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Molecular Organogels. Soft Matter Comprised of Low-Molecular-Mass Organic Gelators and Organic Liquids†

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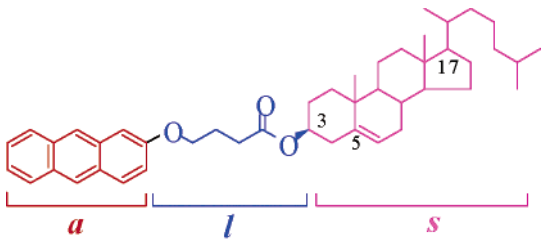
ABSTRACT
This Account presents recent advances in understanding how and why dilute solutions/sols of low-molecular-mass organic gelators (LMOGs) undergo microscopic phase separation to form self-assembled fibrillar networks in molecular organogels. Concepts are illustrated structurally at the subnanometer (molecular) to several millimeter (bulk) length scales and dynamically over time scales that follow the assembly of supersaturated solutions/sols into gel phases. Examples include both structurally complicated (**ALS** molecules with **a**romatic, **l**inking, and **s**teroidal groups) and simple (*n*-alkanes or *n*-alkanes along whose chains a hetero-group has been inserted) LMOGs in a wide range of organic liquids.

A. Introduction

Molecular gels, one type of soft matter, have generated enormous interest recently for basic scientific and technological reasons: many can be cycled thermoreversibly with their free-flowing sols by heating above and cooling below a characteristic temperature, T_g, that is related to the super-saturation temperature;[1] they have potential applications involving nanomaterials (such as sensors, molecular electronics, and catalysts) and delivery or modification agents for paints, inks, cleaning agents, cosmetics, polymers, drugs, etc.[2,3] Before that potential can be realized fully, the relationship between the structures of low-molecular-mass organic gelators (LMOGs) and the structural (especially at shorter distance scales) and rheological properties of their self-assembled fibrillar networks (SAFINs)[2] must be understood much better. This Account highlights studies with one type of LMOG molecules containing **a**romatic−**l**inker−**s**teroid (**ALS**; see **CAB**, for example) groups and their gels with organic liquids. A similar but less extensive description of gels based on the structurally simplest LMOGs, derived from *n*-alkanes[4−6] and including the one with the lowest known molecular mass, *N,N*′-dimethylurea (MW 88),[7] is also presented.



CAB

Although there are many definitions of gels, none seems to encapsulate *all* of their properties. According to Flory,[8] a gel has a continuous structure with macroscopic dimensions that is permanent on the time scale of an analytical experiment and is solid-like in its rheological behavior below a certain stress limit. It is viscoelastic and comprised of an organic liquid (in organogels) or water (in hydrogels) as the major component and a low concentration of an immobilizing agent, a "gelator". As implied, any gel must develop a three-dimensional network that permeates its volume and remains stable within

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† Dedicated to Professor Giovanni Gottarelli on the occasion of his retirement from the Dipartimento di Chimica Organica "A. Mangini", Alma Mater Studiorum, Universita di Bologna.

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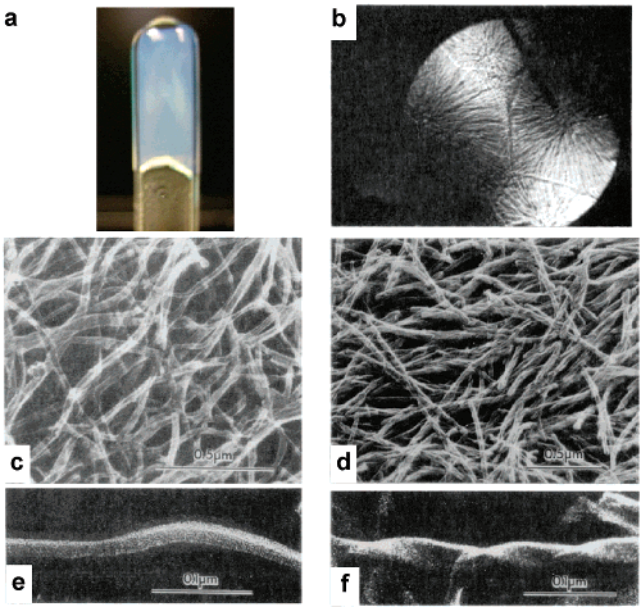


FIGURE 1. **CAB**/1-octanol (1.3 wt %) gel (a), optical micrograph of a 2.2 wt % **CAB**/*n*-dodecane gel (spherulite diameters ≈ 200 μm) (b), and electron micrographs of **CAB** gels in *n*-dodecane (2.2 wt %) (c,d) and 1-octanol (1.9 wt %) (e,f) showing SAFINs (c,e) and individual strands (d,f). Note the junction zone in panel f. Reprinted in part from ref 27 with permission. Copyright 1989 American Chemical Society.

specific ranges of concentration and temperature. In molecular gels, the networks immobilize their liquid component *macroscopically*, by surface tension and capillary forces,[9] even though liquid molecules are able to diffuse *microscopically* relatively freely. An attractive two-dimensional analogy is the *microscopic* movement of water molecules in droplets held in place by the network of a window screen.

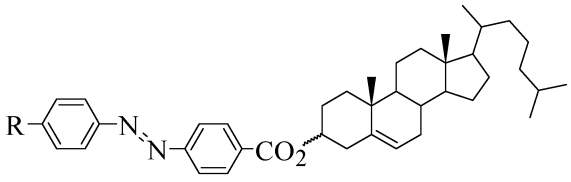
Formation of *polymer* gels progresses from gelating species that are initially held together topologically in at least one-dimension, usually by covalent bonds.[10] By comparison, LMOGs are topologically zero-dimensional objects as viewed on the micrometer scale, but they must possess anisotropy on the molecular scale, which permits specific modes of packing within the fibrillar objects of their three-dimensional SAFINs; an example of a SAFIN is shown in Figure 1 at different magnifications. It will be discussed in more detail in section C. Packing within fibers is determined by a balance among the same weak physical interactions (such as London dispersion forces, intermolecular H-bonding, electrostatic forces, and $\pi-\pi$ stacking[9a,b]) that control packing in bulk crystals or surfactant assemblies. Frequently, the degree of branching within a SAFIN increases with LMOG concentration.

Whereas "normal" crystallization leads to two- or three-dimensional objects, the fiber-like constituents of SAFINs must involve enhanced growth along one axis and severely attenuated growth along the other axes. The packing within the fibers may be amorphous or crystalline depending upon the LMOG[2] and even the liquid component of the gel.[11] Several models have been developed to explain the transition of amphiphilic LMOGs from their molecular to primary and secondary aggregate structures,[12−15] and some models developed for other purposes may be pertinent to gelation.[16,17] The small number of studies performed to date does not indicate a single mechanism for LMOG self-assembly; examples of spontaneous nucleation (where aggregates form at almost the same early time)[18−20] and continuous nucleation (where aggregates form throughout the micro-phase-separation process)[21,22] of LMOGs are known, and noncrystalline SAFINs undergo rapid fiber-making/breaking throughout the lifetimes of their gels.[23,24] Additional studies probing the mechanism of gelation are needed to understand the initial steps in transitions from solutions/sols to gels.

B. ALS Gelators

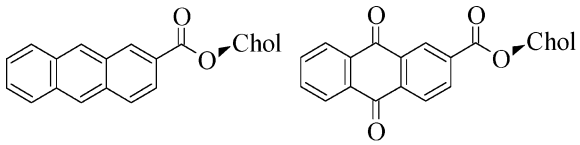
There are many types of LMOGs.[2,9] We focus here on **ALS** molecules because the extensive studies performed with them allow interesting comparisons and conclusions to be made; see **CAB** for structural designations and positions on the **S** part. For the purposes of this Account, the pragmatic factors dealing with gelator efficiency, including T_g, critical gelator concentration, range of liquids gelled, lifetime of gels at room temperature, etc., will not be treated explicitly here. They are addressed in the references cited and in several reviews.[2,9]

B.1. Shape Considerations. Generally, **ALS** molecules are more efficient gelators when they are rod-like in shape. Thus, gels from (rod-like) *trans*-**1** become sols upon UV

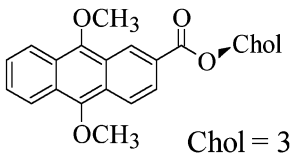


trans-**1** R = −O(CH$_2$)$_n$H, n = 1-5,10
−N((CH$_2$)$_n$H)$_2$, n = 1-3

irradiation as the azobenzene group (the **A** part) isomerizes to *cis*-**1** (bent).[25] The gel state is reestablished by reisomerization to the trans isomer. The efficiency of an **ALS** as a gelator also depends on the anomeric nature at C3 of the **S** part.[24,26] For example, the (more rod-like) β-anomer of *trans*-**1** gelates a wider variety of organic liquids the than the (more bent) α-anomer.[25] Also, none of the liquids gelated by **2a** could be gelated when its



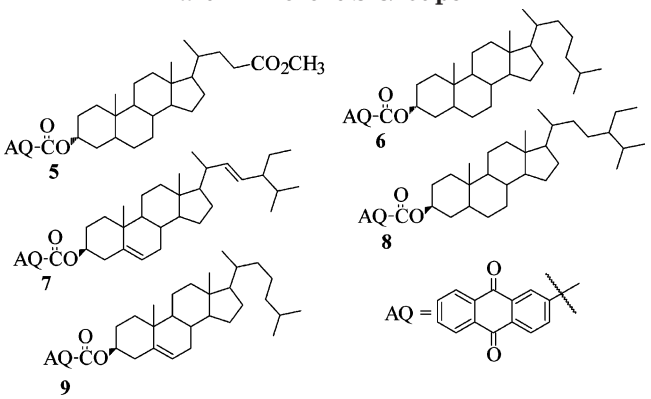
2a **2b**



Chol = 3β-cholesteryl

2c

Table 1. Gelation of Liquids by 2 wt % ALS Gelators with Different S Groups[a]



liquid	5	6	7	8	9	10[21]	11[21]
methanol	I	I	I	I			P
ethanol	I	I	I	I		I	G (3 wt %)
1-propanol	I	E				G*	G
1-butanol	P	E				G*	G
tert-butyl alcohol	I		I				
1-pentanol	P	E	G	G		G*	G
4-heptanol	P	E	G	G	G		
1-octanol	P	E	G	G		P	G
2-octanol	P	E	G	G			
1-decanol	P	P	G	G			
2-decanone		S	P	P			
n-hexane	I	P	I	I			
n-dodecane	I	P	G	G	G	G	PG
n-hexadecane	P	P	G	G		G	G
cyclohexane	I	P	G	B		G (3 wt %)	P (3 wt %)
benzene	S	S	S	S		S	S
styrene	S	S	S	S		S	
toluene	S	S	S	S			S
methyl acrylate			P	B			
methyl methacrylate			B	G			
acetonitrile			I	I			P
benzyl alcohol	P	P	G	G		P	G
ethyl acetate	P		I	I		P	G
CCl_4	S	S					
dichloromethane	S	S	P	S			
chloroform	S	S	S	S			S
silicone oil			P	G			

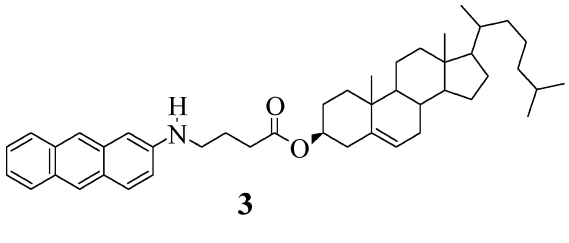
[a] See refs 26 and 27 for experimental details. B = broken gel; E = emulsion; G = gelation at room temperature; G* = gelation at less than −10 °C and gel stable at <0 °C; I = gelator insoluble or nearly so at boiling temperature of liquid; P = gelator precipitated upon cooling; S = solution/sol at room temperature.

2-anthryl **A** part was replaced by phenanthryl, pyrenyl, or 9-anthryl.[27] Also, the projections of the **A** and **S** parts with respect to each other are forced to be very different when odd and even numbers of methylene groups are in the **L** part and they are *all-transoid*.[28]

B.1.a. Aromatic Part (A). Molecules, such as the excellent gelator **CAB**, but in which the three linearly fused rings of the **A** part are truncated to 2-naphthyl or phenyl, are not LMOGs for reasons that probably involve diminished $\pi-\pi$ stacking. They form neat liquid-crystalline phases (as do many other **ALS** gelators[26,27,29,30]) but precipitate from or are soluble in organic liquids that are gelated by **CAB**.[26] However, if stacking of **A** parts leading to strong intermolecular interactions along one axis of a SAFIN fiber[31] is strongly promoted by electrostatic or other factors, **ALS** molecules that are not rod-shaped can still be good gelators.[25,28,32,33]

Although **2a** and **2b** gelate several organic liquids, **2c** (with a less rod-like and more electron-rich **A** part) does not. However, 1-octanol gels of **2b** become thixotropic (i.e., rheoreversible)[30] when a small amount of **2c** is added.[30] Charge transfer between the 9,10-anthraquinonyl and 9,10-dimethoxyanthyl groups enhances **A**−**A** interactions, and the **2b**/**2c** complexes are thought to reside preferentially at "junction zones" (i.e., where fibers of the SAFINs intersect; see Figure 1) for entropic reasons. When mechanical perturbations break the junction zones, the fibers are able to reassemble with time at points of high local charge transfer. Usually, significant thixotropy is found in gels with SAFINs that are not highly crystalline, such as giant worm-like micelles.[34,35] Creation of charge-transfer complexes near junction zones is one strategy to induce thixotropy in gels with highly crystalline SAFINs.[36]

B.1.b. Linker Part (L). The **L** group frequently contains an ester, ether, amide, urea, or carbamate functionality at one or both ends of a chain with zero to four CH_2 units.[25−28,37] As mentioned, the number of methylene units in the **L** part can be very important in controlling the overall **ALS** shape and, therefore, gelation efficiency. Usually, **L** parts with amide or carbamate groups are preferred because they are able to construct intermolecular H-bonding networks that add stability to the SAFINs. However, when the H-bonding network is not easily established for steric reasons or it leads to undesirable packing patterns for fiber growth, no gels are obtained.[30,36,37b,38] As a case in point, **3**, the analogue of **CAB** in which the ether oxygen



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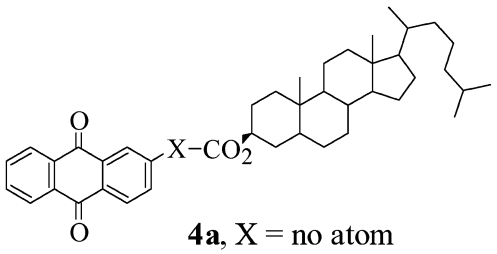


4a, X = no atom
4b, X = O

is replaced by a potential H-bond donor and acceptor (NH),[37b] is not a successful gelator, but replacement of the ether oxygen by an NR (R = bulky group!) does yield LMOGs.[39]

B.1.c. Steroid Part (S). There has been no comprehensive study of the relationship between **ALS** gelator efficiency and either the nature of **S** or even the length, branching, and functionality of the steroidal chain at C17. Table 1 contains some information on **ALS** molecules in which only the **S** groups differ. Although some molecules with long hydrocarbon chains that deviate from the C_8H_{17} tail of cholesterol are LMOGs,[26,37g] gelation has not been observed when an alkyl chain at C17 is very short.[27]

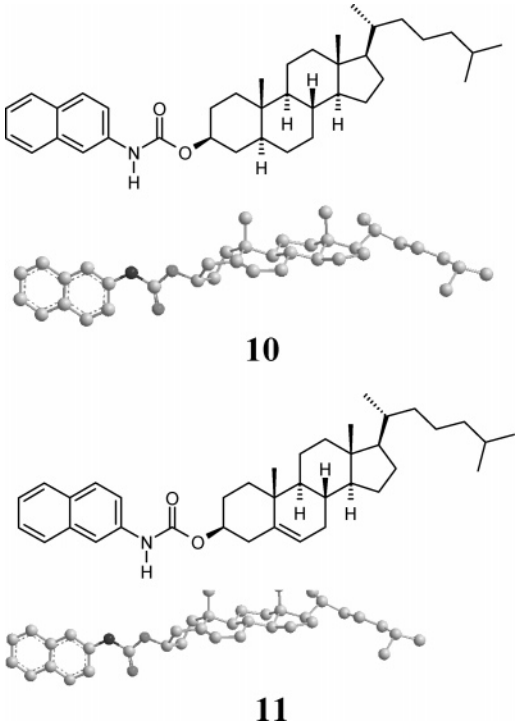


FIGURE 2. Compounds **10** and **11** with PM3-generated 3-D structures (H-atoms absent). Nitrogen and oxygen atoms are blue and red, respectively.

The data in Table 1 for LMOGs **10** and **11** exemplify how small changes in the **S** part can affect the gelating properties.[21] Although it is difficult to trace the specific reason(s) for these differences, the presence or absence of a double bond at C5 alters significantly the shape of the **S** group (Figure 2) and, therefore, how the molecules can pack in the SAFINs. However, the range of liquids gelated by each suggests that the presence or absence of a double bond at C5 has some influence on the overall solubility of these LMOGs. The generality of this conclusion will require additional investigation.

C. Formation and structures of SAFINs

Few insights into the packing of **ALS** molecules in their SAFINs have been possible from X-ray diffraction studies because the fibers themselves are too small for single-crystal analyses and their powder patterns frequently show that the morph responsible for the SAFIN and for a single crystal (when available) are not the same.[29] Synchrotron beams[40] and advanced computational methods[41] may eventually resolve the current analytical problems. For the same reason, caution is advised when recording electron diffraction images of SAFINs of xerogels (i.e., gels in which the liquid component has been removed) unless it can be established, as with cryo-TEM methods, that no phase change has occurred.[42]

Even more challenging is to follow the structural changes of LMOGs as they aggregate and transform sols into gels below T_g. SAFIN formation involves competition between dissolution of **ALS** molecules into the liquid component and phase separation (proceeding from aggregation and nucleation to precipitation into fiber-like objects). No *specific* liquid−gelator interaction has been identified during the transformation, and T_g depends mainly on the solubility of the gelator in the liquid.[37b]

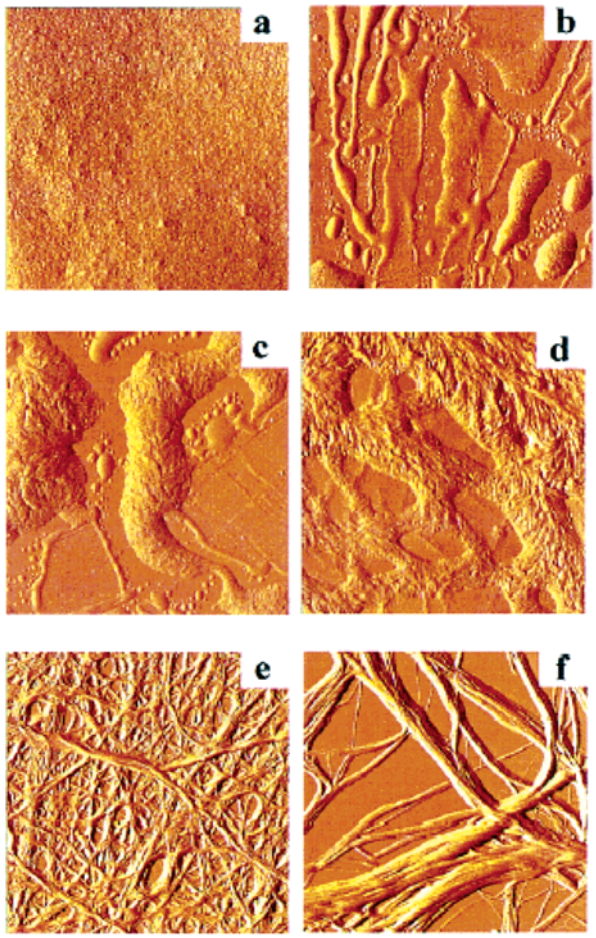
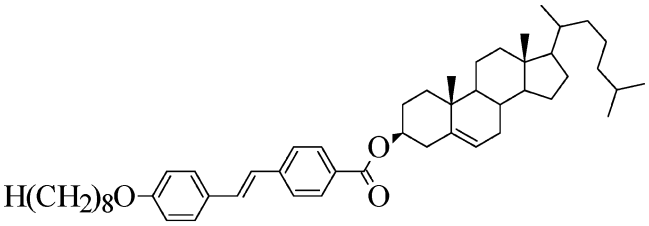


FIGURE 3. AFM images (12 × 12 μm^2) of 1.6 wt % **12**/1-octanol sol cooled to room temperature for (a) 0, (b) 10, (c) 15, (d) 18, (e) 21, and (f) 31 min. Reprinted with permission from ref 43. Copyright 2000 American Chemical Society.

In one of the very few studies of its kind, the temporal evolution of gels of **12** in different liquids was followed



12

by atomic force microscopy (AFM) (Figure 3).[37a,43] Gelation of 1.6 wt % **12**/1-octanol is initiated by dewetting from the hydrophobic graphite surface (Figure 3b), indicating that gelator−liquid interactions are enhanced. The eventual fibrous bundles in the SAFIN contain approximately 30% of liquid molecules that cannot be replaced by a second liquid.[42] Since tubules[15,44] from LMOGs containing cholesteric groups are known in related systems,[45] they may be present here as well.

SAFINs from **CAB** gels in 1-octanol and in the lower polarity liquid *n*-dodecane (Figure 1) are illustrative of the

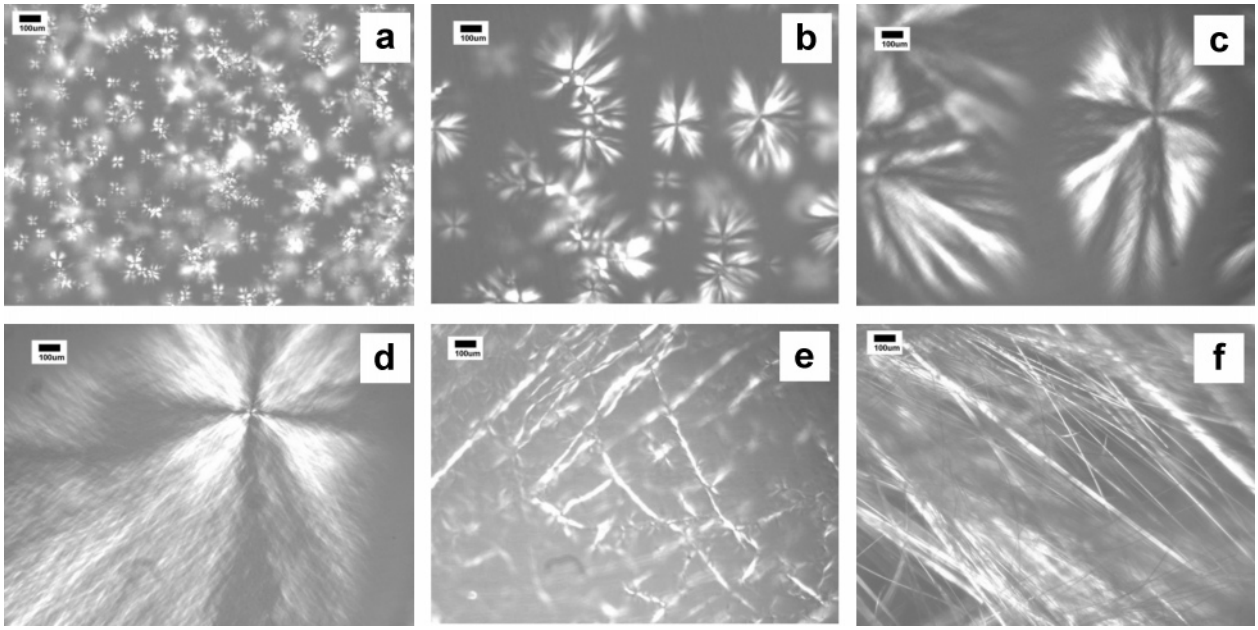


FIGURE 4. Polarizing optical micrographs of 1.0 wt % **10**/*n*-octane gels after incubating sols at (a) 0.0, (b) 15.6, (c) 25.1, (d) 31.6, and (e) 37.4 °C; sol (f) incubated at 42.3 °C is not a gel due to insufficient cross-linking of parallel fibrils. Space bars = 100 μm. Reprinted with permission from ref 18. Copyright 2005 American Chemical Society.

dependencies of **ALS** and other LMOGs on the liquid component and the protocol for transforming their sols to gel phases.[27] Both gels appear to have a bluish haze from a Tyndall effect that indicates scattering from nanometer range objects. Under low magnification, the presence of spherulitic objects, whose diameters depend on the liquid component—ca. 200 μm for *n*-dodecane and 6−8 μm for 1-octanol—are evident. No gel phase can form until the spherulitic objects entangle and establish a network that pervades the volume of the sample. Also, no gels are obtained from *n*-dodecane sols placed in a 50 μm wide cell because it prohibits development of the 200 μm spherulites.[46]

At higher magnifications, the highly branched networks of the SAFINs and their "junction zones" (Figure 1f) become visible. The cross-sectional dimensions of both the *untwisted* fibers in *n*-dodecane (21 nm × 10 nm) and *twisted* ones in 1-octanol (26 nm × 8 nm; pitch ca. 120 nm) are monodisperse. One of the most remarkable and least well understood aspects of SAFINs is the frequent (*but not universal*) monodispersity of their cross-sections. Twisting is induced when liquid-surface energies at the cross-sectional faces of a fiber are very different.[12]

Based on electronic spectra[25,27,47] and single-crystal structures of related **ALS** molecules,[37b] **CAB** molecules in fibers are proposed to be organized in partially interdigitated bilayers in which the anthryl groups are stacked head-to-tail and the cholesteric groups of neighboring molecules are located on opposite sides of a bilayer or a twisted helical structure with the aromatic parts at the core.[25,27] This is an efficient packing mode because the van der Waals thickness of an aromatic ring is about one-half that of a steroid.[37b,48]

Somewhat different **CAB** fibers in *n*-dodecane and 1-octanol gels are also evidenced by spectroscopic and T_g measurements. At ~80−90/20−10 (vol/vol) 1-octanol/*n*-hexadecane liquid compositions, *one* SAFIN type (but not a mixture of both!) was obtained by changing the rate of cooling of the sol phase.[46] Outside this composition range, one SAFIN type is obtained, regardless of the cooling rate.

The delicate balance between the kinetics of gelation and the thermodynamic properties of different morphs is even more evident in **10**/*n*-alkane systems. Spherulitic or rod-like SAFINs are observed depending on the temperatures below T_g at which sols are incubated (Figure 4).[18] Surprisingly, analyses of the temporal changes in fluorescence, circular dichroism, and rheology data during gelation by a modified Avrami equation (eq 1 in which X

$$1 - X = \exp(-Kt^n) \qquad (1)$$

is the volume fraction of the gel at time t, K is a rate parameter, and n is an indicator of the mode of growth)[49] (see, for example, Figures 5 and 6) indicate one-dimensional, interface-controlled fibril growth and "instantaneous nucleation" at all temperatures in Figure 4. However, the temperature ranges where spherulitic and rod-like SAFINs form correspond roughly to very small and very large temperature-dependent regions for K (Figure 7).[18]

In ethyl acetate gels of **11** (**10** with an unsaturated **S** group), SAFIN growth remains rod-like and K is the same at all incubation temperatures examined. However, the values of n provide evidence for a change from spontaneous to homogeneous nucleation at a distinct temperature![21] These results may be grounded in thermodynamic factors related to the degree of super-saturation and the driving energy for phase separation at each temperature.[13a,19] Additional studies of this type using non-**ALS**

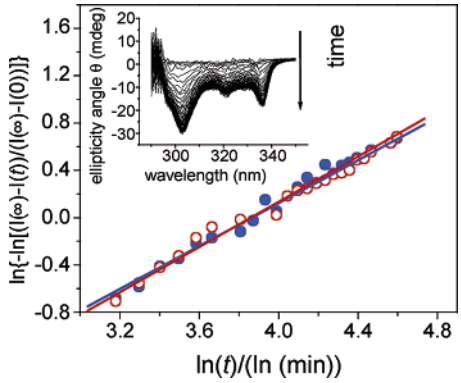


FIGURE 5. Avrami plots[46] of CD spectral intensities at 303 (○; slope = 0.96) and 336 nm (●; slope = 0.91) of a 1.0 wt % **10**/*n*-octane sol versus time (0−277 min) at 40 °C and best linear fits. The inset contains the spectra. Adapted with permission from ref 18. Copyright 2005 American Chemical Society.

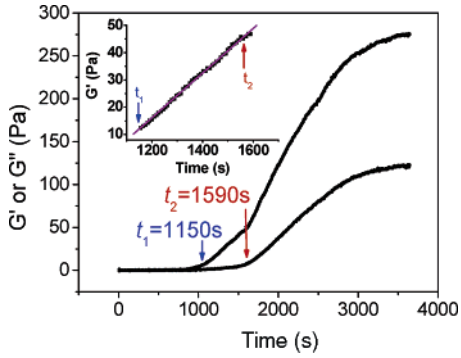


FIGURE 6. Evolution of elastic (*G*′; ○) and viscous (*G*″; ●) moduli for a 1.0 wt % **10**/*n*-dodecane sol incubated at 40.0 °C. The insetshows *G*′ versus time during the t_1-t_2 period (ascribed to formation of fibrils before network formation); slope = 0.08 Pa/s. Adapted with permission from ref 18. Copyright 2005 American Chemical Society.

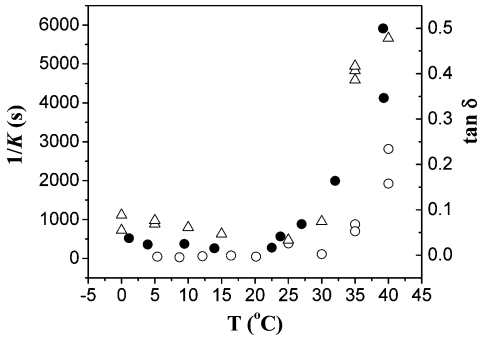


FIGURE 7. 1/*K*[48] from fluorescence (●) and CD (○) data and tan δ (△, *G*″/*G*′) versus temperature. Samples were 1.0 wt % **10** in *n*-octane (fluorescence and CD measurements) or *n*-dodecane (rheology measurements). Reprinted with permission from ref 18. Copyright 2005 American Chemical Society.

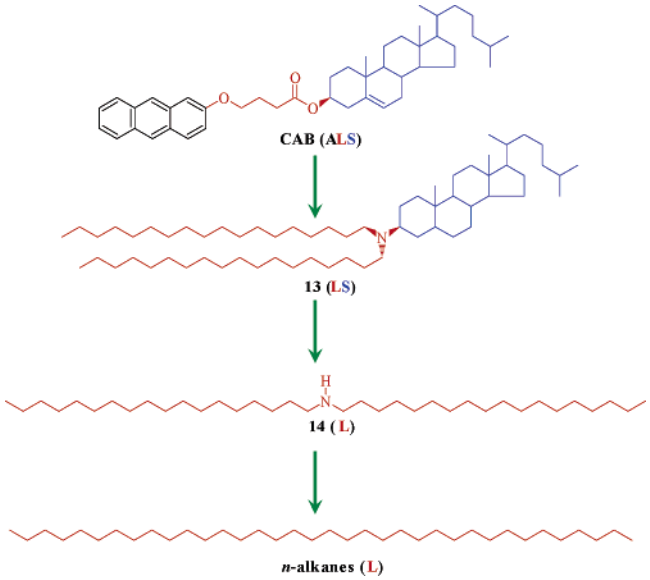
LMOGs and different approaches to data interpretation[12−17,19] are needed to place these observations into a clearer context.

D. Which Liquids Are Gelated?

As noted in section C, whether a gel forms depends on intimate interactions between LMOG and liquid molecules during SAFIN formation, and the details of those interactions are still not well understood. However, a thermally and temporally stable gel requires that the bulk melting point of the gelator be high and its solubility in the liquid be low. For example, at 0.8 wt % **CAB** (mp 204−206 °C[50]), the T_g is 43 ± 2 °C in *n*-alkanes from C_7 to C_{16}; temporally unstable gels with lower T_g values are obtained in cyclohexane and methylcyclohexane, and much more stable gels are formed in alkanols.[27] In gels comprised of gelators with **LS** parts similar to those of **CAB** but a more polar 9,10-anthraquinon-2-yl **A** group, the more stable gels are obtained with *less* polar liquids.[37a]

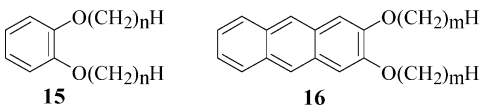
The stability of some organogels where the SAFINs are noncrystalline can be controlled more by specific functional groups of the liquid molecules than by their bulk polarity. Thus, gels of bis(2-ethylhexyl) sulfosuccinate/*p*-chlorophenol gelator and non-hydroxylic liquids, where the SAFIN structure depends acutely on H-bonding networks, are destroyed upon addition of very small amounts of water.[51]

Scheme 1



E. A Quest for the Simplest LMOG Structures

Scheme 1 presents an example of how structural simplifications can be accomplished conceptually when starting with complex (**ALS**-type) molecules. The principal driving force for gel formation and stabilization of SAFINs of $\mathbf{AL}_2$ gelators, such as **15** and **16**,[52−55] is $\pi-\pi$ stacking of the

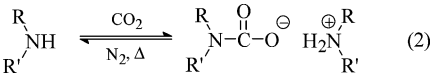


15 **16**

aromatic units and London interactions of the alkyl chains. **LS** gelators, such as **13** and related salts[56] and simple cholesteryl esters,[57] appear to self-assemble into SAFINs when van der Waals packing interactions are sufficiently strong and, of course, solvent−LMOG interactions are much weaker. Some relatively simple molecules with only an **S** part,[58−61] including cholesterol,[62] also gelate

various liquids.[59b,63] In each, there is at least one hydrophilic functional group that prefers to be separate from the lipophilic steroidal rings. Packing constraints imposed by the large, rigid shapes of the steroid rings and the desire of the hydrophilic groups to remain in contact appear to allow these molecules to self-assemble into SAFINs.

Removal of the cholestanyl moiety of **13** leaves di-*n*-octadecylamine, **14**, an **L** LMOG of *n*-alkanes, primary alcohols, aromatic liquids, and silicone oil.[64] Molecules such as **14** are conceptually an *n*-alkane into which an amino group has been inserted. H-bonding among the N−H groups and London dispersion forces between *n*-alkyl chains lead to fibers in which the LMOGs are arranged in lamellae. Bubbling CO_2 (or other X=Y=X triatomic molecules[65]) through solutions of **14** or long-chained primary amines creates ammonium−carbamate pairs (eq 2) with strong electrostatic heterogroup interac-



(2)

tions.[64] As a result, both the range of liquids gelated and the T_g values can be increased dramatically by CO_2 addition. Also, these gels are chemoreversible since bubbling nitrogen through them below their T_g reconverts them to solutions/sols by displacing the CO_2. Strengthening molecular interactions within SAFINs can be accomplished also by enhancing H-bonding among the heterogroups, such as by changing amides to ureas. Thus, even the *very* small molecule, *N,N′*-dimethylurea, is an LMOG for several liquids![7] Urea itself self-aggregates in long *n*-alkanes and similar liquids to form clathrates.[66] Appending one methyl group on each nitrogen atom changes the H-bonding networks from roughly three-dimensional (clathrate channels) to one-dimensional (fibers).

Finally, removal of the **14** heteroatom yields hexatriacontane, which gelates short-chained *n*-alkanes (because long *n*-alkanes are almost insoluble in short ones) and other liquids.[4−6] The only stabilizing interaction available within the SAFINs of *n*-alkanes is London dispersion forces. Since each CH_2/CH_2 interaction is worth ∼8 kJ/mol,[67] their sum within lamellae of hexatriacontane is substantial, allowing the network to immobilize liquids. *n*-Alkanes (the simplest LMOGs structurally) and their gels with short *n*-alkanes (the simplest class of organogels) are a departure point for designing more complex LMOGs from simpler ones conceptually by reversing the arrows in Scheme 1!

F. Perspectives and Prospects

Although this Account has focused on **ALS**-type molecules, very diverse LMOGs structures are known,[2,9a] and new ones seem to be discovered daily. As the body of information grows, so does our ability to design molecules with a high probability to be LMOGs. The transformation of this science from serendipitous discovery to molecular engineering is approaching.[9d,68]

To reach that goal, additional studies will be required, especially those dealing with the kinetics and mechanisms of organogel formation. Without them, it will be very difficult to refine current models of how nucleation and crystallization occur, how liquids interact with growing fibrillar surfaces, and how fibers interact to form SAFINs.[12−17] In turn, those models are needed to develop predictive tools for when and how a particular system will yield a gel. Being able to design a priori LMOGs for specific liquids that impart predetermined rheological and thermodynamic properties to their gels is currently not possible.

The authors hope that this Account will catalyze others to attack some of these outstanding problems. Much has been learned about LMOG gels and their SAFINs during the last 20 years; much more must be learned in this burgeoning field before it reaches its potential.

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