Chemically Reversible Organogels: Aliphatic Amines as "Latent" Gelators with Carbon Dioxide

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Thermally reversible organogels, consisting frequently of ≤ 2 wt % of a low-molecular mass gelator (**LMOG**) and an organic liquid,[1] are microheterogeneous phases that self-assemble in a wide variety of modes expressed from the molecular to the micrometer-distance scales. When sols or solutions of any of these systems are cooled below the characteristic gelation temperature (T_g), the **LMOG**s aggregate into fibers, strands, tapes, and so forth which join at "junction zones"[1f] to form networks that immobilize the liquid component.[1c] The unusual structural and diffusional properties of organogels have led to several interesting applications.[2] An exceedingly broad range of organic liquids, including quasi-liquids such as supercritical CO_2, has been gelled,[3] and very diverse types of **LMOG**s—ranging from two components (acting via specific H-bonding interactions) or single species whose structures can be salts to multifunctional molecules or even simple long-chained *n*-alkanes—are known.[1a,c,4]

Here, we report a new type of **LMOG**, ammonium carbamates (**2**), and a new, reversible organogelation process based on the *rapid and isothermal* (at room temperature) uptake of CO_2 by a "latent" **LMOG**, an amine (**1**), and loss of CO_2 from its ammonium carbamate (**2**) upon heating (Scheme 1). Key to the success of this approach is the known reversible uptake of CO_2 by many primary and secondary amines.[5] The neat ammonium carbamates in Scheme 1 lose CO_2 when heated to ≥ 100 °C for several minutes. Experimentally, CO_2 is bubbled through an amine solution for several minutes to form the gel, and N_2 is bubbled through the heated gel (to avoid reformation of **2** on cooling) to destroy it; the gelation/degelation cycle can be repeated many times without detectable degradation of the system. When CO_2 is lost from **2** in a closed vessel so that it can recombine with **1**, formation of the ammonium carbamate and gelation are thermally reversible. To ensure homogeneity, gels were sealed in glass tubes and then heated and cooled rapidly under tap water twice before measurements were made.

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Scheme 1
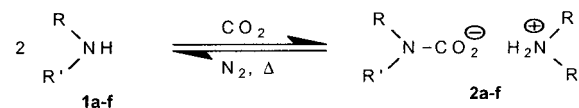
	R	R′		R	R′
a	$C_{18}H_{37}$	H	d	C_8H_{17}	C_8H_{17}
b	$C_{16}H_{33}$	H	e	$C_{18}H_{37}$	CH_3
c	$C_{10}H_{21}$	H	f	$H_2NC_{12}H_{24}$	H

In situ evidence for the presence of **2** in gels was obtained from FT-IR spectroscopy. The similarities between the relative intensities and positions of carbamate absorbances of neat solids of **2a** or **2b** (1645 and 1567 cm^{-1}) and of their 2−5 wt % gels with silicone oil[6] (1648 and 1568 cm^{-1}) suggest similar aggregation structures on a molecular level.

Generally, the amines[7] in Scheme 1 are transformed from nongelators (or not very inefficient ones[4b]) to ammonium carbamates[8] that are at least somewhat more efficient **LMOG**s as indicated by the variety of liquids[7] gelled, the periods over which the gels persist in sealed tubes at room temperature, and the T_g values (taken to be the temperatures at which gels, inverted in sealed glass tubes, fell under the influence of gravity when heated[9]). Qualitatively, longer *n*-alkyl chains of primary amines produced better ammonium carbamate gelators: although even 2 wt % of **2a** was able to gel about half of the liquids in Table 1, the same concentration of **2b** gelled 4 of the liquids, but with much lower T_g values and (except for silicone oil) stability periods of <1 week, and **2c** gelled only silicone oil and with a much lower T_g and period of stability than **2b**. Whereas 2 wt % of the symmetrical amine, **1d**, was able to form a partial, unstable gel only in silicone oil, T_g of the corresponding **2d** gel was ca. 50 °C higher. The unsymmetrical and slightly longer secondary amine, **1e**, produced gels with silicone oil, nitrobenzene, and DMSO that persisted for less than 1 week and its ammonium carbamate, **2e**, was not an appreciably better gelator. Neither the diamine, **1f**, nor **2f** was a good gelator; each gelled silicone oil poorly, and **1f** made an unstable partial gel additionally with octane (T_g <0 °C). At 0.5−1.0 wt %, only **2f** was dissolved in boiling water; the solutions yielded unstable, quasi-gels when cooled.

The properties of gels employing **1a** and **2a** are described in greater detail. **1a** is a very poor **LMOG**, even in relatively large concentrations.[4b] It formed unstable gels only with DMSO and silicone oil. By contrast, all of the liquids listed in Table 1 (except nitrobenzene) provided gels of **2a** that persisted for >3 months at room temperature. T_g measurements on 2 wt % silicone oil gels indicate that the **1a→2a** transformation is complete after only ca. 30 s of CO_2 bubbling at room temperature and that **2a→1a** requires ≤ 2 min N_2 bubbling at 60 °C. According to differential scanning calorimetry (DSC) thermograms of gels containing <2 wt % **2a** in silicone oil, gelator strands dissolve (i.e., disassemble) at <70 °C.

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(6) Tetramethyltetraphenylsiloxane (Dow silicone oil 704) was selected as the liquid for structural studies here because its very low volatility allows gels to be handled in the air without sample loss.

(7) Solvents were reagent grade or purer. Amines (Aldrich) were heated under N_2 atmospheres to remove traces of carbamates, or they were distilled and stored under nitrogen, depending upon their initial purity. Ammonium carbamates were isolated by passing CO_2 gas through a chloroform solution of the corresponding amine for 15 min; hexane was the solvent for 1-decylamine and dioctylamine. The precipitates were then filtered and dried. Melting points of the amines and carbamates are reported as Supporting Information.

(8) Although **1d→2d** and **1e→2e** using this technique, another secondary amine with longer alkyl chains, *N,N*-dioctadecylamine, was not converted appreciably to its ammonium carbamate in a variety of liquids. Clearly, there are limitations to the amine structures that can be converted efficiently to ammonium carbamates for gelation.

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Table 1. Gelation Properties[a] of 2 and 5 wt % **1a** and **2a** in Various Liquids[b]

	1a		**2a**	
liquid	2 wt %	5 wt %	2 wt %	5 wt %
hexane		P	P	OG (54−56)
n-octane		P	P	OG (56−60)
silicone oil	TG (25)	TG[b] (35)	TG (59−60)	TG (80)
ethanol		P	P	OG (54−56)
1-butanol		P	P	OG (49−50)
1-pentanol	S	S	PG (<0)	OG (52−55)
1-octanol		P	P	OG (40−42)
benzyl alcohol		S	TG (44)	TG (53)
toluene		S	TG (47−48)	TG (56)
nitrobenzene		S		PG (<10)
DMSO	TG (50−52)	TG (48−50)	TG (74−76)	TG (90−92)
CCl₄	P	P	P	TG (40−42)

[a] S = solution, P = precipitate, PG = partial gel, TG = turbid gel, and OG = opaque gel. [b] All gels were stable at room temperature in closed tubes for >3 months unless indicated otherwise. values of T_g (°C) are in parentheses. [c] Stable < 1 week.
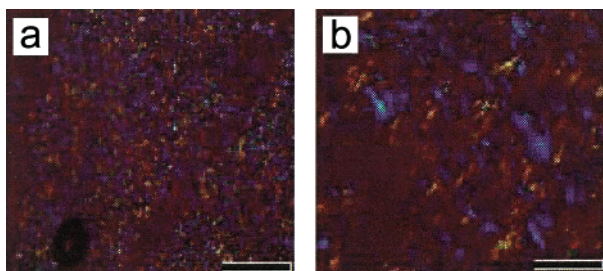
Figure 1. Polarizing optical micrographs at room temperature of 2 wt % gels in silicone oil: (a) **1a**; (b) **2a**. The space bars are 100 μm.
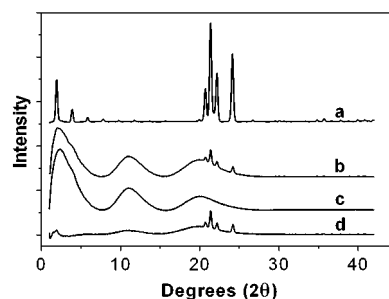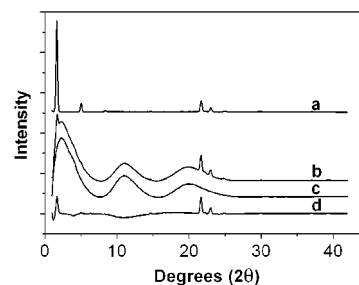
Polarizing optical micrographs of **1a** and **2a** silicone oil gels are presented in Figure 1. The aggregates from the **2a** gel are clearly more elongated and strand-like than those from **1a**. On this basis alone, the **2a** assembly should be able to immobilize a liquid better than that of **1a**. The higher dissolution temperatures (i.e., lower solubilities) of **2a** in silicone oil also predict that its gels will be more stable those of **1a**.

After subtraction of the "amorphous" scatter from the liquid component, X-ray diffraction patterns[10] of 5 wt % silicone oil gels of **1a** and **2a** match those of their neat powders (Figures 2 and 3); the packing in the neat crystals and gel strands must be the same.[4a,11] The same morphs have been found in the gels and neat solids of several (*but not all*) of the other **LMOG**s in Scheme 1, also. The presence of a low-angle peak in the gels from many **1** and **2** is consistent with lamellar organizations within their strands. For instance, the length of a fully extended molecule of **1a**, 26.0 Å,[12] is slightly more than half the lamellar spacing in its gel strands (silicone oil) and neat powder, 45.4 Å as determined from Bragg's law. These data suggest that the lamellar thickness is determined by pairs of **1a** molecules in a head-to-head arrangement with either a slight deviation from orthogonality between their long axes and the lamellar planes or some chain bending. Since the extended length calculated for octadecylam-

Figure 2. X-ray diffraction patterns at room temperature of (a) **1a** powder, (b) 5 wt % **1a** in silicone oil gel, (c) silicone oil, and (d) diffractogram b subtracted from diffractogram c.

Figure 3. X-ray diffraction patterns at room temperature of (a) **2a** powder, (b) 5 wt % **2a** in silicone oil gel, (c) silicone oil, and (d) diffractogram b subtracted from diffractogram c.

monium octadecylcarbamate, 55.0 Å,[12] is very close to the lamellar thickness in strands of its silicone oil gels[13] or its neat powder, 52.4 Å, molecules of **2a** must be fully extended with their long axes orthogonal to the lamellar planes. Although the exact nature of the packing cannot be ascertained with the information in hand, the match between the diffraction patterns in Figures 2 and 3 and the absence of solvent molecules in the powders require that the gel strands of both **1a** and **2a** not be swollen with silicone oil.[14] Efforts to make single crystals of any of the **1** or **2** suitable for X-ray analyses have been unsuccessful thus far.

In summary, we have developed a new method for the reversible formation of organogels employing "latent" organo-gelators (amines) and a gas (CO₂). In addition, most of the ammonium carbamates examined produce a wider variety of gels that are more stable than their corresponding amines. It should be possible to develop other gelators that respond analogously to different gases. For instance, a pH-sensitive system based on latent gelators of carboxylic acids in which the active gas is ammonia or a volatile amine may be possible.

Supporting Information Available: Melting points of amines and their carbamates and DSC thermograms of **2a** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

(10) XRD data were collected on a Rigaku R-AXIS image plate system with Cu Kα X-rays (λ = 1.54056 Å). Data processing and analysis were performed using MDI-Jade (version 5) software.

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(12) Calculated by Hyperchem (version 5.1) molecular modeling system at the PM3 level, adding the van der Waals radii of the terminal atoms.

(13) A distance of 52.6 Å can be estimated from the low-angle peak in Figure 3d, but the uncertainty of this value is much larger than the 0.2 Å difference between it and the distance based in Figure 3a.

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