Chemically and Physically Induced (Reversible) Gelation of Organic Liquids by Monomeric and Polymeric Gelators

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Summary: The properties of several types of organogels that can undergo a chemical transition during gelation or while in the gel phase are described. The transitions can be physically induced by light or chemically triggered by the addition of an acid or a neutral molecule such as CO_2 or CS_2. In some cases, the gelation properties of the new species formed are markedly different from those of the precursors. The link between molecular structure and the nature of the gel networks as well as results obtained from the multidisciplinary tools used to study them are discussed.

Keywords: amines; ammonium carbamates; diacetylenes; organogels; polyamines; supramolecular assembly; trialkylphosphine oxides

Introduction

The last several years have witnessed an enormous increase of interest in low molecular-mass organic gelators (**LMOG**s) and their thermally-reversible gels.[1-4] Organogels are prepared typically by heating a small amount of a solid gelator in an organic liquid until it dissolves and the gel forms as the solution/sol is cooled. During this process, the gelator molecules undergo a preferential one dimensional growth to form fibers, tapes, strands, or other aggregates with high aspect ratios. These elongated objects are usually crystalline in nature. They link at "junction zones"[5] to form three-dimensional networks that immobilize the liquid component, primarily by capillary forces and surface tension.[2] Unlike polymer gels, the networks of **LMOG**-derived gels disassemble when their organogels are heated above a characteristic (gel-sol transition) temperature, T_g.

Both structurally simple and complex molecules have been found to serve as **LMOG**s.[1,6-9] However, few reports describe the changes in the gelation properties upon *in situ* structural modifications of the gelator molecules. In our lab, those changes have been accomplished chemically or photochemically.[10-15] We report here results from three classes of our gelators that undergo chemical transformation during gelation or in the gel phase.

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Results and Discussions

Chart 1

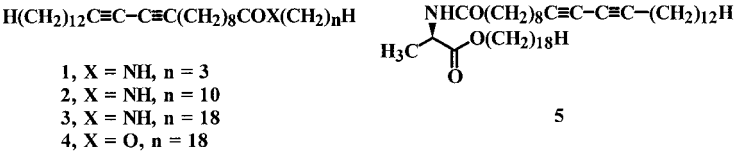


Table 1. Gelating abilities, appearances,[a] and T_g values (°C; in parentheses) of 2 wt% **1-5** in different liquids.

Liquid	1	2	3	4	5
hexane	S	P	P	S	jelly
n-octane	S	P	P	S	jelly
n-decane	TG[b,c] (56)	P	jelly	S	OG[b] (39)
silicone oil[d]	TG[b] (49-56)	jelly	TG[b] (69)	jelly	TG[b] (51)
ethanol	P	jelly	TG[b,f] (69)	jelly	OG[b] (49)
1-butanol	S	P	TG[g] (48)	OG[g] (34-36)	OG[b] (43)
1-octanol	S	P	TG[b] (46)	OG[b] (28)	OG[b] (34)
benzyl alcohol	S	P	TG[b] (55)	TG[b] (51)	TG[b] (40-43)
nitrobenzene	P	P	TG[h] (33-37)	TG[h] (23-25)	TG[b] (30-39)
toluene	S	P	S	S	P
DMSO	TG[b] (48-50)	TG[b,e] (41-45)	TG[b,e] (82)	jelly	TG[b] (28-35)
CCl_4	S	P	P	S	P

[a] P-precipitate, S-solution, TG-turbid gel, OG-opaque gel.
[b] Stable for >2 years.
[c] Syneresis after 1 month.
[d] Tetramethyltetraphenylsiloxane; Dow silicone oil 704.
[e] Pale blue color.
[f] Syneresis after 9 months.
[g] Stable for 1 year.
[h] Stable for <1 month.

Diacetylenes. The diacetylene derivatives (Chart 1)[14] can undergo 1,4-topochemical polymerization in the solid phase when neighboring molecules lie within the geometric boundaries for efficient reaction.[16-18] **1-5** form gels in different liquids with good thermal and temporal stabilities (Table 1).[14] After radiation-induced polymerization (> 300 nm), the thermal stability of most of the gels remained similar to that of their unpolymerized analogues. Except for those of **3**, the irradiated gels are intensely colored and the color can be changed by heating the polymerized gel (causing conformational changes of the polymerized chains[19]).

Powder X-ray diffractograms indicate that the morphologies of the gelator networks in the neat powder samples and the gels are the same and they remain the same in their polymerized states; see, for example, Figure 1. The diffraction peaks in the low angle region and higher order reflections of them indicate that these **LMOG**s are arranged in lamellae. The appearances of the aggregates before and after polymerization of the gels were similar. An example is shown in Figure 2.

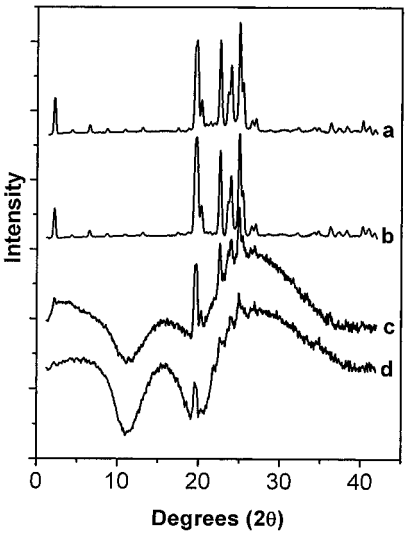


Figure 1. X-ray diffraction patterns (room temperature) of **3** as a neat powder (a,b) and in a 2 wt% silicone oil gel (c,d) before (a,c) and after (b,d) irradiation for 60 min. The diffractogram of silicone oil has been subtracted from that of the gels in (c,d).

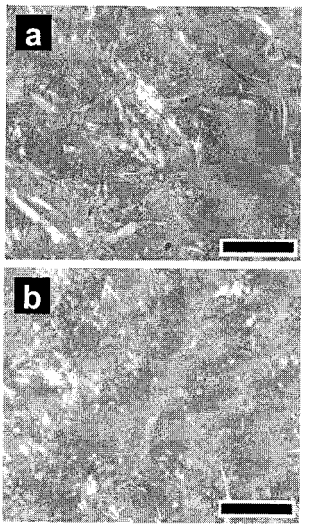


Figure 2. Polarizing optical micrographs (room temperature) of 2 wt% **3** in a benzyl alcohol gel (a) before and (b) after irradiation. Black space bars are 200 μm. The images were taken with a full-wave plate.

Helical aggregates are formed when the chiral amidoester **5** is used as the gelator (Figure 3).[14] Due to the high optical densities below 300 nm, the spectra in that region are not useful analytically. Neither a 1 wt% chloroform solution of **5** nor the silicone oil used for gelation showed any CD signal (Figure 3d,e).[20,21] A two-fold increase in the first negative Cotton effect was observed when the irradiated gel was heated. This may be due to additional polymerization, an increase in the helicity of the polymer aggregates caused by annealing (specifically, from conformational changes of the polydiyne parts[19a]), or a combination of the two factors.

Alkylamines, phosphines, and phosphine oxides as latent gelators. Chemically reactive organogelators discussed here are either alkylamines (that are reactive towards neutral triatomic molecules such as CO_2 or CS_2[11,22-26,27]) and phosphine oxides (that form salts or zwitterions with Brønsted or Lewis acids, respectively); see Schemes 1 and 2.[10-13]

Depending on the basicity of the phosphine oxide and the strength of the protic acid, either hydrogen-bonded complexes (i.e., adducts) or hydroxyphosphonium salts were formed.[13] Hydroxyphosphonium salts were obtained when the pK_a of the Brønsted acid, such as CF_3CO_2H, is $\leq$ 0.2; no salt formation was observed with acids of p$K_a \geq 5$ (e.g., CH_3CO_2H). NMR and thermal studies of the hydroxytrialkylphosphonium chloride salts (i.e., made upon addition of HCl gas) indicate an inhomogeneous distribution of HCl in the initially formed salt. The salt is not thermally stable and loses HCl when kept in an open container for long period or heated.[13] Zwitterions made by addition of the Lewis acid, BF_3, are much more stable to heat (up to 90 °C) than the hydroxyphosphonium salts. The ^{31}P chemical shifts of the phosphonium oxide-BF_3 adducts are similar to those of the hydroxylphosphonium salts, indicating that interaction of BF_3 with the phosphoryl oxygen induces a large increase of positive charge at the phosphorus atom.[13]

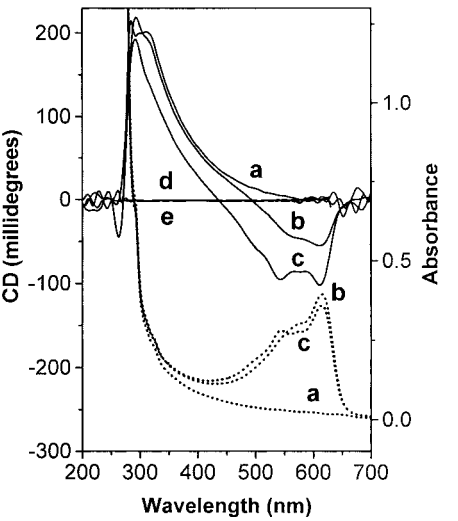
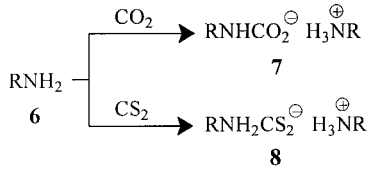


Figure 3. UV-vis absorption (dotted lines) and CD (solid lines) spectra of 1 wt% **5** in a silicone oil gel (a) before irradiation, (b) after irradiation for 1 min, and (c) after heating the irradiated gel to ca. 70 °C for ca. 2 min. CD spectra of a solution of 1 wt% **5** in chloroform (d) and of neat silicone oil (e) are also included.

Differences in the gelation ability of these classes of **LMOG**s before and after a chemical transformation are attributed mainly to the modifications of the nature of the intermolecular interactions. Because the electrostatic interactions in the salts and zwitterions are stronger than the dipolar and/or H-bonding interactions of the parent neutral compounds, the former are the more efficient gelators. Gelation ability also increases with increasing alkyl chain lengths on **6** or **10** due to greater London dispersion forces. Table 2 summarizes the gelation properties of 5 wt% **6**-**11** and **13** (R = $-(CH_2)_{18}H$).

The alkylamine–ammonium carbamate system is chemically reversible, also (i.e., the

Scheme 1



Scheme 2

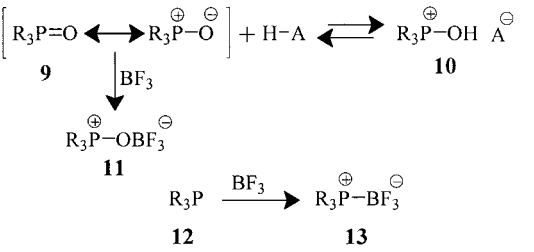


Table 2. Appearances[a] and gel-sol transition temperatures (T_g, °C) of gels formed from 5 wt% neutral gelators (**6**, **9**) and their charged analogues (**7**, **8**, **10**, **11**, **13**) in different liquids. The R group in all of the cases presented here is $H(CH_2)_{18}$-.

liquid	***6***	***7***	***8***	***9***	***10 (A = Cl)***	***11***	***13***
hexane	P	OG[d] (54-56)	P	P	P		
n-octane	P	OG[b] (56-60)	OG[e] (72-78)	P	P	P	
silicone oil	TG[b] (35)	TG[b] (80)	TG[c] (88)	TG[h] (57-68)	TG[h] (62-64)	TG[c] (47-53)	TG[i] (52-55)
ethanol	P	OG[b] (54-56)	P	P	P	P	
1-butanol	P	OG[b] (49-50)	OG[f] (62)	Jelly	P	P	P
1-pentanol	S	OG[b] (52-55)		Jelly	TG[h] (34-40)	P	jelly
1-octanol	P	OG[b] (40-42)	OG[f] (63)				
benzyl alcohol	S	TG[b] (53)	TG[f] (61)	TG[i] (51)	TG[f] (39-43)	TG[c] (33-40)	jelly
DMSO	TG[c] (48-50)	TG[b] (90-92)	TG[g] (71-76)	P	P		
toluene	S	TG[b] (56)	PG	P	jelly	P	
CCl_4	P	TG[b] (40-42)	OG[e] (56)		S		

[a] P-precipitate, S-solution, TG-turbid gel, OG-opaque gel.
[b] Stable for >3 years.
[c] Stable for 1 month.
[d] Phase separation after 3 months.
[e] Stable for 2 weeks.
[f] Stable for >2 years.
[g] Stable for >2 years, pale yellow color after 5 months.
[h] Stable for >1 year.
[i] Stable for 2 months.

ammonium carbamate gel reverts to the amine gel when nitrogen is bubbled through the former at a slightly elevated temperature (to facilitate the displacement of CO_2). This cycle between the amine and ammonium carbamate gels can be repeated many times without any noticeable degradation. By contrast, the ammonium dithiocarbamate gels (made by addition of CS_2 to the amine gels) lose H_2S upon heating and form thiourea derivatives[26] which are also organogelators.[11]

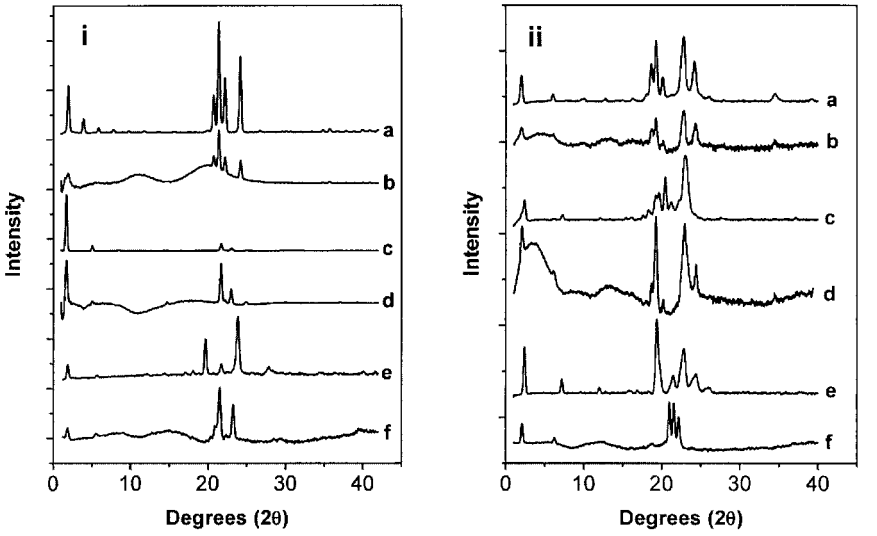


Figure 4. X-ray diffraction patterns (room temperature) of neat (a,c,e) and 5 wt% gels in silicone oil (b,d,f) of (i) **6** (a,b), **7** (c,d), and **8** (e,f) and (ii) **9** (a,b), **10** (c,d), and **11** (e,f). The contribution from the silicone oil is subtracted in the gel spectrum in each case.

Powder X-ray diffraction patterns of neat **6-11** and their gels in silicone oil are shown in Figure 4. The latter are obtained as the difference between the normalized diffraction patterns of a gel and its neat liquid component.[28] The morphology of the **LMOG**s as neat powders and in their gel networks has been analyzed by comparing the positions of the diffraction peaks in these two cases; if the sharp peaks of the difference pattern and of the neat gelator are the same, so are their molecular packing arrangements. This is the case for gels of the amine, its ammonium carbamate salt (Figure 4a), and the neutral **9** (R = $-(CH_2)_{18}H$) gels in silicone oil, 1-nonanol, and benzyl alcohol as the liquids (Figure 4b). However, the dithiocarbamate and the other phosphonium salts are arranged differently in their neat solid and gel phases. In fact, it is more common for the morphology of packing of an **LMOG** to differ in the gel and its bulk solid phases than to be the same.[28]

The hydroxytrialkylphosphonium salts are not always the species constituting the gel networks. In several cases, the diffractogram of the gel samples formed from a hydroxytrioctadecylphosphonium salt is identical to that of the parent trioctadecylphosphine oxide (e.g., Figure 4iic,d).[13] The stability of the salts and their equilibrium constants with their acid and phosphine oxide components are very dependent

Table 3. Appearances[a] and gel-sol transition temperatures (T_g, °C) of polyethyleneimines in different liquids.

liquid	PE-L		PE-H		PE	
	wt %	appear. (T_g, °C)	wt%	appear. (T_g, °C)	wt %	appear. (T_g, °C)
hexanes	2.4	P	2.9	P	3.4	P
n-decane	3.1	P	3.3	P	3.6	P
toluene	3.2	OG[b,c] (66-70)	2.7	P	3.8	OG[b,g] (70-79)
chlorobenzene	3.9	OG[b,c] (40-49)	2.9	OG[b,e] (58-75)	3.9	OG[b,g] (64-70)
chloroform	2.5	OG[c] (30-49)	2.9	OG[f] (41-52)	3.2	OG[g] (40-50)
ethanol	3.3	OG[d] (64-69)	2.9	OG[e] (52-54)	3.3	OG[g] (55-60)
1-butanol	3.3	OG[c] (71-75)	3.0	OG[c] (74-85)	3.3	OG[g] (65-80)
1,2-propanediol	3.4	S	2.7	S	3.4	S
benzyl alcohol	2.8	S	2.9	S	3.0	S
1-nonanol	2.9	TG[c] (88-90)	3.0	TG[c] (82-89)	3.5	TG[g] (70-85)
silicone oil	3.1	TG[c] (68-69)	3.8	S	3.7	OG[g] (75-90)

[a] P-precipitate, S-solution, TG-turbid gel, OG-opaque gel.
[b] Exhibits syneresis.
[c] Stable for >10 months.
[d] stable for 10 months.
[e] Stable for 3 weeks.
[f] Stable for 1 month.
[g] Stable for >8 months.

on the nature of the solvent. Interestingly, some of the phosphine oxides that are not able to gelate a liquid alone are able to do so (as evidenced by the X-ray diffraction data) when nucleation leading to the networks is mediated by the acid!

Diffractograms of the fluoroborate zwitterions (**11**, **13**) indicate that the morphologies are different in their neat solid and gel phases. The differences are not always a consequence of morphology since these salts react slowly at room temperature with several liquids.[13]

Polyamines. The alkylamine–ammonium carbamate chemistry has been extended to polyallylamine[12] and other polyamines. The gelation abilities of the ammonium carbamates from three polyamines, low (**PE-L**: M_n *ca.* 600; M_w *ca.* 800) and high (**PE-H**: M_n *ca.* 10,000; M_w *ca.* 25,000) molecular weight polyethylenimine and a linear polyethylenimine (**PE**, M_n *ca.* 400) are summarized in Table 3. The amines are liquids at room temperature and did not gelate any of the liquids investigated. When CO_2 was bubbled though the amine solutions, gels were formed in some cases.

Thermally irreversible gelation has been observed when solutions of polyallylamine in aliphatic alcohols and 1-methyl-2-pyrrolidone are saturated with CO_2 gas.[12] The irreversible de-gelation temperatures (the temperature at which CO_2 is liberated from the ammonium carbamate salt) of the gels were strongly dependent on the number of carbon atoms in the alkyl chains of the alcohol liquids, and increased with increasing the chain length.

Conclusions

Gelation of solutions/sols of monomeric and polymeric amines exposed to CO_2 involves enhanced electrostatic interactions between the ammonium (cationic) and carbamate (anionic) parts of the salts. Molecules of the liquid component with monomeric amines are expelled from the sols, allowing the aggregates to crystallize as lamellae and eventually form three-dimensional networks. It is currently unknown the exact stage at which this expulsion occurs. Unlike the thermal and chemical reversibility of gels of monomeric ammonium carbamate salts, gels of ammonium carbamates of polyamines and, of course, polymerized diyne derivatives cannot be cycled with their sol phases. However, the ammonium carbamate salts of the polyamines do eliminate CO_2 at considerably higher temperatures than those of the ammonium carbamate **LMOG**s. In low polarity liquids, the electrostatic interactions between the charged centers of the polymer salts are more localized and stronger; increasing de-gelation temperatures are found as alkyl chain lengths of alcohol liquids become longer.

Hydroxytrialkylphosphonium salt **LMOG**s can undergo two types of chemical transformations: reaction with the liquid component; thermal dissociation, leading to the parent neutral phosphine oxide and acid. As a result of the latter, the nature of the species included within the fibrillar networks depends on the relative rates of nucleation/precipitation of the phosphine oxide and its salt and the rate of reassociation of the phosphine oxide and Brønsted acid. Interestingly, the presence of the acid component must have an influence on the formation of the fibrillar network because several liquids were gelated by the phosphine oxide

(when added as the salt) even though they were not in the absence of acid.

In essence, we have explored several structural features that determine whether small organic molecules with different functional groups, such as conjugated diynes, alkylamines, trialkylphosphine oxides, and polymers bearing amino groups can become more efficient organogelators upon introduction of a physical or chemical perturbation. The gelation ability of an **LMOG** generally increases with increasing alkyl chain length and the networks of the gels are stabilized primarily by London dispersion forces and one or both of electrostatic forces and intermolecular H-bonding. Clearly, there are many other ways to modulate gelation and degelation of **LMOG**-containing mixtures. We have emphasized our own work here, but many others have applied very clever techniques to achieve the same end.[15] In addition to being interesting for fundamental scientific reasons, these systems may have several practical applications, such as in art conservation.[29]

Experimental Section

Instrumentation. Instruments for analyses of the gels have been described elsewhere.[11-14]

Materials. Commercially available solvents and reagents were used as received. Diyne derivatives **1-5** were prepared from 11,12-pentacosadiynoic acid.[14] Alkylammonium alkylcarbamates (**7**) and alkylammonium alkyldithiocarbamates (**8**) were prepared from the amine and CO_2 or CS_2.[11,30] Salts from trialkylphosphine oxide or trialkylphosphine (**10**, **11** and **13**) were prepared by standard procedures.[13]

Preparation of gels and determination of gel-sol tranistion temperatures. Weighed amounts of a liquid and a solid were placed in a glass tube (5 mm i.d.) that was flame-sealed to avoid evaporation. Gels for polarizing optical microscopic 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.

T_g values were determined by the inverse flow method.[31] A gel in a sealed glass tube was immersed in a stirred water bath in an inverted position 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.

Acknowledgment

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