tr>
<tr>
<td>14DREA</td>
<td>orthorhombic</td>
<td>Pmma</td>
<td>7.7, 8.7, 28.4</td>
<td>57.7</td>
<td>29.5, 14.2, 9.5, 8.3, 7.4, 6.8, 6.0, 5.7</td>
</tr>
<tr>
<td>18DREA</td>
<td>tetrahedral</td>
<td>I4</td>
<td>44.0, 44.0, 27.5</td>
<td>63.0</td>
<td>31.1, 16.1, 13.8, 11.1, 9.9, 8.0, 6.1, 5.3</td>
</tr>
</tbody>
</table>

[a] The gels of ammonium salts were prepared in nitrobenzene, whereas the ones of D-REA were prepared in octane or silicone oil. [b] Extended molecular lengths (including van der Waals radii of terminal atoms; Figures 6.12 and 6.13) were calculated after geometry optimization using MM2. [c] See Section 2.2 for details about unit cell indexing.
6.3.5 *H-bonding information from FT-IR spectra*

FT-IR was used to probe the type of H-bonding within the neat solid (Figures 6.14a) and the SAFiN phases (Figures 6.14b and 6.15) of D-REA and D-12HSA. In the neat solid state, the frequencies of the OH stretch of D-REA (~3330 and 3241 cm\(^{-1}\)) are higher than those of D-HSA (~3290 and 3200 cm\(^{-1}\)), indicating that the inter-molecular H-bonding interactions of D-REA are weaker.\(^{258,259}\) Based on FT-IR spectra, the same conclusion is reached for the comparative hydroxyl H-bonding strengths in the octane gels of D-REA and D-12HSA. The weaker inter-molecular interactions in the SAFiNs of D-REA may be responsible for the lower energy needed to melt or mechanically break the SAFiN network and the weaker SAFiN structures as indicated by the rheological data.

![Figure 6.14](image-url) Vertically offset FT-IR spectra showing relative peak transmittances: (a) neat D-REA (black) and D-12HSA (red); (b) fast-cooled gels of 5 wt % D-REA (black) and D-12HSA (red) in octane. In the gel spectra, the peaks attributable to the liquid component have been subtracted empirically, as described in Section 2.2.
Figure 6.15 Vertically offset FT-IR spectra showing relative peak transmittances of gels of 5 wt % D-12HSA (black) and D-REA (red) in octane without subtraction of the liquids.

Figure 6.16 Vertically offset FT-IR spectra showing relative peak transmittances: (a) neat C4REA (black), C10REA (red), and C18REA (blue); (b) neat 12DREA (black), 14DREA (red), and 18DREA (blue).

There is no discernible frequency difference between the OH stretching bands in the spectra of neat D-REA and C18REA; the strengths of their inter-molecular H-bonding
interactions are comparable. These data are consistent with the similarity of the non-interdigitated bilayered packing arrangements proposed on the basis of the PXRD data. Thus, the superior gelating ability of C18REA is assumed to be a consequence of its stronger London dispersive interactions and additional electrostatic interactions. However, the H-bonding stretching peaks of C4REA and C10REA appear at ~3400 cm⁻¹, which may correspond to weaker OH-OH or NH-OH H-bonding interactions (Figure 6.16). Based on the proposed antiparallel or parallel bilayered packing arrangement of the gelator molecules suggested by the PXRD data in the SAFiNs, the peaks at ~3400 cm⁻¹ probably are from NH-OH hydrogen bonded stretches. Regardless, the higher frequencies of the hydrogen bonded stretching peaks of C4REA and C10REA than those of C18REA imply that the H-bonding interaction of C18REA is stronger than that of C4REA and C10REA. Such stronger inter-molecular H-bonding interactions may be another reason why the SAFiN network of C18REA is more robust than those of C4REA and C10REA.

However, 12DREA, 14DREA, and 18DREA have very similar hydrogen-bonding OH stretching frequencies (Figure 6.16b). In addition, the similar stretching frequencies indicate that the strengths of their inter-molecular H-bonding interactions are like that of C18REA. This similarity and that in the range of liquids gelated support our hypothesis of similarly layered packing arrangements for 12DREA and 14DREA, proposed on the basis of the PXRD data. Furthermore, the FT-IR data indicate that the 12-hydroxyl groups of all three alkane-α,ω-diammonium salts interact inter-molecularly with the 12-hydroxyl group of another gelator molecule.
6.4 Conclusions

The trans-unsaturated fatty acid, D-REA, is a more efficient gelator than its cis- (and naturally occurring) isomer, D-RA. This observation is related to the fact that trans-unsaturated fatty acids typically exhibit higher melting temperatures and lower solubilities in most liquids than their corresponding cis-isomers. The ability of the D-REA chain to adopt an extended all-trans-like conformation—whereas D-RA cannot (due to the presence of its cis-double bond)—is a very important factor in explaining these observations: efficient packing of all-trans-like chains disfavors solubilization and is more conducive to aggregation, crystallization, and thus SAFiN formation.

However, D-REA is a weaker gelator than the saturated fatty acid, D-12HSA. Solubility of these gelators in many liquids increases with the degree of unsaturation. The same trends are found in alkane/alkene analogues and among a number of methyl esters of long-chain fatty acids (including methyl stearate and methyl oleate) in both high and low polarity solvents. In addition, the strength of the inter-molecular hydroxyl H-bonding interactions was weakened (according to FT-IR spectral data) by the introduction of a trans-double bond along the alkyl chain of D-12HSA (i.e., making D-REA).

The gelating abilities of both the alkylammonium and the alkane-α,ω-diammonium salts of D-REA are better than that of the parent acid, especially in high polarity liquids. Electrostatic interactions clearly aid aggregation and formation of SAFiNs. In addition, the increased London dispersion interactions afforded by the alkylammonium salts with longer chains aid formation of and stabilize SAFiNs. Surprisingly, our proposed packing models for the alkylammonium salts, based on the PXRD and the FT-IR results, predict that the packing arrangements of the gelators change with different alkyl chain lengths, and that C18REA favors the inter-molecular H-
bonding networks to a greater extent than does C4REA or C10REA. By contrast, the data indicate that the alkane-α,ω-diammonium salts with different linker lengths exhibit similar gelation efficiencies and similar strengths of inter-molecular H-bonding interactions. In addition, the similarity in the layered packing arrangements and the strengths of inter-molecular H-bonding interactions of the alkane-α,ω-diammonium salts and C18REA are suggested as the dominant reasons for their ability to form gels in a similar range of liquids. However, the reason for the slightly better gelation ability of 14DREA cannot be explained with the data currently in hand.

In sum, the results demonstrate that the degree of unsaturation and the stereochemical nature of the double bond along the C18 chain, the introduction of charge centers, and the length of the alkyl chains on the ammonium groups are key factors in controlling gelation efficiency for gelators derived from D-12HSA. These factors result in different packing arrangements, different strengths of the H-bonding interactions and different London dispersion interactions. Simple structure derivatization of the carboxylic acid groups, other than the formation of ammonium salts, is expected to yield additional insights and interesting gelators.
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