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Review

The Quest for the Simplest Possible Organogelators and Some Properties of their Organogels

David J. Abdallah and Richard G. Weiss

Department of Chemistry, Georgetown University, Washington, DC 20057-1227, USA

Nesse trabalho é apresentada uma revisão sobre esforços recentes na busca pela classe mais simples de moléculas orgânicas capazes de gelificar grandes volumes de líquidos, com ênfase na abordagem adotada pelos autores. Apresentam-se, também, propriedades de alguns destes compostos bem como de seus organogéis. Alguns dos desafios futuros para o desenvolvimento desta área são discutidos.

The search for the simplest structural class of organic molecules capable of gelling large amounts of organic liquids is reviewed with an emphasis on the approach taken by the authors. The properties of several of the gelators, as well as their gels with various organic liquids, are presented. Some challenges to future developments in the field are mentioned.

Keywords: gels, organogels, organogelators, gelators, X-ray diffraction

Introduction

This review[1] focuses on recent research at Georgetown University on **l**ow **m**olecular-mass **o**rganic **g**elators (**LMOG**s, molecules whose molecular masses are $\leq$ 3000 g mol L^{-1}) and their organogels. It describes our efforts to reduce the structural complexity of the **LMOG**s -- leading eventually to the simplest class of organogelators possible -- and approaches taken to discern the structures of their gels at various length scales.

"What is an organogel?" is a question that has been addressed without a very satisfactory answer for more than a century. There are several types of organogels, and each requires a definition with somewhat different qualifications.

Unfortunately, the statement by Jordan Lloyd more than 70 years ago, "…the colloid condition, the gel, is easier to recognize than to define"[2], was prophetic. In fact, many gels are not colloidal! Flory's[3] definition of gels[4] attests to their complexity; it is rigorous, but very difficult to apply on a routine basis. Even gels with polymeric gelators are difficult to define[5]. For the purposes of this review, organogels must be composed of a low concentration (usually $\leq$ 2 wt%) of an **LMOG** in an organic liquid and meet two loosely defined criteria:

(1) They may be distorted in shape by an applied stress (below a certain limit) but must return to their original form when relieved of the stress.

(2) Although being composed predominately of liquid and being fluid at the microscopic scale, they must appear solid-like macroscopically.

In addition, all **LMOG** organogels are thermally reversible (that is, they can be cycled repeatedly with their pregelation (sol) phases by heating and cooling) unless there is a chemical reaction that occurs along with the physical changes.

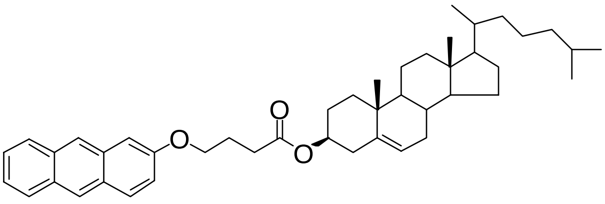
Understanding how **LMOG** molecules nucleate and assemble in the sol phase and whether the lyotropic structures in the sol resemble those in the gel are keys to learning the mechanisms for organogel formation. Such considerations need not be addressed to understand polymer gels and many hydrogels. In this regard, it is important to distinguish the critical aggregation concentration (CAC; i.e., when **LMOG**s aggregate in the sol) and the critical gelator concentrations (CGC; i.e., the lowest concentration of **LMOG** molecules capable of gelling a liquid at room temperature)[6,7]. The aggregation process leading to gelation has been studied by optical spectroscopic methods[7] and, in a few cases, by small angle neutron scattering (SANS)[8,9], electron spin resonance (ESR)[8], and atomic force microscopy (AFM)[10].

LMOGs self-assemble usually via *one-dimensional* growth modes to form fibers, strands, or tapes which are frequently crystalline. Recent examples of gelator structures based on microplatelets indicate that *two-dimensional* growth patterns by the nucleating species are also possible[11]. Although it is generally assumed that strong intermolecular forces such as H-bonding, electrostatic attractions, or π-π stacking interactions are necessary to stabilize **LMOG** assemblies, recent observations[11] have demonstrated that London dispersion forces, alone, can be sufficient. The primary nanoscale objects, regardless of their shapes, join in three-dimensional networks that encapsulate the liquid component and inhibit its flow. "Junction zones"[1a] between fibers, strands, tapes, or microplatelets provide rigidity to the microstructure.

Many of the solid structures are colloidal in nature and gelation occurs when the individual colloids interact physically while pervading the liquid volume. Regardless, the highly porous superstructure of the linked nanoscale objects immobilizes a large volume of liquid via surface tension and related forces[12]. In addition, a few **LMOG** gels are reported to be *thixotropic*[13,14].

A personalized history of the recent development of ***LMOG*** *research*

***ALS** and related **LMOG**s*. Our entry into the field of organogels was serendipitous. It resulted from an observation by Y. -C. Lin during a photochemical investigation[15] that small concentrations (typically < 2 wt%) of 3(β)-cholesteryl 4-(2-anthryloxy)butanoate (**CAB**) gelled a wide variety of organic liquids[16] . Initially, we looked upon the gels as an undesirable nuisance! At room temperature in a closed vessel, some **CAB** gels are stable for years and others separate macroscopically to a solid and a liquid after no more than a few minutes.



CAB

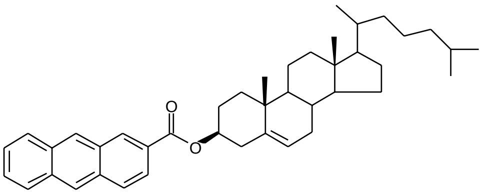
The **CAB** gel superstructure has been characterized in detail[7b]. The size of its colloids depends upon the nature of the liquid and the rate at which the sol is cooled to below T_{gel}, the sol↔gel transition temperature. For instance, colloids from gels with 1-octanol are < 10 μm in diameter while those with *n*-alkanes are more than one order of magnitude larger. As a result, gels are not formed by **CAB** and *n*-alkanes when one dimension of the vessel in which they are contained is ≤ 100 μm[17]. The substructures of the colloids are elaborately branched strands whose rectangular cross-sections range from 10 to 20 nm in size and are nearly monodisperse within one gel. The uniform cross-sections in these and other gels[1a] suggest that growth beyond certain limits along two axes is prohibited, but essentially unlimited growth is allowed along the third! An attractive hypothesis to explain this observation is that "building blocks" within the sol phase combine only along selected faces to create long stacks. In addition, strands of **CAB** from 1-octanol gels are twisted with a pitch of ca. 120 nm while those from *n*-alkane gels are not twisted. A particularly elegant example of the control of helicity and chirality is found in **LMOG** tapes based on 12-hydroxyoctadecanoic acid[7d,18].

Subsequent investigations have shown that **CAB** is only one member of a class of molecules with an **a**romatic, **l**inking, and **s**teroidal part (i.e., **ALS** molecules), and many of them function as **LMOG**s[7a,b]. Structural changes have been made to each part of the **ALS** structure, including the stereochemistry at C3 and the nature of the chain at C17 of the steroidal part. 2-Substituted-9,10-anthraquinones, cinnamate, N-substituted anilines, 2-naphthyl, 1-pyrenyl, and *p*-substituted phenyl have been introduced as the aromatic part. The length and functionality of the linker have been modified, also. Of the more than 40 **ALS** molecules synthesized by us, 19 are able to gel at least some organic liquids. In addition, others have synthesized **ALS** gelators containing substitiuted azobenzenes[7c], squarines[44h], and stilbenes[44h].

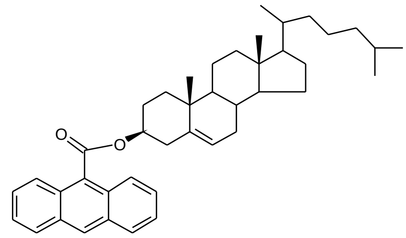
It has been possible to derive several important conclusions concerning the nature of **LMOG** organogels from these investigations: (1) H-bonding, even when possible, may be absent in **LMOG** assemblies when other packing contributors (e.g., π-π interactions and London dispersion forces) dominate[7a], (2) charge-transfer interactions *within gelator strands* can stabilize gels[14b,19], (3) thixotropy[13] can be induced by adding a small concentration of a second (non-gelling) **ALS** molecule whose size and shape are similar to those of a good **ALS** gelator[14b], (4) the fraction of **ALS** gelator within the solid network is dependent on temperature and the solubility of the gelator in the liquid component[7b,20], (5) the bulk properties of a liquid mixture, rather than the properties of the individual components, determine the dimensions and shape of the gelator assemblies[21], and (6) subtle changes in molecular shape can alter profoundly the ability of an **ALS** to gel organic liquids (e.g., **2-CA** is an excellent gelator of many types of organic liquids but **9-CA** did not gel any of the same liquids[7b]).

Unfortunately, the complexity of the **ALS** structures has not allowed a clear, broadly applicable link between molecular structure and gelation ability to be established. However, it is clear that **LMOG** structure alone does not govern gelation ability. Widely applicable correlations between structure and function must be derived from **LMOG**s that are simpler than the **ALS**.

With this goal in mind, others[22] and we[7b,14b] have examined the gelling abilities of **AL** molecules (i.e., containing an **a**romatic group and *one* "**l**inking" chain, but lacking a **s**teroidal group) with very little success[23].

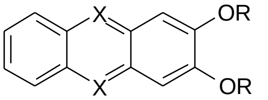


2-CA



9-CA

However, several $\mathbf{AL_2}$ molecules (i.e., containing one **a**romatic and *two* **l**inker groups) are efficient **LMOG**s. An example, 2,3-di(dodecyloxy)anthracene (**DDOA**), gels several organic liquids especially at low temperatures[22]. When the length of its alkyl chains were shortened, the oxygen atoms were removed, the chain lengths were mismatched, or the aromatic part was truncated to naphthyl, the gelating ability of **DDOA** was either lost or severely reduced. However, hydrogenation of one of the anthryl rings of **DDOA**[24] or replacement of it by a phenazine (**DNON** and **DUON**)[25a] or an anthraquinone (**DDOQ**)[25b] produced **LMOG**s whose efficiencies are similar to that of the parent. In addition, a fullerene containing $\mathbf{AL_2}$ molecule gels methanol, but only when sols stand undisturbed for protracted periods[26]. Its gelating ability may derive more from its two trimethylammonium bromide groups that terminate the two **L** chains than from the fullerene **A** part[27].



Gelator	X	R
DNON	N	n-C_9H_{19}
DUON	N	n-$C_{11}H_{23}$
DDOA	CH	n-$C_{12}H_{25}$
DDOQ	CO	n-$C_{12}H_{25}$

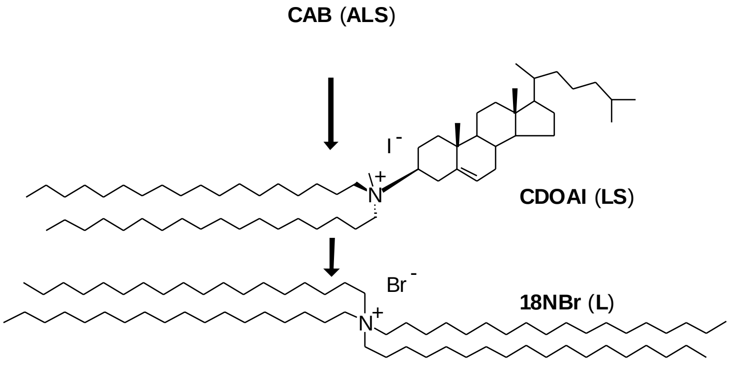
Some **LS** molecules (*i.e.*, containing a “linking” chain and a steroidal group) have also been examined. Although several cholesteryl alkanoates do not gel simple organic liquids[7b], cholesteryl laurate gels some silicone oils[28], and several steroidal amines and their salts[27] have been shown to be efficient **LMOG**s. Even some **S** molecules (i.e., consisting of only a steroidal group) are good **LMOG**s. Examples include dihydrolanosterol[29] and lithocholic acid salts[30]. Gels of some 17-azahomosteroids of isoandrosterone[31] have been investigated in great detail by Terech and coworkers using scattering and rheological techniques[32]. In spite of the simplifications introduced by removal of the **A**, **S**, or both parts of the **ALS** gelators, it is still difficult to correlate their specific structural changes with variations in the properties of their organogels.

LMOG salts

For this reason, we attempted to discover **LMOG**s consisting essentially of only an **L** part (i.e., alkyl chains with minimal functionalization). The simplest **LMOG** structures known before 1997[11,33] were long, partially fluorinated *n*-alkanes[34], but they gel a limited number of liquids and require rather large concentrations to do so. The first approach to further simplifications was suggested by the efficiency of cholesteryl tri-*n*-alkyl ammonium **LS** gelators (*e.g.*, **CDOAI**; Scheme 1)[35]. When the cholesteric group was replaced by another *n*-alkyl chain, several of the *tetra-n*-alkylammonium salts were very efficient **LMOG**s, especially when three or four groups are “long”; in the first examples, octadecyl chains were employed (e.g., **18NBr**; Scheme 1)[27]. However, these **LMOG**s are unstable at elevated temperatures due, probably, to Hofman-type elimination reactions. Replacement of the nitrogen atom of the cationic head group with phosphorus, another Group VA atom, provided much more stable phosphonium salts[36] whose gelation efficiencies are somewhat different from the corresponding ammonium salts[37].

The gelling properties of salts with four equivalent chains, $H(CH_2)_{\mathbf{n}})_4\mathbf{Y}^+\mathbf{X}^-$ (**nYA**, where **n**, the number of carbon atoms in each alkyl chain, is varied from 7 to 18, **Y** is **N** or **P**, and **A** is **Cl**, **Br**, **I** or $\mathbf{ClO_4}$), will be discussed in some detail. The influence of **n** and **Y** are emphasized; we have not been able to discern a correlation between the size or type of **X** group and the ability of an **nYA** salt to be an **LMOG**.

Comparisons between identically prepared **nYA** gels demonstrate that the ammonium salt **LMOG**s have higher T_{gel} values, are stable for longer periods in sealed vials at room temperature, and require lower CGCs than the corresponding phosphonium salts. Stronger $\mathbf{N^+}$ $\mathbf{A^-}$ than $\mathbf{P^+}$ $\mathbf{A^-}$ interactions are believed to be largely responsible for these observations. Polarizability differences between ammonium and phosphonium cationic centers do not appear to be important since the valence shell electrons about the hetero-atom of the $\mathbf{nY^+}$ parts are well shielded from the anion by the four alkyl chains. However, greater ionic interactions can result from tighter packing of the α and β



Scheme 1.

methylene units (i.e., those nearest nitrogen). Since N-C covalent bond distances (~1.53 Å) are shorter than P-C ones (~1.81 Å), an **N$^+$** center can approach its anions more closely than can **P$^+$** [38]**.** Additionally, the larger inductive effects[39] of nitrogen make the α and β methylene hydrogen atoms of the **nN$^+$** cations more acidic (*i.e.*, they bear a larger partial positive charge) than those of the **nP$^+$** cations; stronger hydrogen-bonding and, therefore, shorter hydrogen-anion contact distances are expected for the ammonium salts.

From single crystal x-ray diffraction studies on several of these salts, the separation between cationic and anionic centers minus the van der Waals radius of nitrogen or phosphorus, as appropriate, is always smaller for the **nNA** salts than the corresponding **nPA** salts[38]. However, we are reluctant to draw a strong conclusion from this observation because the morph of an **LMOG** in its gels may differ from that in solids obtained by bulk recrystallizations[40] .

The magnitudes of the London dispersion forces (that supplement the stronger **Y$^+$A$^-$** electrostatic interactions) are responsible for greater gelation efficiencies by **nYA** salts with longer chains. The **nNBr** salts exemplify the trends. Due to its high solubility in all of the liquids tested, **7NBr** was unable to form a gel. Relatively high concentrations (~0.2 mol L^{-1}) of the slightly longer **10NBr** gelled hexadecane (stable at room temperature for ≤ 2 days) and glycidyl methacrylate, but not benzene, 1-octanol, carbon tetrachloride, or styrene. Generally, as **n** of the **nNBr** increased, the CGC decreased and T_{gel} values increased. In addition, the melting temperatures of the salt gelators parallel T_{gel} of their gels. Gels from salts with shorter chains usually had wider T_{gel} transitions because they are solubilized more gradually as temperature is increased than salts with longer chains. Consequently, a clear assignment of T_{gel} was not always possible for salt gels with shorter chains.

In addition to increasing T_{gel} and lowering the CGC, longer chain lengths of salt gelators increase the periods of gel stability. For instance, some hexadecane gels with **16NBr** and **18NBr** gelators have persisted for more than 2 years in closed vials at room temperature! By contrast, hexadecane/**12NBr** gels with the same wt% composition survived less than 2 days. Gels of the other liquids in Table 1 follow qualitatively the same trend. CCl_4/**16NBr** and CCl_4/**18NBr** gels, which require > 5 wt% gelator, persisted less than 1 week. They became yellow with time, indicating that some decomposition had occurred.

Thermograms of **nNBr** gels (Figure 1) illustrate further the dependence of alkyl chain length on gelation ability. Salts with the longest chains provide gels with the lowest CGCs and the highest T_{gel} values, regardless of cooling protocol. If the packing of gelator molecules in gel strands is microscopically separated into lipophilic and lipophobic regions, as in their bulk solid states[38], longer alkyl chain lengths will increase the aggregate stabilities as a result of larger London dispersion forces.

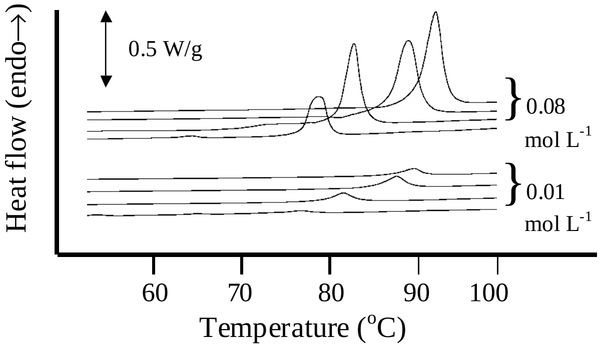


Figure 1. DSC heating thermograms of fast-cooled (See Table 1) **nNBr**/hexadecane gels at 0.01 and 0.08 mol L^{-1} gelator concentrations. The values of **n** for each concentration are in the order 12→14→16→18 from bottom to top[37].

The dependence of cooling protocol on T_{gel} and gelation is evident in Figure 2. T_{gel} is higher for slowly cooled gels. However, gelation is facilitated by quickly cooling sols. Dilute, fast-cooled gels of **nYA LMOG**s are more translucent than slow-cooled ones, also. The networks of

Table 1. Transition temperatures, T_{gel} (^oC), and periods of stability (at room temperature)[a] of gels with **nNBr** gelators.

		Concentration		Cooling rate[b] (T_{gel}, ^oC)		
Liquid	Gelator	wt %	mmol L^{-1}	slow	moderate	fast
Hexadecane	**7NBr**		: 200		p	
	10NBr	14.57	200		58 (<2d)	
	12NBr	1.96	20	78	79 (<2d)	54-77
	14NBr	1.13	10	74	73 (2w)	65-67
		2.23	20	74	73 (>2y)	74
	16NBr	1.28	10	76-77	80 (>2y)	73
	18NBr	1.41	10	84-86	79-85 (>2y)	73
Dodecane	**7NBr**		: 200		p	
	12NBr	1.02	10		p	
		4.89	50	74	g (<2d)	g
	14NBr	2.43	20	p	p	pg
		5.56	50	pg	g (<2d)	g
	16NBr	1.31	10	75-79	p	p
		2.59	20	75-81	74 (>2y)	75
	18NBr	1.50	10		p	
		2.87	20	g	74 (>1m)	78
Benzene	**7NBr**		: 200		s	
	10NBr	13.1	200		s	
	12NBr	3.00	35	p	p	30
		4.23	50	29	29 (<2d)	30
	14NBr	1.00	10	39-43	40 (1d)	38-41
		3.42	35	39-40	43 (2y)	38
	16NBr	1.13	10	45	43 (<2d)	47
		3.83	35	50-53	52-53 (>2y)	50-51
	18NBr	1.25	10	60	56 (>3w)	55-56
		2.47	20	59	58 (>2y)	56
1-Octanol	**7NBr**		: 200		s	
	10NBr	13.8	200		s	
	12NBr	6.13	70		s	
	14NBr	6.96	70		s	
	16NBr	2.28	20		p	
		7.77	70	38-44	g (>2y)	42
	18NBr	2.60	20	49	p	49
		6.28	50	50-55	g (>2y)	53
CCl_4	**7NBr**		: 200		s	
	10NBr	7.6	200		s	
	12NBr	4.60	100		s	
	14NBr	5.25	100		s	
	16NBr	1.24	20		p	
		5.88	100	45	41 (3d)	45
	18NBr	1.38	20		s	
		6.50	100	g	48 (>1w)	g
MMA[c]	**7NBr**		: 200		s	
	10NBr	12.34	200		pg 35	
	12NBr	0.82	10	p	p	pg 21-35
		3.96	50	47	43	39
	14NBr	0.94	10	p	45-46	pg 39-48
		1.85	20	50	47-49	39-50
	16NBr	1.05	10	58	51-58	pg 42-48
		2.08	20	60	60-62	48
		5.05	50	68	65-66	64-69
	18NBr	1.17	10	67	65	26-48
		2.31	20	70-73	69	69-74
Styrene	**7NBr**		: 200		s	
	10NBr	12.66	200	s		
	12NBr	1.67	20	p	p	26-29
		6.36	80	30	31	30
	14NBr	0.96	10	p	p	31-33
		4.63	50	40	39	37
	16NBr	1.08	10	48-51	48	44-46
	18NBr	1.20	10	p	pg 59	56
		2.38	20	60-61	59-60	57

(cont.) Table 1.

		Concentration		Cooling rate[b] (T_{gel}, °C)		
Liquid	Gelator	wt %	mmol L^{-1}	slow	moderate	fast
GMA[d]	**7NBr**		: 200		s	
	10NBr	11.23	200	44		
	12NBr	0.73	10	p	p	34
		1.46	20	p	43	39
		3.57	50	p	41-45	40
	14NBr	0.84	10	p	50	44
		1.67	20	62	58	46
	16NBr	0.95	10	74-75	68	54
	18NBr	1.05	10	76	77	59
		2.08	20	76	84	71-75

[a]Periods of stability in parentheses: h = hour; d = day; w = week; m = month; y = year. [b]Cooling protocols for samples in sealed tubes: slow -- submerged in initially boiling water until room temperature achieved; moderate -- removed from the boiling water and placed in the air; fast -- removed from the boiling water and placed under a stream of water at 20°C. [c]MMA = methyl methacrylate. [d]GMA = glycidyl methacrylate. g = gel formed but T_{gel} not determined; pg = partial gel. Where gels did not form: s = solution; p = solid + liquid.

the former are more intricate and have larger surface/gelator-mass ratios that allow them to entrap a larger volume of liquid by surface tension[37]. For example, fast-cooled sols of **18PBr** or **18PI** in aromatic liquids provide translucent gels with a bluish tint (Tyndall effect), but the same sols yield white and opaque gels when slowly cooled.

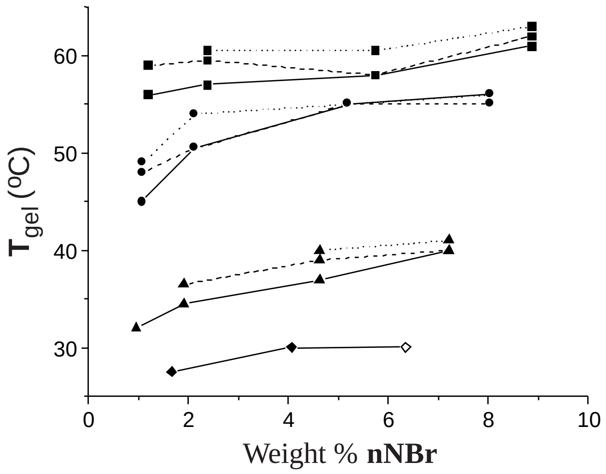
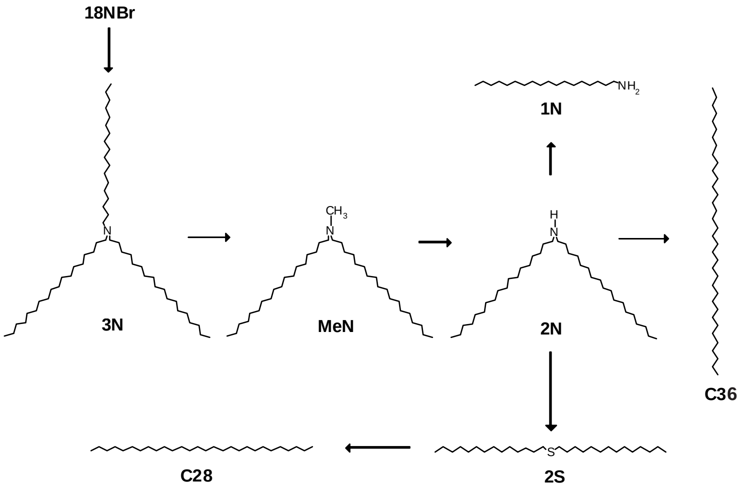


Figure 2. The influence of cooling rates of **nNBr**/styrene sols on the T_{gel} values of their gels: n = 18 (■), 16 (●), 14 (▲), 12 (◆,); fast (———), moderate (-------) and slow (•••••••) cooling; see Table 1. Averages are reported when ranges of melting were noted. The value is the same for fast, moderate and slow cooling[37].

***LMOG**s with one hetero-atom (Scheme 2)*

Each of the ammonium or phosphonium **LMOG**s has a *minimum* of two hetero-atoms—the cationic center and its anion. Removal of one of the salt chains leads to molecules with only one hetero-atom and three chains. Due to the instability of phosphines in air, the gelling characteristics of only the amines were explored. As expected, tri-*n*-octadecylamine (**3N**), a tertiary amine with three long *n*-alkyl chains, is a much less efficient **LMOG** than its quaternary analogue, but it is able to gel some organic liquids[41]. Methyl-di-*n*-octadecylamine (**MeN**), in which one of the octadecyl chains has been truncated to methyl, is less efficient than **3N**, but truncating the methyl group further to hydrogen as in di-*n*-octadecylamine (**2N**) increases gelator efficiency. **2N** can act as both a donor and acceptor of H-bonds; the presence of H-bonds was confirmed in strands of **2N** gels by infrared spectroscopy[41]. **3N**, **MeN**, and di-*n*-tetradecylsulfide (**2S**), another single hetero-atom **LMOG**, may be less efficient than **2N** because they are able to accept H-bonds only. However, 1-octadecylamine (**1N**), capable of being an H-bond donor and acceptor like **2N**, did not gel any of the liquids tested. We suspect that the molecular packing arrangement of its solid may not be amenable to formation of gels and that the presence of some octadecylammonium octadecylcarbamate, invariably present when **1N** is exposed to air[42], may catalyze the nucleation of morphs that are not amenable to strands or other gel-related motifs[41].

Unfortunately, the organization of these **LMOG**s in their gel strands is not known. However, the positions and appearances of the IR absorption bands for the N-H stretch of **2N** in gels suggest that the same solid morph may be responsible for its bulk solid at least in siloxane gels. Since the melting temperature of neat **2N** is the highest of the five single hetero-atom gelators examined, its intermolecular interactions may be strongest, at least in the bulk solid phase. On a per octadecyl chain basis, the enthalpy (and entropy) of melting of the four amines as bulk solids follow the order: **1N** (73.3 kJ mol-chain^{-1} (226.5 J mol-chain^{-1} K^{-1})) > **2N** (60.3 kJ mol-chain^{-1} (182.9 J mol-chain^{-1} K^{-1})) > **3N** (45.3 kJ mol-chain^{-1} (141.5 J mol-chain^{-1} K^{-1})) > **MeN** (39.0 kJ mol-chain^{-1} (125.5 J mol-chain^{-1} K^{-1})). The higher enthalpy and entropy per octadecyl chain for **1N** and **2N** are consistent with strong hydrogen-bonding interactions that are not possible in the other



Scheme 2.

gelators. This is most apparent when comparing the structurally comparable gelators, **2N** and **MeN**, where the transition enthalpy and entropy of the H-bonding molecule are 55 % and 46 % greater, respectively, than those of the methylated one.

At equal molar concentrations of single hetero-atom **LMOG**s, T_{gel} of 1-alkanol gels decreased as the chain length of the liquid was increased. Not inconsequentially, these gelators are more soluble in the longer alcohols, and **2S**, **MeN**, and **3N** remained solubilized when placed in n-alkane liquids (that mimic the polarity effect of making alkanol chains infinitely long).

*n-Alkanes, **LMOG**s with no hetero-atoms*

Stabilization of the gel assemblies of **2S**, a molecule whose chain length equals that of **1N,** but which cannot donate H-bonds, must rely heavily on van der Waals forces[41]. On that basis, we wondered whether *n*-alkanes with long chains might serve as **LMOG**s. To our amazement (and joy), several organic liquids, including shorter *n*-alkanes, have been gelled thermoreversibly by low concentrations of longer *n*-alkanes (**Cn** with n = 24–36)![11] Gelator efficiency increases with alkane chain length.

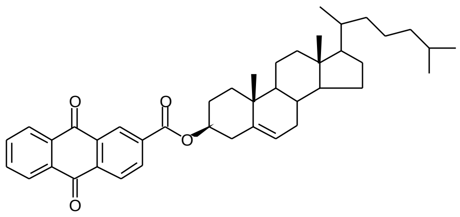
Hexatriacontane (**C36**), the longest *n*-alkane examined as an **LMOG**, gelled a wide variety of liquids. Although CGC's were not determined in most cases, > 5.1 wt% (> 0.12 mol L^{-1}) of *n*-tetracosane (**C24**), > 2.1 wt% (> 0.04 mol L^{-1}) *n*-octacosane (**C28**), 2.3 wt% (0.04 mol L^{-1}) *n*-dotriacontane (**C32**), and 1.3 wt% (0.02 mol L^{-1}) **C36** formed gels, albeit rather unstable ones, with *n*-dodecane as liquid. A dodecane gel with 0.02 mol L^{-1} **C36** was stable at room temperature for ~ 1 h; one with 0.04 mol L^{-1} **C36** has persisted for several months. By contrast, only 1.3 wt% (0.04 mol L^{-1}) **C24**, 0.91 wt% (0.025 mol L^{-1}) **C28**, 0.96 wt% (0.023 mol L^{-1}) **C32**, and *only* 0.19 wt% (0.004 mol L^{-1}) **C36** were necessary to make gels with Dow Corning 704 silicone oil that are stable for at least one week. Since the **C36** concentrations correspond to > 400 (silicone oil) and > 200 (dodecane) liquid/gelator molecular ratios, direct gelator-liquid *molecular* interactions cannot be responsible for these and the other alkane gels. Several studies have demonstrated that the vast majority of liquid molecules in **LMOG** organogels behave microscopically as though in their neat liquid states[1].

Some comparisons can be made between *n*-alkane and single hetero-atom *n*-alkane **LMOG**s. **2S** is **C28** with an S atom inserted at its center, and the structure of **2N** is **C36** with an N (and hydrogen) atom at its center. Both **2S** and **C28** are much more soluble than their longer chain analogs. We have been able to gel only alcoholic liquids with **2S** and **C28** above room temperature, and **2S** is unable to gel several alcohols that can be by **C28**. However, neither molecule is as efficient an **LMOG** as its longer chain analogs. Both **C36** and **2N** form gels that are stable above room temperature with most of the liquids tested. The more polar **2N** has lower T_{gel} and periods of stability in alcoholic liquids and the less polar **C36** has lower T_{gel} and periods of stability in non-polar liquids. Again, these trends are related to the solubility of the **LMOG**s in the liquid components. Additionally, **2N** is more soluble and formed less stable gels in liquids capable of donating or accepting hydrogen bonds than **C36**.

*The structures of **C36** organo gel assemblies at Ångstrom to micrometer distance scales*

Recently, we determined the first complete description of the packing of an **LMOG** in its organogels[43]. Prior attempts have not been completely successful for several reasons, including the polymorphism of many organogelators and the difficulties in making diffraction quality single crystals of others. Structural information on **LMOG** packing at the molecular level has been inferred from conventional techniques, such as nuclear magnetic resonance spectra[44a], semi-empirical calculations[7c] or assumptions that the gelator superstructure is the same as the xerogel morph[44b] or the morph analyzed by single-crystal X-ray diffraction (in the relatively few cases where this is available)[44c,d,e]. At the supermolecular scale, information can be gained by SANS, SAXS, electron microscopy, and atomic force microscopy[7b,44f,g,h]. Unfortunately, extrapolation from the supermolecular to the molecular scale using any of these methods is not definitive.

Previously, a method was devised in our group to provide molecular packing information of **LMOG**s within their gel superstructures by relating the X-ray diffraction (XRD) pattern *of a gel* to that of its neat solid phase[40]. When the two patterns are the same and the single-crystal structure of the **LMOG** is also available, packing in the gel is determined unambiguously. In its first application[40], the method demonstrated that the morph of the **LMOG**, 3(β)-cholesteryl anthraquinone-2-carboxylate (**CAQ**), exists in gel strands in the same morph as the solid derived from the melt, *but different from the morph derived from bulk crystallization*. Unfortunately, molecular structural information is available only for the latter.



CAQ

Using this same approach, we have identified the single morph (of the *four* that are known[45]) of the **LMOG**, **C36**, that is responsible for gelation of several liquids[43]. The match between the XRD patterns of the **C36** gels and that of the neat B_O (orthorhombic) phase (Figure 3) is definitive. In addition, using optical microscopy methods that have been known for more than a century[46] , the orientation of the long molecular axes of individual molecules has been shown to be orthogonal to the planes defined by the microplatelets that constitute the building blocks of the supermolecular assembly. This is the first time a complete structural determination of the solid component of a gel has been made.

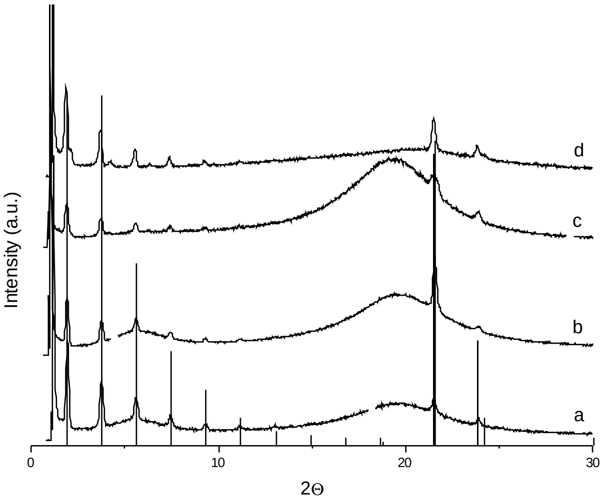


Figure 3. Overlay of the column graph representation of XRD data for crystalline **C36** in its B_O phase[45] and the XRD patterns for gels composed of **C36** at (a) 4 wt% in 1-octanol, (b) 2 wt% in 1-octanol, (c) 4 wt% in hexadecane and (d) 4 wt% in glycidyl methacrylate (adapted from ref 43).

Conclusions and prospects for the future

Careful scrutiny of the literature indicates that engineers involved in fuel transport have been aware of a phenomenon like gelation for many years, and view it as a nuisance to crude oil flow[47]. In cold climates, diesel-burning automobiles are equipped with heaters for the fuel tanks in order to avoid gelation by the long *n*-alkane components. Terms such as 'wax-appearance' and 'cloud point' are used in the fuel community to describe what others[33] and we have concluded are gelation processes.

n-Alkanes are structurally the simplest **LMOG**s possible and their gels with *n*-alkanes as liquids are the simplest organogels that can be made. The existence of these gels demonstrates that London dispersion forces alone can provide solid networks whose strength is sufficient to immobilize liquids against the pull of gravity. The currently accepted paradigm[1a] (formulated in part by the elder and less wise of the two authors) does not predict the existence of such organogels.

Over more than one decade, we have progressed (or regressed?) from very complex **ALS** structures to the simplest **LMOG**s possible, *n*-alkanes. Thus, we are finally in a position to examine systematically the relationship between structural changes in an **LMOG** and the stability of its gels. However, many of the remaining questions concerning <u>*why*</u> **LMOG** gels form can be answered only through investigations of the processes leading from sols to the gels, including the nucleation of **LMOG** aggregates and the assembly of the aggregates into the colloidal superstructures. Despite the progress made, many challenges lie ahead.

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