Urea and Thiourea Derivatives as Low Molecular-Mass Organogelators

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Dedicated to Dr. J. Donald Weber on the occasion of his 70th birthday

Abstract: The properties of a series of organogels consisting of a urea or thiourea derivative with one or two *n*-alkyl substitutuents at the nitrogen atoms (a low molecular-mass organogelator (LMOG)) and an organic liquid are described. They include *N*,*N*′-dimethylurea, the LMOG of lowest molecular mass (M_W 88) we are aware of. The efficiencies of the LMOGs, based the diversity of liquids gelated, the minimum amount required for gelation of a liquid at room temperature, and the temporal and thermal stabilities of the gels formed, have been investigated as a function of the number, length, and substitution pattern of their *n*-alkyl chains. The gels are thermally reversible and require generally very low concentrations (<2 wt%) of an LMOG. Some of the LMOGs with shorter chains are more efficient than their longer chained analogues. The structural and thermodynamic properties of the gels have been examined by IR, DSC, and X-ray diffraction techniques. Polarizing optical microscopic analyses of the gels show that the nature of gelator aggregates depends mainly on the alkyl chain length. Changes in the aggregation ability have been examined systematically by perturbing the molecular structure.

Keywords: gels · hydrogen bonds · ureas

Introduction

The aggregation behavior of urea has been studied extensively.[1,2] It is known to form inclusion complexes with *n*-alkanes (≥7 carbon atoms)[3–6] and some functionalized long-chain molecules.[3,7–11] In these complexes, the urea molecules self-assemble through intermolecular hydrogen bonds and orient in a helical lattice into which the guest molecules fit. Thiourea, in a similar way, combines with several substrates to form non-stoichiometric complexes analogous to the urea inclusion complexes.[3–6,12] By contrast, we are unaware of inclusion complexes in which *N*-alkyl or *N*,*N*′-dialkyl ureas serve as the hosts. However, *N*,*N*′-disubstituted ureas, in which the substituents are more complex than an *n*-alkyl chain, can form α-networks (i.e., with one degree of translational symmetry[13]),[14,15] and some of these have been shown to lead to gels[16,17] with organic liquids and water.[18–29] Among the latter, few contain only one urea moiety.[18,19,23] In addition, supramolecular two-dimensional arrays can be driven by the self-assembly of molecules containing urea and similar groups capable of donating and accepting intermolecular hydrogen bonds.[15,30–33]

Some bisurea derivatives possessing aliphatic[22,24,34–37] or aromatic[38–44] groups have been shown to be efficient gelators as well.[45] Most of these LMOGs contain functional groups in addition to ureas. LMOGs containing more than two urea groups have been reported recently,[29,46,47] and a few thiourea derivatives are also known to gelate organic liquids.[34,48] Finally, many structurally more complex LMOGs than those investigated here have been demonstrated to derive their modes of aggregation or solid-state packing in large part from intermolecular hydrogen bonding of urea and thiourea groups.[38,39,45,49–50]

As part of our ongoing effort to design structurally simple LMOGs that are *n*-alkanes with one inserted heterofunctionality, we report here the gelation properties of some very low molecular mass and structurally simple *N*-alkyl, *N*,*N*′-dialkyl, and *N*,*N*-dialkyl ureas and thioureas

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Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author: Gelation properties of urea and thiourea derivatives, Ferry–Eldridge plots, DSC thermograms, optical micrographs, IR, and XRD patterns of several gels and neat powder samples.

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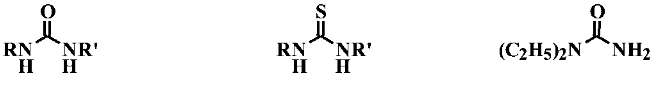

1a-h

a, R = R' = CH_3
b, R = R' = C_2H_5
c, R = R' = n-C_3H_7
d, R = R' = n-C_4H_9
e, R = n-C_3H_7, R' = H
f, R = R' = n-$C_{10}H_{21}$
g, R = R' = n-$C_{18}H_{37}$
h, R = n-$C_{18}H_{37}$, R' = H

2a-e

a, R = R' = CH_3
b, R = R' = C_2H_5
c, R = R' = n-C_3H_7
d, R = R' = n-$C_{10}H_{21}$
e, R = R' = n-$C_{18}H_{37}$

3

Scheme 1. Structures of the urea and thiourea derivatives.

(Scheme 1) with a wide variety of organic liquids. The urea or thiourea functional group has been inserted at a chain end (i.e., *N*-alkylureas) or in the chain center (i.e., *N,N'*- or *N,N*-dialkylureas depending on the mode of insertion). In addition, the urea **1a** (M_W 88) is the lowest molecular mass organogelator known to us. Urea **1a** and some of its short-chained homologues are more efficient gelators than the longer-chained ureas and thioureas. The results indicate that the fibrillar networks needed for immobilization of the liquid components in organogels need not have significant London dispersion interactions when the stronger hydrogen bonding forces can be directed to promote requisite intermolecular contacts.

Results and Discussion

Gelation studies: Several general observations can be made from the data in Tables 1 and 2 with respect to the gelation properties of LMOGs **1–3**. Perhaps, as a consequence of the stronger hydrogen bonding of ureas than thioureas, the gelation abilities of short-chain urea derivatives are significantly better than those of the corresponding thioureas. Urea and thiourea form ribbon and chain structures by intermolecular hydrogen bonding interactions.[51,52] For urea, the calculated energies for hydrogen-bonding interactions are $37.30\,kJ\,mol^{-1}$ for the ribbon structure and $44.80\,kJ\,mol^{-1}$ for the chain structure. For thiourea, the values are 36.55 and $32.62\,kJ\,mol^{-1}$, respectively.[52] In longer-chained ureas and thioureas, this distinction is muddled somewhat by the increased importance of London dispersion forces that also stabilize intermolecular interactions. London dispersion forces can become the dominant interaction when the length of the alkyl chains is ≥ 10 methylene units and neighboring chains are extended and parallel since the attractive dispersion energy is about $8\,kJ\,mol^{-1}$ per methylene unit for *n*-alkanes in their crystalline state.[53]

All of the LMOGs listed in Scheme 1 except **2a** were able to gelate silicone oil and, in most cases, the T_g values of the gels were far above room temperature. As the chain length of the alkyl groups of the *N,N'*-dialkylureas increased from **1a** (dimethyl) to **1c** (dipropyl), the gelation efficiency increases, and then decreases as the chain length becomes longer (i.e., **1d**, dibutyl). However, **1f–h** (i.e., ureas with the longest alkyl chains) are able to gelate a much wider variety of liquids than **1a–c**. In **1h**, the presence of both a primary amido group (which can be involved more efficiently in intermolecular hydrogen bonding than the secondary amido group) and the long alkyl chain of the secondary amido group combine to make it a slightly better LMOG than the somewhat analogous *N,N'*-disubstituted ureas, **1f** and **g**.

Another interesting comparison is among the three much shorter ureas, the isomeric *N,N'*- and *N,N*-diethylureas (**1b** and **3**) and the nearly isomeric *N*-propylurea (**1e**). Again, the *N,N'*-dialkylated urea, **1b**, is a slightly better gelator empirically than both **1e** and **3** (Table 1). Although the primary amide groups in **1e** and **3** should offer more efficient intermolecular hydrogen-bonding interactions than a secondary one, it appears that the stability of the aggregates formed depends on the substitution on the nitrogen atoms. For LMOG **3**, the steric factors associated with the tertiary amide may also destabilize its gelator aggregates. The decreased relative importance of London dispersion forces in the packing of these gelators is probably responsible for the observed order of efficiencies; packing within the solid phases and intermolecular hydrogen-bonding interactions may be accommodated best when the urea group is at the end of the "*alkane chain*", allowing its N–H bonds to be directed toward the C=O bond of a neighboring molecule and its alkyl chain to interact with that of the same or a different neighboring molecule at one extremum.

As emphasized above, one can view **1f–h** as long *n*-alkanes with a substituent placed at one chain end (**1h**) or inserted in the middle (**1f**, **g**). In other studies, where a simpler amino group is the substituent "inserted" on an end of octadecane ($C_{18}H_{38}$; in analogy with **1h**) or in the middle of hexatriacontane ($C_{36}H_{74}$; in analogy with **1g**), the more efficient LMOG was found to be the symmetrical secondary amine rather than the terminal primary amine.[54] Similar results have been observed for alkylammonium alkylcarbamate salts in which the ionic moieties can be considered to be inserted in the middle of an alkane chain. The ammonium carbamates with *n*-alkyl groups are much more efficient gelators than their parent primary amines as a result of the stronger ionic interactions of the charged species.[55,58] Insertion of a urea moiety into a long *n*-alkane induces greater attractive forces than does an amino functionality due to the presence of both dipolar and hydrogen-bonding interactions (involving N-H and C=O groups) in the latter. It also requires greater intermolecular specificity for the energetic stabilization from these interactions to be realized, and we believe that it is the need for specificity that determines the order of gelator efficiencies within the group of long-chained ureas.

The observation that **1a**, the lowest molecular mass organogelator of which we are aware, can gelate silicone oil and carbon tetrachloride at concentrations as low as 2 wt % indicates that a gel network can be stabilized predominantly by intermolecular hydrogen bonding; most organogels have a different balance between London dispersion and hydrogen-

Table 1. Gelation properties of urea derivatives **1a**–**h** and **3** in different liquids. Melting points of neat gelators and T_g values of the gels [°C] are given in parentheses.[a]

Liquid	**1a**		**1b**		**1c**		**1d**		**1e**	
	(103.1–104.0)		(108.7–109.8)		(107.3–107.9)		(74.1–74.9)		(110.9–111.9)	
	2 wt%	5 wt%	2 wt%	5 wt%	2 wt%	5 wt%	2 wt%	5 wt%	2 wt%	5 wt%
hexane	P	P	P	TG[e] (55–60)	PG[c] (20–22)	TG[e] (60)	P	P	P	P
n-octane	P	P	P	P	PG[g] (20–22)	TG[e] (68)	P	P	P	P
silicone oil	TG[b] (87)	TG[b] (85–90)	TG[e] (74)	TG[e] (80)	TG[h] (71)	TG[e] (75)	TG[c] (34)	TG[j] (40)	TG[k] (60–71)	TG[k] (76–82)
ethanol	S	S	S	S	S	S	S	S	S	S
1-butanol	S	S	S	S	S	S	S	S	S	S
1-octanol	S	S	S	S	S	S	S	S	S	S
benzyl alcohol	S	S	S	S	S	S	S	S	S	S
toluene	P	PG[c] (26)	PG[f] (20–25)	PG[f] (28)	TG[c] (23–26)	TG[i] (30)	S	S	TG[c] (68–73)	TG[c] (68)
DMSO	S	S	S	S	S	S	S	S	S	S
CCl_4	TG[c] (41)	TG[d] (47)	S	S	S	S	S	S	P	P
water	S	S	S	S	P	P	P	P	S	S

Liquid	**1f**		**1g**		**1h**		**3**	
	(97.4–98.0)		(111.4–113.6)		(109.6–110.7)		(73.5–74.4)	
	2 wt%	5 wt%	2 wt%	5 wt%	2 wt%	5 wt%	2 wt%	5 wt%
hexane	P	P	P	P	P	OG[n] (48)	P	P
n-octane	P	P	jelly (75)	OG[l]	jelly (52)	OG[l,m]	P	P
silicone oil	TG[j] (67)	TG[l] (72)	TG[l] (89)	TG[l] (>95)	OG[l] (64)	OG[l] (72)	TG[c] (40)	TG[k] (47)
ethanol	P	OG[g,m] (42)	jelly	OG[l,m] (84)	P	OG[l,m] (29)	S	S
1-butanol	P	P	P	OG[l,m] (68)	P	OG[l,m] (35)	S	S
1-octanol	P	P	P	OG[l] (67)	P	OG[l] (38)	S	S
benzyl alcohol	P	TG[l] (38)	TG[l] (72)	TG[l] (79)	jelly	TG[l] (60)	S	S
toluene	P	P	P	P	P	jelly	S	P
DMSO	TG[l] (25)	jelly (68)	TG[l]	OG[c,m] (41)	OG[c] (70)	S (72–76)	S	
CCl_4	P	P	P	OG[l] (35–42)	jelly	OG[l] (43)	S	P
water	I	I	I	I	I	I	S	S

[a] P: precipitate, S: solution, I: insoluble, TG: turbid gel, PG: partial gel. [b] Stable for >23 months, syneresis after three weeks. [c] Stable for one week. [d] Stable for five months, syneresis after one week. [e] Stable for >23 months. [f] stable for two weeks. [g] Stable for two months. [h] stable for >23 months, syneresis after six months. [i] Stable for >23 months, syneresis after one week. [j] stable for 13 months. [k] stable for two weeks. [l] stable for >eight months. [m] syneresis. [n] stable for >eight months, syneresis after 2 months.

bonding interactions in their networks,[16] and very few rely exclusively upon London dispersion forces.[17] As noted above, the substitution pattern of the alkyl group also plays a crucial role in the gelation properties of urea derivatives.

N,*N*′-Dialkylthioureas with shorter alkyl chains (**2a**–**c**) are poorer organogelators than their longer-chained homologues (Table 2) or their urea analogues (Table 1). Whereas 2 wt% of **1a** gelates two of the liquids investigated, the same concentration of **2a** did not gelate any of them. However, **2e**, the thiourea with the longest alkyl chains, gelates several liquids in Table 2 with remarkable thermal and temporal stabilities. These results and those with **1** indicate that although gelation can be effected when the LMOG fibrillar network is stabilized primarily by intermolecular hydrogen-bonding interactions, London dispersion forces can certainly help when they are oriented correctly within a structural matrix.

Dependence of gelator concentration on gel stability: The properties of gels of **1a**,**c** and **2c** in silicone oil and CCl_4 (**1a** only) were compared at different LMOG concentrations (Table S2 in the Supporting Information). Those with silicone oil are displayed in Figure 1. At concentrations as low as 0.5 wt% of **1a** in silicone oil, turbid gels with high thermal (T_g 65 °C) and temporal (two months) stabilities are produced. However, a turbid gel is formed in CCl_4 only at concentrations ≥2 wt% of **1a**. Although both **1c** and **2c** gelate also silicone oil at low concentrations, the T_g values of the **1c** gels are much higher and they plateau at concen-

Table 2. Gelation properties of thiourea derivatives **2a**–**e** in different liquids. Melting points of neat gelators and T_g values of the gels [°C] are given in parentheses.[a]

Liquid	**2a** (61.3–62.1)		**2b** (76.6–77.6)		**2c** (70.6–71.3)		**2d** (67.3–67.9)		**2e** (95.1–95.8)	
	2 wt %	5 wt %	2 wt %	5 wt %	2 wt %	5 wt %	2 wt %	5 wt %	2 wt %	5 wt %
hexane	P	P	P	P	P	P	P	P	P	P
n-octane	P	P	P	P	P	P	P	OG[b] (30–35)	P	P
n-decane	P	P	P	P	P	P	P	OG[c] (50)	P	P
silicone oil	P	P	TG[b] (51–53)	TG[b] (58)	TG[b] (47)	TG[c] (55)	TG[d] (52)	TG[d] (56)	TG[d] (50)	TG[d] (82)
ethanol	S	S	S	S	S	S	P	P	P	OG[d] (69)
1-butanol	S	S	S	S	S	S	S	P	OG[d] (56)	OG[d] (61)
1-octanol	S	S	S	S	S	S	S	P	OG[c] (48)	OG[d] (60)
benzyl alcohol	S	S	S	S	S	S	S	P	TG[d] (64–66)	TG[d] (69)
toluene	S	S	S	P	S	P	P	P	P	P
DMSO	S	S	S	S	S	S	P	OG[e] (30)	OG[c] (68)	OG[c] (70–74)
CCl_4	P	P	S	PG[b] (20–22)	S	S	P	P	P	P
water	S	S	S	S	P	P	I	I	I	I

[a] P: precipitate, S: solution, I: insoluble, TG: turbid gel, PG: partial gel. [b] Stable for one week; [c] Stable for three months. [d] Stable for >23 months, syneresis after one week. [e] Stable for two months, syneresis after one week.

trations >3 wt% (Figure 1). The T_g values of the corresponding **2c** gels increase linearly with concentration in the 1.0–5.0 wt% range and then become independent of concentration up to at least 9 wt%. The nature of the changes in Figure 1 are commonly observed for organogels.[16] Plots of these data for **1c** and **2c** according to the Ferry–Eldridge equation (i.e., log[LMOG] versus $1/T$)[56,80] gave nearly straight lines, whereas **1a** exhibited an upward concavity in the <2 wt% concentration region (Figure S1 in the Supporting Information). This nonlinearity may be attributed to the formation of junction zones having low heats of interaction between the gelator molecules,[80] to some of the gelator molecules remaining outside the solid network, or to the non-ideality of the sol phase obtained at $T > T_g$. The heats of gelation calculated from the linear plots, 0.012 J g^{-1} for **1c** and 0.019 J g^{-1} for **2c**, are much lower than the heats of melting of the neat gelators, 98.9 and 118.9 J g^{-1}, respectively, as determined by DSC measurements. The much lower heats of gelation indicate that the networks dissolve directly into the liquid component rather than melting and then dissolving.

The dependence of LMOG concentration on gel properties of the ureas with two (**1g**) or one (**1h**) *n*-octadecyl chain and the thiourea with two *n*-octadecyl chains (**2e**) was examined in silicone oil, 1-butanol, benzyl alcohol, and DMSO (Table 3 and Table S3 in the Supporting Information). In each liquid, LMOG **1g** is a slightly better gelator than the monosubstituted **1h**, and both are more efficient than the thiourea.

Thermal properties of gels: Differential scanning calorimetry (DSC) thermograms of silicone oil gels have been obtained at different concentrations of selected LMOGs. Representative sets of thermograms with **1c** and **2c** as the LMOGs are shown in Figure 2; Figure S2 in the Supporting Information contains thermograms for gels with **2e**. Unlike the "falling drop" measurements of T_g, that are determined by a partial *loss* of strength of the gel networks,[80] the transition temperatures observed by DSC measure the *melting* of the crystalline fibrils of the gelator networks. Here, they are almost independent of concentration. In other work, we have observed a more marked dependence of DSC-determined transition temperatures on both LMOG concentration and the cooling protocol for preparation of the gel from its sol.[54] The lack of a clear urea or thiourea concentration dependence on these transition temperatures strongly suggests that solubilization of the gelators by the liquids has a very pronounced temperature dependence; virtually all of

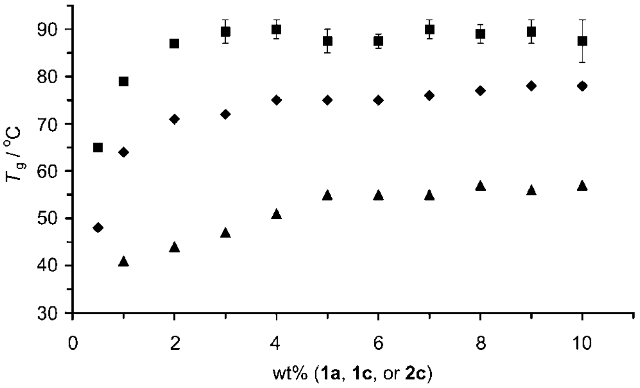

Figure 1. T_g values [°C] of **1a** (■), **1c** (◆), and **2c** (▲) gels in silicone oil as a function of gelator concentration.

Table 3. Gelation properties of **1g** and **1h** in silicone oil, 1-butanol, benzyl alcohol, and DMSO as a function of gelator concentration. The T_g values [°C] are given in parentheses.[a]

wt %	Silicone oil		1-Butanol		Benzyl alcohol		DMSO	
	1g	**1h**	**1g**	**1h**	**1g**	**1h**	**1g**	**1h**
0.50	TG[b] (69)	jelly	P	P	P	S	P	P
1.0	TG[b] (85)	TG[b] (67)	P	P	jelly	S	P	P
2.0	TG[c] (95)	TG[c] (77)	P	jelly	TG[c] (70)	TG[d] (26)	jelly	jelly
3.0	TG[c] (97)	TG[c] (80)	P	TG[c] (33)	TG[c] (77)	TG[d] (42)	TG[e] (31)	TG[c] (56)
4.0	TG[c] (>97)	TG[c] (82)	TG[c] (46)	OG[c] (38)	TG[c] (80)	TG[c] (44)	TG[e] (35)	TG[c] (60)
5.0	TG[c] (>97)	TG[c] (85)	OG[c] (67)	OG[c] (43)	TG[c] (80)	TG[c] (47)	TG[e] (41)	TG[c] (63)

[a] P: precipitate, S: solution, TG: turbid gel. [b] Stable for three weeks. [c] Stable for > three months. [d] Stable for two weeks. [e] Stable for one week.

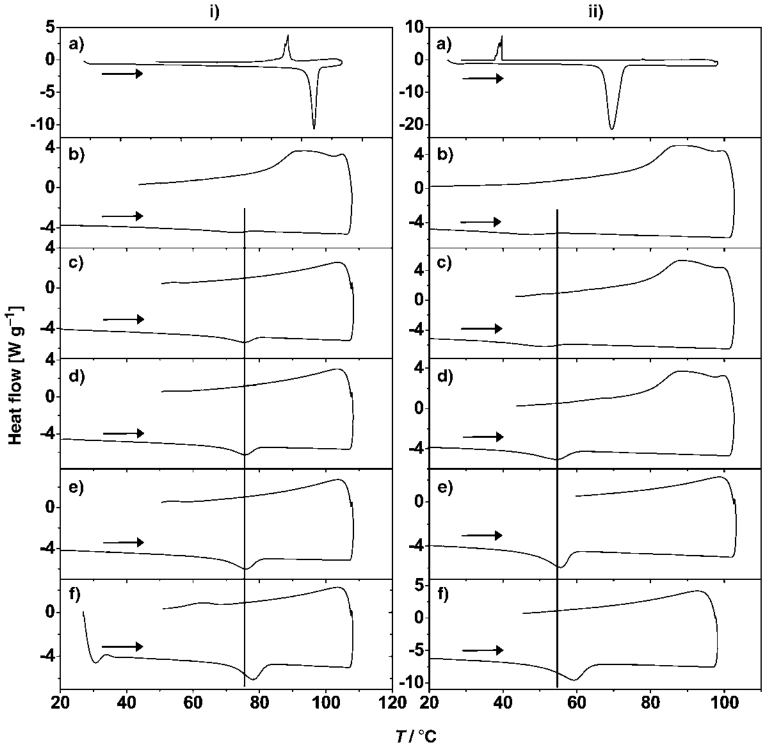

Figure 2. DSC thermograms of the first heating and cooling cycle of i) **1c** and ii) **2c** neat solids (a) and their gels in silicone oil at b) 1 wt %, c) 2 wt %, d) 3 wt %, e) 4 wt %, and f) 5 wt % concentrations. Arrows indicate the direction of temperature change. The gels wee prepared from their hot sol phases by the fast cooling protocol (see Experimental Section).

the gelator molecules must be incorporated within the fibril network below T_g, and they remain there up to T_g. Note also that these temperatures are significantly lower than the melting temperatures of the neat gelators. Regardless, the strength of a network is dependent on the number and strength of fibers as well as the strength of junction zones where individual fibrils intersect to form a three-dimensional network.[16] Clearly, the DSC data reflect the melting of fibrils and provide little or no information concerning the retention of junction zones. However, in most cases, the T_g from "falling drop" experiments and DSC measurements follow the same trend.[54–59]

Polarizing optical microscopy (POM) studies: Pertinent optical micrographs (OMs) of gels containing the LMOGs listed in Scheme 1 are shown in Figures 3–6 and Figures S3–7 in the Supporting Information. The nature of the aggregates depends on the type of gelator, its alkyl chain length, and the cooling protocol. From theoretical studies that emphasize differences in intermolecular hydrogen-bonding energies, elongated aggregates are favored by urea and ribbons are favored by thiourea.[51,52] Three different cooling protocols were used to prepare the gels for POM studies (see Experimental Section for details) because the nature of the aggregates depended on the cooling rate from the solution/sol phase. For instance, elongated and strandlike aggregates are seen in the image of the 2 wt % gel of **1a** prepared by slowly cooling its hot CCl_4 solution, and shorter objects are observed when the gel was prepared by fast- or moderate-cooling rates. Temperature-induced transitions from spherulitic to rod-like growth patterns of gels have been observed in other systems as well.[60,61]

The lengths of the aggregated objects are also reduced considerably when the alkyl chain lengths of the gelator substituents are increased. For example, elongated fibrils of **1c**, **2c** and **3** are found in silicone oil gels (Figure 4), but highly dispersed, small aggregates are present in the silicone oil gels of **1f–h** (Figure 5) and **2e** (Figure 6). Some plate-like microcrystals were evident in a 5 wt % **3** in silicone oil gel (Figure S7 in the Supporting Information); microcrystals were not detected in any of the other gels at LMOG concentrations up to 5 wt %. Although the best distinction between a gel network and an aggregation of microcrystals (i.e., Figures 3c and 4a, bottom row) is based on rheological measurements, our visual observations of how the samples "melt" during the "falling drop" experiments indicate that our assignments are correct.

Regardless of the cooling protocol employed, the three-dimensionality of the gel networks appears to be due to a combination of extensive branching, leading to intertwining of colloid-like objects (as in Figure 3a) or physical junction zones in which long rod-like objects intersect with each

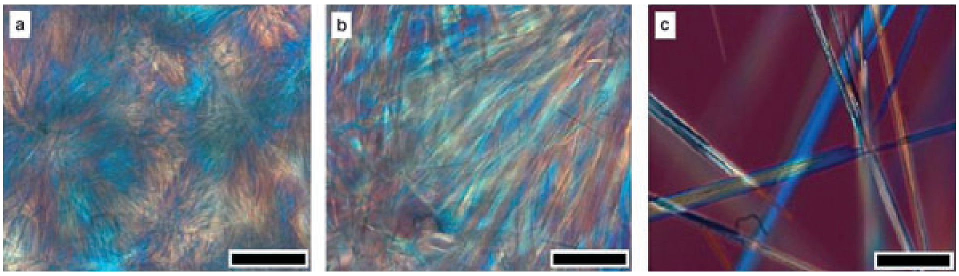

Figure 3. Polarizing optical micrographs (room temperature) of gels of 2 wt % **1a** in CCl_4: a) fast cooling, b) moderate cooling, and c) slow cooling. Black space bars are 200 μm.

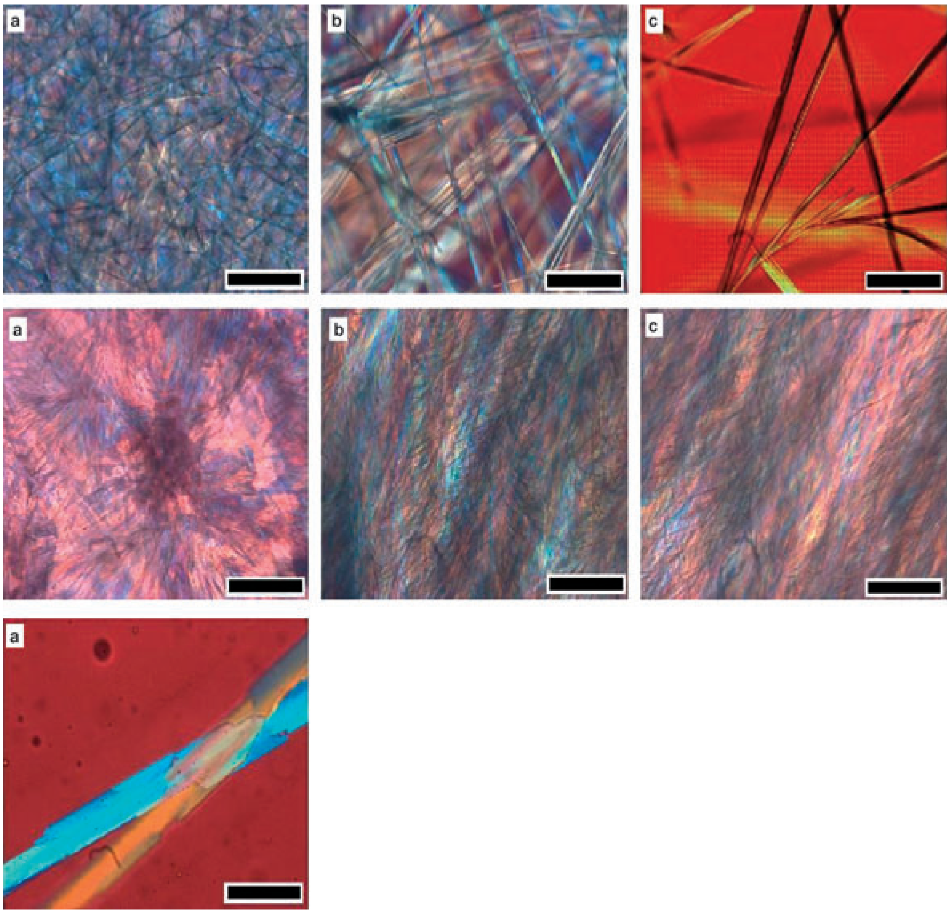

Figure 4. Polarizing optical micrographs (room temperature) of gels comprised of 2 wt % **1c** (top row), 5 wt % **2c** (middle row), and 2 wt % **3** (bottom row) in silicone oil. Protocols: a) fast cooling, b) moderate cooling, and c) slow cooling. Black space bars are 200 μm.

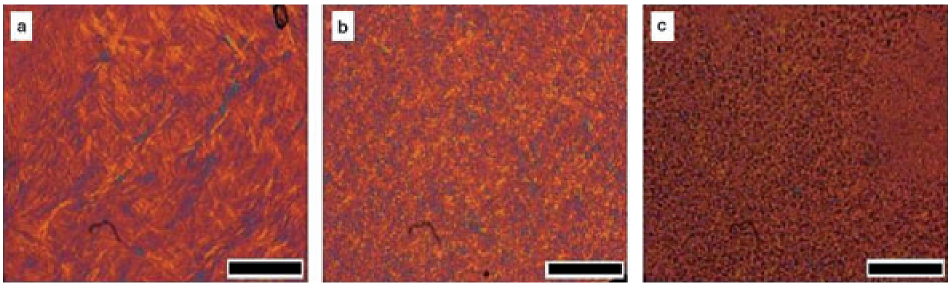

Figure 5. Polarizing optical micrographs (room temperature) of silicone oil gels. a) 2 wt % **1f**, b) 2 wt % **1g**, and c) 5 wt % **1h**. The gels were made by the fast cooling protocol. Black space bars are 200 μm.

other (as in Figure 3c). The natures of these junction zones have been discussed previously.[16] They probably are produced during the nucleation and growth steps as sols are reduced to temperatures below T_g and objects increase in length along specific trajectories (defined by their long axes) until they collide with another rod-like object.

Although the optical micrographs of several of these gels are very dependent on the protocols used to cool their solutions/sols, the transition temperatures (temperatures of maximum heat flow on heating) from DSC analyses are not. Figure 7 contains DSC thermograms of gels of 2 wt % **1c** or **2c** in silicone oil from the fast and moderate cooling methods. The heat flow maxima occur in the same temperature ranges for gels with each LMOG. As mentioned previously, the transition temperatures of other gels whose LMOGs have somewhat related structures *do* depend markedly on the protocol for gel preparation.[54]

Atomic force microscopic (AFM) studies: An AFM image of a gel of 2 wt % **1c** in isooctane that was allowed to dry (i.e., a xerogel; see Experimental Section) is shown in Figure 8. Domains of fibrils stacked on top of each other are clearly visible. An optical micrograph of the same xerogel sample (Figure S8a in the Supporting Information) and that of the gel (Figure S8b in the Supporting Information) appear to have the same morphology of fibrils. On this basis, we believe that the fibrils of the gel maintain their structural identity in the xerogel; the AFM images represent the network structure of the gel.

The topography of the sample from the 2 wt % **1c** in

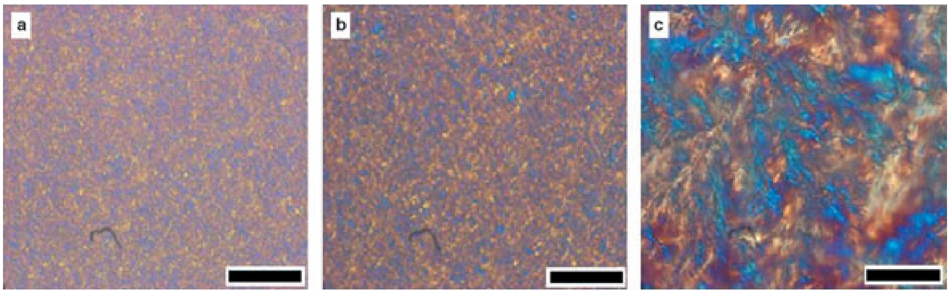

Figure 6. Polarizing optical micrographs (room temperature) of gels of 2 wt % **2e** in silicone oil. a) Fast cooling, b) moderate cooling, and c) slow cooling. Black space bars are 200 μm.

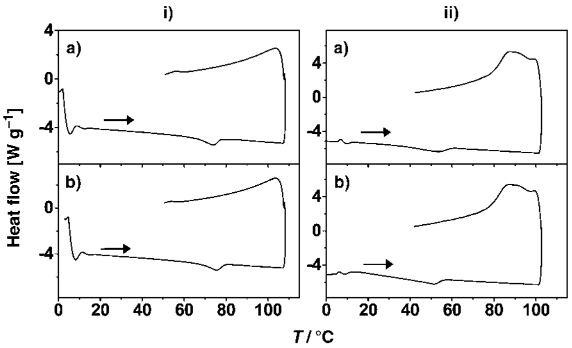

Figure 7. DSC thermograms (first heating and cooling cycles) of silicone oil gels containing 2 wt % of i) **1c** and ii) **2c** prepared by a) fast and b) moderate cooling protocols. Arrows indicate the direction of temperature change.

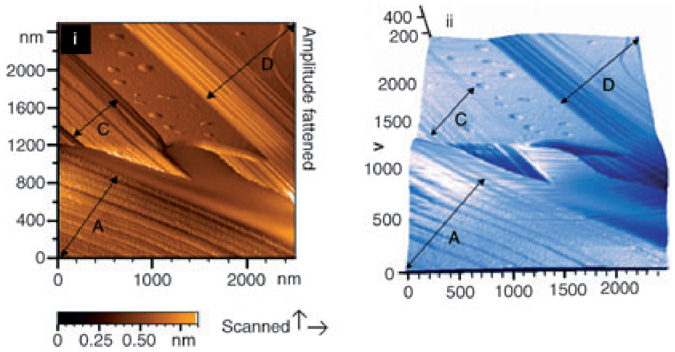

Figure 8. i) Amplitude AFM image of a xerogel prepared from a gel of 2 wt % **1c** in isooctane and ii) a 3D view of the topography of the same surface used in i). The full scale is 2.5 micron × 2.5 micron.

isooctane gel suggests that the aggregates consist of flat sheets of varying thickness that are stacked on top of one another (Figure 8). The sheets are formed from bundled, long fibrils, each of thickness less than 10 nm. Since the diameter of **1c** is about 3.7 Å (as calculated from the volume, 154.2 Å^3,[62] and length, 14.1 Å,[63] of a fully extended molecule), each fibril has about 27 **1c** molecules stacked along its shortest axis. The stacked sheets project out of the plane with height about 50 nm for aggregate A and about 100 nm for D (indicated by arrows). A slight dip in the middle of the structure (region C) is clearly visible in the image.

Scanning electron microscopy (SEM) studies: Scanning electron micrographs of xerogels prepared from gels of 2 wt % **1a** in CCl_4 and 2 wt % **1c** in *n*-octane are shown in Figure 9. Fibrils of about 2–5 μm thickness are present in the **1a** sample and thicker fibrils are seen for **1c**. Close inspection of these micrographs and information gleaned from the AFM images strongly indicate that much narrower fibers are bundled to make these objects. Stacks of layers are clearly visible in the SEM image of **1c**.

IR spectral studies: The modes of stabilization of aggregates of several urea derivatives have been studied extensively. Comparison of IR spectra of their neat, solution, and gel phases indicate the importance of intermolecular hydrogen bonding.[34–37,64–67] The same conclusion is reached here. The NH and CO or CS group absorbances of IR spectra of LMOGs as neat solids and in their silicone oil gels appear at the same frequencies; see for example, Figures 10 and 11, and Figures S9 and S10 in the Supporting Information. From this observation, we infer that the nature of the intermolecular hydrogen bonding is the same in the solid and gel. However, because the NH stretching bands in the gel spectra are slightly broader than those of the solid, there must be somewhat more disorder in the gel fibrils. The broadness may arise from the relatively large populations of gelator molecules at the surfaces of the fibrils and at junction zones.

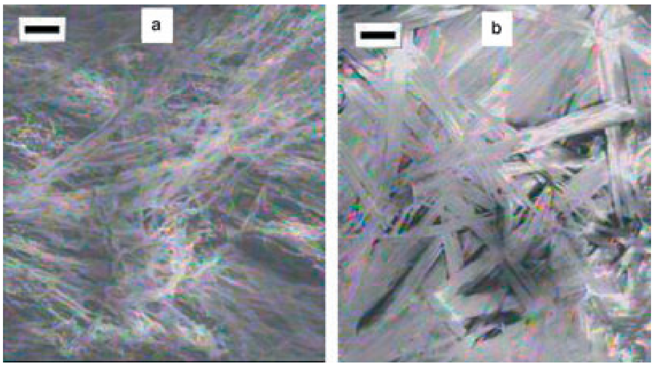

Figure 9. SEM images of xerogels prepared from gels of a) 2 wt % **1a** in CCl_4 and b) 2 wt % **1c** in octane. Black space bars are 20 μm in a) and 50 μm in b).

X-ray diffraction (XRD) studies: Diffraction peaks of the gel network assemblies of **1–3** were obtained by subtracting

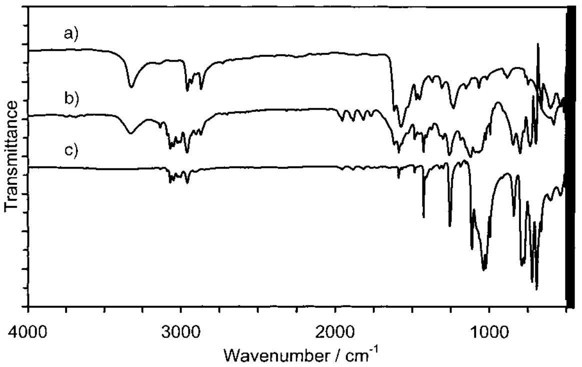

Figure 10. IR spectra of a) neat **1c**, b) a gel of 5 wt% **1c** in silicone oil, and c) silicone oil. The approximate contributions from the silicone oil have been subtracted from the spectrum in b).

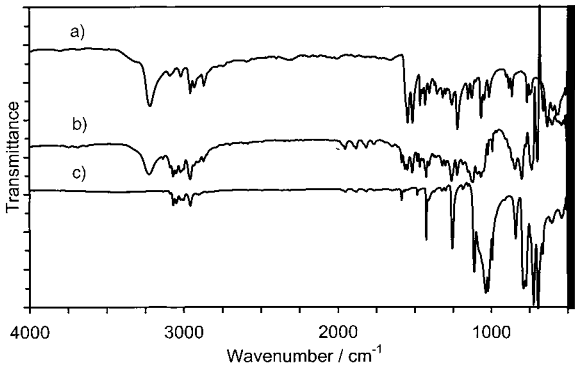

Figure 11. IR spectra of a) solid **2c**, b) a gel of 5 wt% **2c** in silicone oil, and c) silicone oil. The approximate contributions from the silicone oil have been subtracted from the spectrum in b).

the "amorphous scatter" of the liquid components from the total diffractograms of the gels.[68] The subtracted diffractograms were then compared with diffraction patterns of the solid LMOGs (Figures 12–14 and Figures S11–S15 in the Supporting Information) to determine whether the molecular packing arrangements in the two are the same. This analysis is possible because the gelator networks of these LMOGs are crystalline in nature; not all LMOG networks are.[16] However, the low concentrations of the LMOGs and the (sometimes) intrinsically weak diffracting power of the fibrils can make these determinations difficult. Despite the weakness of some of the peaks from gels of **1–3**, in most cases they coincide with peaks of the solid LMOGs (Figures S16–S18 in the Supporting Information); the molecular packing arrangements within the gel assemblies and the bulk crystals are the same. In fact, it is more common for the gel and bulk solid morphs of LMOGs to differ.[68]

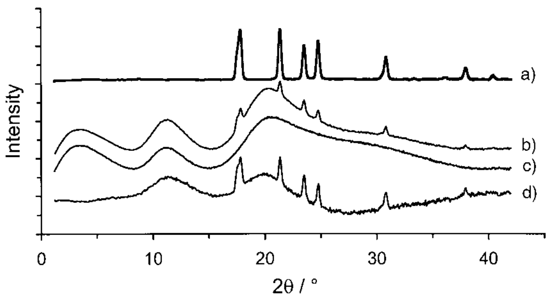

Figure 12. X-ray diffraction patterns at room temperature of **1a**: a) powder, b) gel, 2 wt% in silicone oil, c) silicone oil, and d) diffractogram b subtracted from diffractogram c).

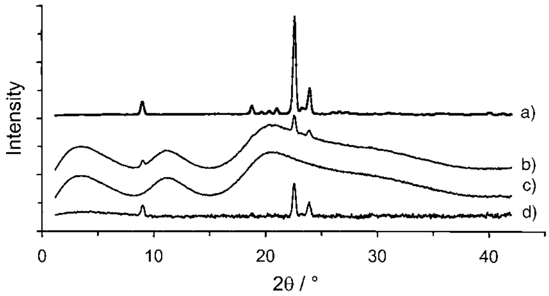

Figure 13. X-ray diffraction patterns at room temperature of **1c**: a) powder, b) gel, 2 wt% in silicone oil, c) silicone oil, and d) diffractogram b subtracted from diffractogram c).

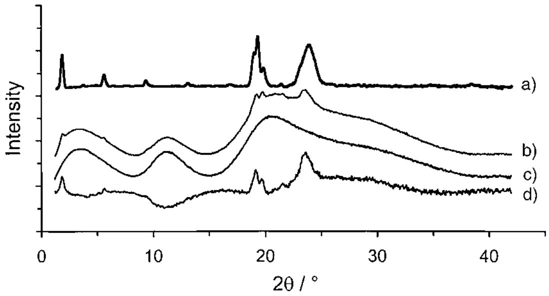

Figure 14. X-ray diffraction patterns at room temperature of **2e**: a) powder, b) gel, 5 wt% in silicone oil, c) silicone oil, and d) diffractogram b) subtracted from diffractogram c).

The presence of a low-angle peak in diffractograms of neat powders and gels whose LMOGs contain long alkyl chains is consistent with lamellar organizations. The Bragg distances (*d*) of the low-angle peaks, representing the thicknesses of the layers and the calculated van der Waals lengths (*l*) of the fully extended urea and thiourea molecules[63] are collected in Table 4.

For the *N,N'*-dialkylureas, the values of *l* vary from much longer to slightly longer than those of *d*. The values of *l* and *d* of the thioureas with two long alkyl chains (**2d,e**) are equal within the limit of experimental error. From this correspondence, **2d,e** must adopt extended conformations and their long axes must be orthogonal to the lamellar planes (Figure 15a). This cannot be the case for the other dialkylated LMOGs in Table 4. They must be in bent conformations, their long axes must be tilted with respect to the layer planes, or they must be interdigitated (Figure 15b). The same possibilities apply to the monoalkylated ureas **1e** and **1h**; a potential interdigitated arrangement is shown in Figure 15c.

Table 4. Lamellar spacings (*d*) from the lowest angle peaks in X-ray diffraction patterns of powders and gels of **1** and **2** and calculated van der Waals extended molecular lengths (*l*).[63] All distances are in Å.

LMOG	**1**		**2**	
	l	*d*	*l*	*d*
a	9.0	5.0	8.9	[a]
b	11.6	8.8	11.6	9.0
c	14.1	9.9	13.8	11.2
d	16.6	13.4	27.8	27.7
e	10.3	9.5	45.1	46.3
f	28.3	25.3		
g	45.1	36.9		
h	28.4	40.8		

[a] Not determined.

We have generated powder diffraction patterns for **1a** and **2b**, the two LMOGs whose single crystal X-ray data[69] are reported in the literature (Figure 16 and Figure S19 in the Supporting Information).[70,71] The complete superposition of the experimental and generated diffraction peaks demonstrates that molecular packing within the gel aggregates is the same as in the bulk (single) crystals prepared from non-gelated solvents. The latter for **1a** contains three-centered intermolecular hydrogen bonds that form infinite rows;[70] **2b** exists as a dimer due to NH···S hydrogen bonding that links molecules to form zigzag chains and two-dimensionally knitted layers (Figure 17).[71]

Conclusion

As part of our ongoing effort to design structurally simple LMOGs that are *n*-alkanes with an inserted hetero-functionality, we have investigated the gelating properties of molecules in which the length of the "alkane" has been changed and a urea or thiourea functional group has been inserted at a chain end (i.e., *N*-alkylureas) or in a chain center (i.e., *N*,*N'*- or *N*,*N*-dialkylureas depending on the mode of insertion). These ureas and thioureas are more efficient gelators than their parent *n*-alkanes, the structurally simplest class of LMOGs.[54,57] Whereas London dispersion forces alone are responsible for the stabilization of the *n*-alkane LMOG networks, and only long *n*-alkanes are successful gelators at room temperature, introduction of one heteroatom (e.g., a sulfur or nitrogen atom) along slightly shorter *n*-alkane chain provides LMOGs capable of gelating a variety of organic liquids because the London dispersion forces are augmented by intermolecular H-bonding and dipolar forces.[54,58]

In the present study, attachment of urea or thiourea groups to the end or their insertion in the middle of an *n*-alkane as short as ethane (**1a**) has resulted in LMOGs! In fact, **1a** is the lowest molecular mass organogelator known

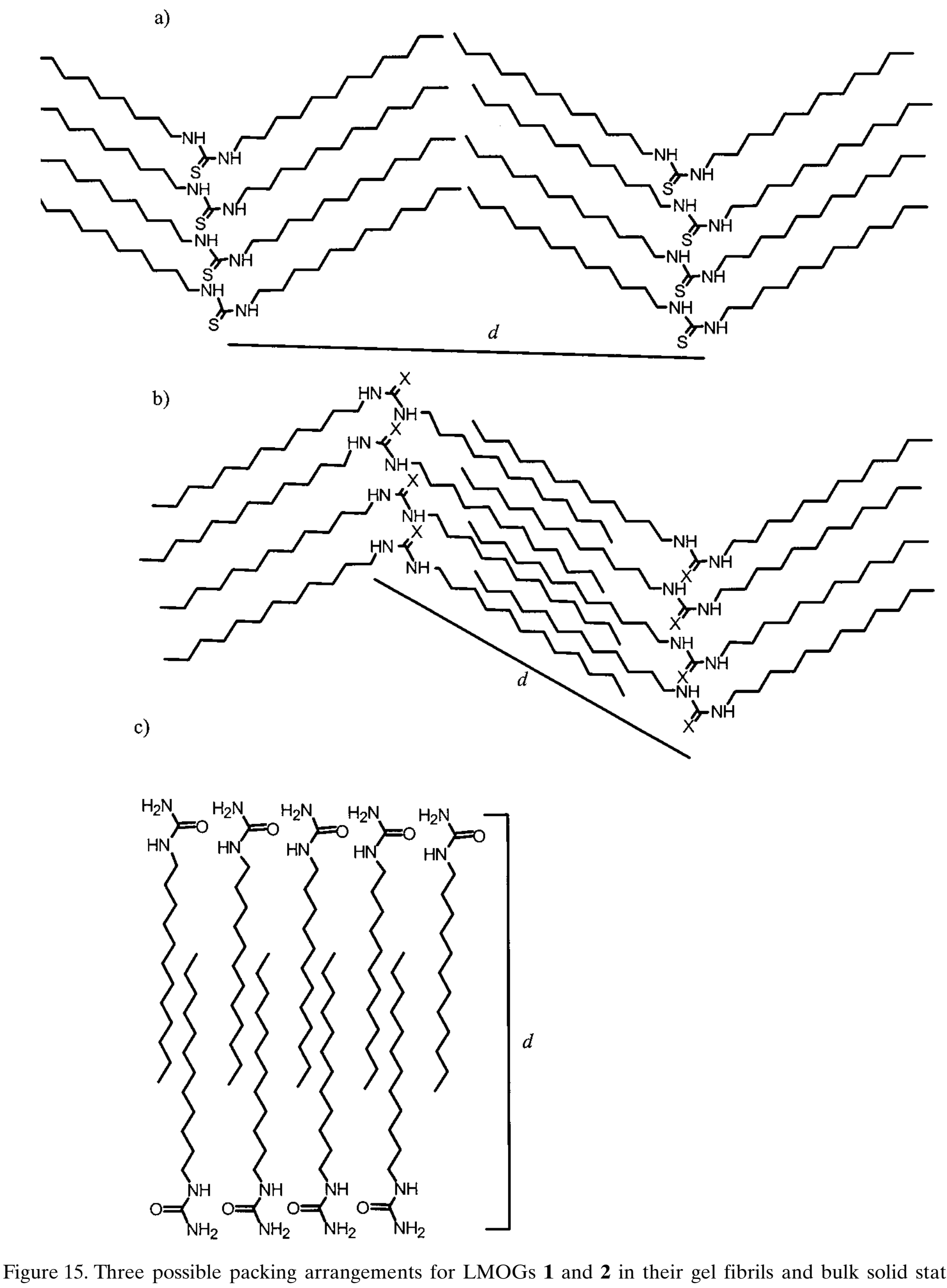

Figure 15. Three possible packing arrangements for LMOGs **1** and **2** in their gel fibrils and bulk solid states.

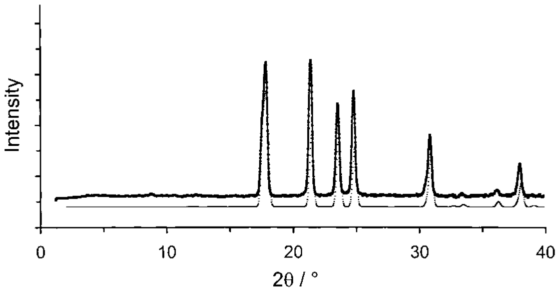

Figure 16. X-ray diffraction of **1a** powder at room temperature (solid line) and generated theoretically from the single crystal parameters (dotted line).[70]

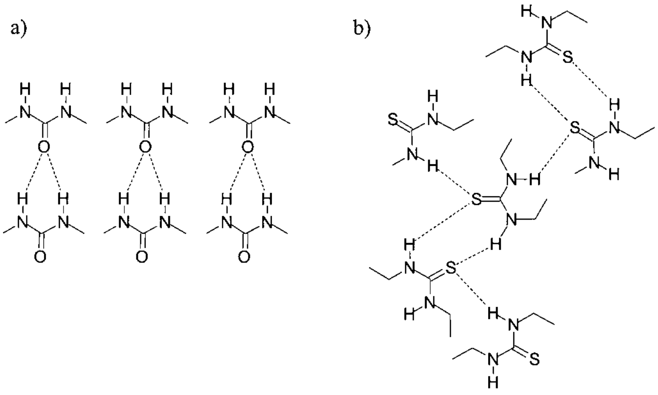

Figure 17. Representation of intermolecular H-bonds indicated by the crystal structures of a) **1a** and b) **2b**. See refs. [70] and [71] for details.

(M_W 88) to the best of our knowledge and some of these very small and structurally simple *N*-alkyl and *N*,*N*′-dialkyl substituted ureas and thioureas are efficient gelators of a variety of organic liquids. Different contributions by hydrogen bonding and London dispersion interactions are responsible for our observation of three types of molecular packing arrangements within the gel fibrils, including lamellar ones. Primarily as a result of their stronger hydrogen-bonding abilities, ureas are more efficient gelators than their thiourea analogues.[51,52]

In future work, we intend to explore an additional perturbation on the structures of these molecules by placing a center of chirality along one or both of the alkyl chains. Chiral fibrils have been observed in the strands of several optically-active LMOGs with complex structures.[72–76] With the exception of the tartrate gelators explored by Oda and co-workers,[77] it is difficult to pinpoint the relationship between molecular and strand asymmetry.[73,74] By using a series of alkylated ureas and thioureas with only one center of chirality and in which that center can be moved systematically along the alkyl chain, it should be possible to determine the relationship between molecular and aggregate chiralities.

Experimental Section

Instrumentation: Melting point determinations (corrected) of neat gelators and polarized optical microscopy (POM) of gels were performed on a Leitz 585 SM-LUX-POL microscope equipped with crossed polars, a Leitz 350 heating stage, a Photometrics CCD camera interfaced to a computer, and an Omega HH503 microprocessor thermometer connected to a J-K-T thermocouple. IR spectra were obtained on a Perkin-Elmer Spectrum One FT-IR spectrometer interfaced to a PC. NMR spectra were recorded on a Varian 300 MHz spectrometer interfaced to a Sparc UNIX computer using Mercury software and were referenced to internal TMS (^{1}H) or internal $CDCl_3$ (^{13}C). Differential scanning calorimetry (DSC) was performed on a TA 2910 differential scanning calorimeter interfaced to a TA Thermal Analyst 3100 controller. All DSC data are reported at temperatures of maximum heat flow. Heating rates were 5 °C min^{-1}; cooling rates were variable and depended on the difference between the cellblock and ambient temperatures. X-ray diffraction (XRD) of samples in thin, sealed capillaries (0.5 mm ∅; W. Müller, Schönwalde, FRG) was performed on a Rigaku R-AXIS image plate system with Cu Kα X-rays ($\lambda = 1.54056$ Å) generated with a Rigaku generator operating at 46 kV and 46 mA. Data processing and analyses were performed using Materials Data JADE (version 5.0.35) XRD pattern processing software.[78] Molecular calculations of lowest energy conformations and molecular dimensions were performed with the semiempirical Parametric Method 3 (PM3)[63a] of the HYPERCHEM package (release 5.1 Pro for Windows from Hypercube, Inc.).

Materials: Silicone oil (Dow silicone oil 704; tetramethyltetraphenylsiloxane) was purchased from Dow Chemical Company and used as received. Other solvents used for the preparation of gels were reagent grade (Aldrich) and used as received. 1-Decylamine (95 %), urea (98 %), *N*,*N*′-dimethylurea (**1a**, 99 %), *N*,*N*′-dimethylthiourea (**2a**, 99 %), *N*,*N*′-diethylthiourea, (**2b**, 98 %), and *N*,*N*′-di-*n*-propylurea (**1c**, 97 %) from Aldrich and *N*,*N*′-diethylurea (**1b**, 97 %), *N*,*N*-diethylurea (**3**, 97 %), *N*-*n*-propylurea (**1e**, 95 %) and *N*,*N*′-di-*n*-butylurea (**1d**, 98 %) from Lancaster were used as received. 1-Octadecylamine (Aldrich) was distilled twice under vacuum prior to use. *N*,*N*′-di-*n*-propylthiourea (**2c**), *N*,*N*′-di-*n*-decylthiourea (**2d**), and *N*,*N*′-di-*n*-octadecylthiourea (**2e**) were prepared as described in the literature.[48] *N*-*n*-octadecylurea (**1h**), *N*,*N*′-di-*n*-decylurea (**1f**) and *N*,*N*′-di-*n*-octadecylurea (**1g**) were prepared by modification of a reported procedure.[79] Melting points and spectroscopic and analytical data for the compounds prepared are collected in Table S1 in the Supporting Information.

Preparation of gels and determination of gelation temperatures: Weighed amounts of a liquid and a solid were placed in a glass tube (5 mm i.d.) that was usually flame-sealed (to avoid evaporation). Gel samples for POM analyses were prepared in closed Pyrex flattened capillary cells (2 mm pathlength). The tubes were heated in a water bath (until all solid dissolved) and cooled rapidly in an ice-water mixture twice to ensure homogeneity. Three different cooling protocols were used to make gels for polarized optical microscopy studies: a hot solution/sol was cooled rapidly by dipping its tube in an ice-water mixture (fast cooling); a hot solution/sol was cooled by leaving the tube in the air at room temperature (moderate cooling); the tube containing a hot solution/sol was left in a hot water bath that was cooled slowly to room temperature in the air (slow cooling).

Gelation temperatures (T_g) were determined by the inverse flow method.[80] A gel in a sealed glass tube was inverted, strapped to a thermometer near the bulb, and immersed in a stirred water bath at room temperature. The temperature of the bath was raised slowly and the range of T_g was taken from the point at which the first part of the gel was observed to fall to the point at which all had fallen under the influence of gravity.

AFM studies: Gels from **1c** (ca. 2 wt %) for AFM imaging were prepared in isooctane. The mixture was heated and cooled 3× prior to casting the gel onto a mica disc placed in a petri dish. The sample was left open to the atmosphere for one day (to allow a large portion of the isooctane to evaporate) before making AFM images. Tapping mode AFM imaging (MAC mode imaging) was performed under ambient conditions on a PicoSPM (Molecular Imaging) instrument by using Type II MAC levers (silicone cantilevers). The tip has the shape of a pyramid and polygon at the base. Its macroscopic cone angle is 40–50° when viewed along the direction of the cantilever axis and 50–60° when viewed from the side. The angle is reduced to less than 20° at the apex of the tip. The tip radius was typically less than 10 nm and its height was 10–15 micron. Typical force constants of 1.2–5.5 nN nm^{-1} were used. Images were acquired with the cantilevers operated at their fundamental resonance frequencies of 60–100 kHz. The tip vibrational frequency was set on the low frequency side of the resonance peak, corresponding to a free air tip amplitude of 70% of the resonance peak height amplitude. Topography, amplitude and phase images were collected at scan rates ranging from 0.4–2 lines s^{-1} and at a scan angle of 0°.

SEM analyses: SEM pictures were obtained on a ZEISS DIGITAL DSM960 scanning electron microscope equipped with an ATI TV capture card. Samples were attached to an Al holder by conductive adhesive tape and dried under high vacuum (ca. 10^{-6} Torr) for ca. 2 h at room temperature prior to analyses.

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