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Low Molecular-Mass Gelators with Diyne Functional Groups and Their Unpolymerized and Polymerized Gel Assemblies

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A series of low molecular-mass organogelators (LMOGs) with conjugated diyne units, R−C≡C−C≡C−R′, has been synthesized from 10,12-pentacosadiynoic acid. R is a long alkyl chain and R′ is a short or long alkyl chain containing an amide or ester group. The gelation efficiencies of these LMOGs and the parent acid (as assessed by the variety of liquids gelled, the amount of gelator needed for gelation, and the temporal and thermal stabilities of the gels) differ widely according to the nature of the substituents. An LMOG with an amide substituent is much more efficient than the corresponding molecule with an ester group, and LMOGs with longer R′ chains are more efficient than those with shorter ones. When irradiated, some gel networks polymerize. In most cases, the polymerized aggregates phase-separate microscopically, but maintain the gel structure macroscopically. These gels are irreversibly photo- and thermo-chromic, and the thermal stabilities of some of the colored polymerized organogel networks are similar to those of the monomeric assemblies. The molecular packing of the LMOGs as neat powders and in gels before and after polymerization has been examined by X-ray diffraction techniques. This and analyses of IR, UV, and CD (in the case of a chiral diyne LMOG) data allow the nature of the aggregate assemblies before and after irradiation to be assessed. These monomeric organogels and their treatment with light and heat afford an approach to the synthesis of microheterogeneous polymerized networks from relatively simple molecules.

Introduction

Interest in low molecular-mass organogelators (LMOGs) and their thermally reversible organogels has increased enormously during the last several years.[1] Organogels usually consist of a small amount of an LMOG and an organic liquid. They are microheterogeneous phases in which the LMOGs self-assemble in a variety of three-dimensional fibrillar networks whose organization can be expressed from the molecular to micron length scales. Typically, a solid LMOG is heated until it dissolves in a liquid and the gel forms below a characteristic gelation temperature, T_g. As the solution/sol cools, the LMOGs aggregate into fibers, strands, tapes, etc., that join at “junction zones”[2] to form the three-dimensional networks, immobilizing the liquid component.[1b] Molecules that are known to act as LMOGs can have very simple[3,4] or very complex structures,[1,5,6] and their assemblies can involve H-bonding interactions,[7] chemical or physical triggers,[8] or van der Waals forces.[3] In addition, an exceedingly broad range of organic liquids (including quasi-liquids such as supercritical CO_2[9]) and water[10] has been gelled. The unusual structural and diffusional properties of orga-

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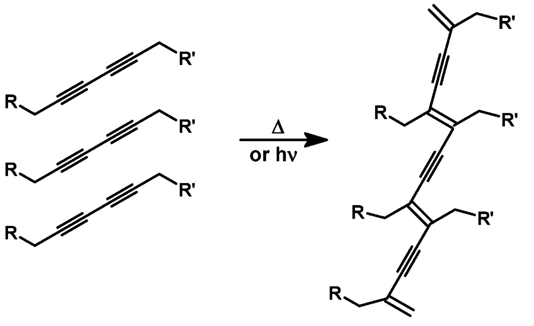
nogels have led to several interesting applications[11−16] and they can be used as structure-directing agents for formation of inorganic nanoparticles.[16a,17]

Recent studies have shown that appropriately substituted diacetylenes can form organogels.[18] Diacetylenes are also known to undergo solid-state polymerization reactions by 1,4-addition reactions when the monomer units are aligned appropriately (Equation 1).[19] Polymerization of the diacetylenic units within LMOG networks need not affect the morphology of the gel, but usually increases its thermal stability.[18b] Polydiacetylenes possess several interesting properties[20] related to electrical conductivity,[21] chromism,[22,23] nonlinear optical generation,[24] fluorescence,[25] and liquid crystallinity.[23b,26] In most cases, they are very insoluble in common organic liquids because of their stiff backbone, and undergo a color transition from blue to red in response to temperature, pH changes, or exposure to some solvents.[27−30]



(1)

Here, we describe the gelation abilities of 10,12-pentacosadiynoic acid **1** and its derivatives **3**−**8**, including a comparison between the amides **3**−**5**, esters **6** and **8**, and the chiral amidoester **7**. Organogels before polymerization are thermally reversible. Polymerization of the diynes in their gel phases leads to insoluble polymers that, with the exception of **6** in silicone oil and **7** in nitrobenzene, retained their gel phase when heated to ca. 70 °C and then cooled to room temperature.

Experimental Section

Instrumentation. Melting points (corrected) of neat compounds and polarized optical micrographs (POM) of silicone oil gels sandwiched between thin cover slides were obtained 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, using an attenuated total reflection accessory. UV−Vis spectra were recorded on a Varian CARY 300 Bio UV−Vis spectrophotometer. Circular dichroic (CD) spectra were obtained on a Jasco J-710 spectropolarimeter interfaced to a computer. Data analyses were preformed using Jasco J-700 software (version 1.10.00) for windows. Gel samples were sandwiched between two quartz plates (separated by a 0.12-mm Teflon spacer) for absorption and CD measurements. High-performance liquid chromatography (HPLC) analyses were performed on an HP Series 1100 chromatograph with a UV−Vis detector (280 and 300 nm detection) and a 4.6 × 250 mm Allsphere 5-μm silica gel column using a 3:7 mixture of hexane and ethyl acetate (unless

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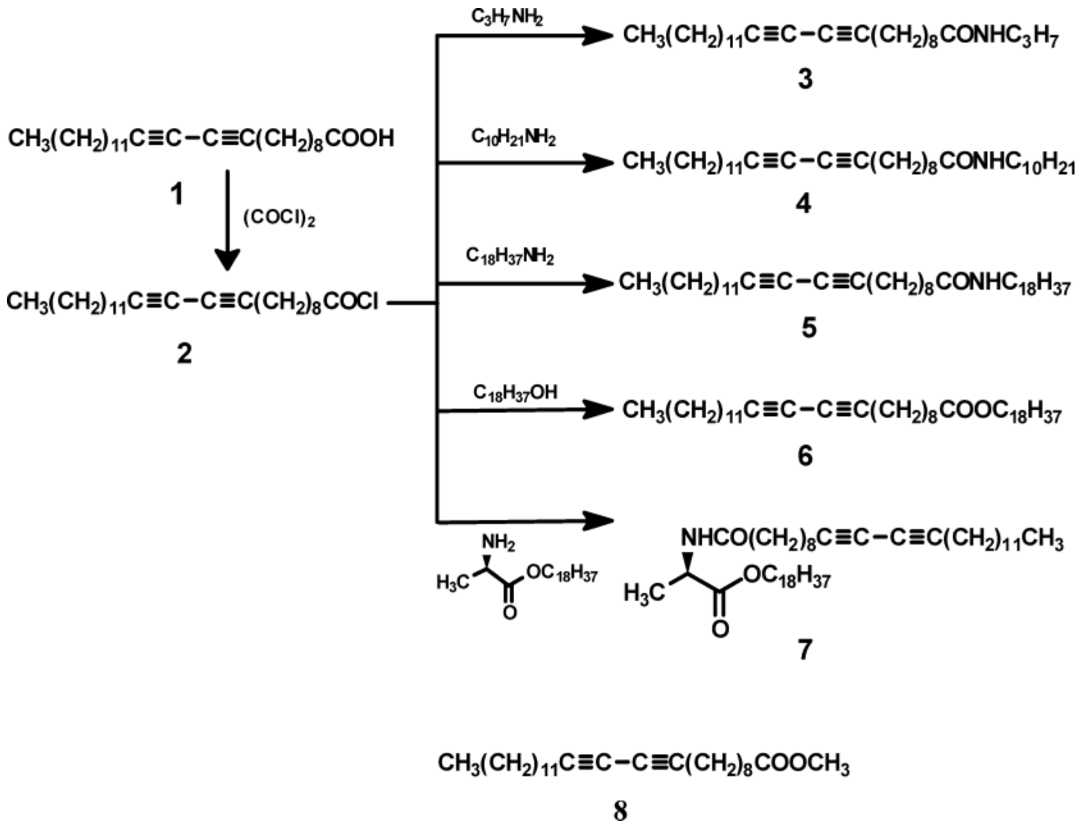
Scheme 1



stated otherwise) as the eluent. Gas chromatography (GC) analyses were performed on an HP Series 5890 gas chromatograph equipped with a DB 35 column (0.25 mm × 15 m). ^{1}H (referenced to internal TMS) and ^{13}C (referenced to chloroform-*d* signal) NMR spectra were recorded on a Varian 300 MHz spectrometer interfaced to a Sparc UNIX computer using Mercury software. Elemental analyses were performed on a Perkin-Elmer 2400 CHN elemental analyzer. X-ray diffraction (XRD) of samples in thin, sealed capillaries (0.5-mm diam.; W. Müller, Schönwalde, Germany) 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 accomplished with Materials Data JADE (version 5) XRD pattern processing software.[31]

Materials. Silicone oil (tetramethyltetraphenylsiloxane; Dow silicone oil 704) was used as received. Other liquids for the preparation of gels were reagent grade or better (Aldrich). 10,12-Pentacosadiynoic acid (mp 62−63 °C; lit. mp 61−62 °C;[32] GFS Chemicals), 1-propylamine (99+%), 1-decylamine (95%), L-alanine (99%, 99% ee), 1-octadecanol (99%), and oxalyl chloride (98%) (all from Aldrich) were used as received. 1-Octadecylamine (Aldrich) was distilled twice under vacuum and stored under a nitrogen atmosphere. Silica gel (60−200 mesh) for column chromatography was purchased from EM Science. Methyl 10,12-pentacosadiynoate (**8**) (96%; Lancaster Chemicals) was passed through a silica column in the dark using nitrogen-flushed dichloromethane as the eluent and the solvent was removed by rotary evaporation under reduced pressure at room temperature in the dark.

General Procedure for the Synthesis of Diacetylene Derivatives. Syntheses of LMOGs **3**−**7** are outlined in Scheme 1. All procedures involving **1** were done under very dim light to inhibit polymerization of the diyne group. Oxalyl chloride (1.69 g, 13.3 mmol) was added slowly to a stirred solution of **1** (500 mg, 1.33 mmol) in dry dichloromethane (10 mL) under a nitrogen atmosphere, and stirring was continued under a nitrogen atmosphere for 12 h. Excess oxalyl chloride and solvent were then removed by distillation under reduced pressure. Hexane (10 mL) was added to the crude acid chloride and distilled 3× under reduced pressure. The acid chloride **2** so-obtained was dissolved in dry dichloromethane (10 mL) and added to the amine or alcohol (1.33 mmol) in triethylamine (5 mL). The mixture was stirred under a nitrogen atmosphere for 12 h, added to an ice−water mixture (300 mL) containing concentrated hydrochloric acid (10 mL), and extracted with chloroform. The product residue after removal of chloroform from the combined extracts was purified either by repeated recrystallization or by column chromatography through silica gel. Only compound **3** underwent polymerization during melting point determinations. All other LMOGs could be melted reproducibly at least three times; thereafter, some developed a pink color, indicative of partial polymerization.

10,12-Pentacosadiynoyl Propylamide. Compund **3** was prepared from **1** (500 mg, 1.33 mmol) and propylamine (79 mg, 1.33 mmol). The crude product (400 mg, 71%) was recrystallized repeatedly from dichloromethane/hexane (1:1) until 97% pure (HPLC). It became a red polymer when heated to 68.0 °C and melted at 218.4 °C. IR (neat): 3294 (NH), 2917, 2847 (CH), 2180, 2142 (C≡C), 1639 (C=O) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 5.45 (br s, 1H, NH), 3.18−3.25 (q, 2H, $J = 6.5$ Hz, NCH$_2$), 2.13−2.24 (m, 6H, O=CCH$_2$ and C≡CCH$_2$), 1.26−1.65 (m, 34H, CH$_2$), 0.86−0.95 (m, 6H, CH$_3$). ^{13}C NMR (CDCl$_3$): δ 172.91, 77.48, 77.34, 65.24, 65.17, 41.15, 36.83, 31.91, 29.65, 29.63, 29.61, 29.48, 29.35, 29.23, 29.17, 29.10, 28.92, 28.86, 28.75, 28.36, 28.29, 25.81, 22.92, 22.70, 19.21, 19.19, 14.15, 11.41. Anal. Calcd for $C_{28}H_{49}NO$: C, 80.90; H, 11.88; N, 3.37. Found: C, 81.13; H, 12.24; N, 3.28.

10,12-Pentacosadiynoyl Decylamide. Compound **4** was prepared from **1** (500 mg, 1.33 mmol) and decylamine (210 mg, 1.33 mmol). Recrystallization from 1:1 dichloromethane/hexane gave 450 mg (66%) of **4** (98% by HPLC), mp 77.6−78.7 °C. IR (neat): 3346 (NH), 2916, 2850 (CH), 2177, 2140 (C≡C), 1636 (C=O) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 5.55 (br s, 1H, NH), 3.20−3.27 (q, 2H, $J = 7.2$ Hz, NCH$_2$), 2.12−2.26 (m, 6H, O=CCH$_2$ and C≡CCH$_2$), 1.26−1.65 (m, 48H, CH$_2$), 0.86−0.90 (m, 6H,

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Table 1. Gelating Abilities, Appearances,[a] and T_g Values (°C; in parentheses) of 2 wt % 1 and 3−7 in Different Liquids and of Gels Irradiated for 10 Min (3) and 60 Min (5 and 6); Before Irradiation the Gels Were White or Turbid

	1	**3**		**4**	**5**		**6**		**7**
liquid	before hν	before hν	after hν	before hν	before hν	after $h\nu$	before hν	after $h\nu$	before hν
hexane	P	S		P	P		S		jelly
n-octane	P	S		P	P		S		jelly
n-decane	P	TG^{b,c} (56)	OG^{e} (59)	P	jelly		S		OG^{m} (39)
silicone oil	TG^{b} (40)	TG^{d} (49−56)	OG^{e} (55)	jelly	TG^{g} (69)	TG^{f} (70)	jelly		TG^{m} (51)
ethanol	S	P		jelly	Tg^{g,h} (69)	TG^{f} (70)	jelly		OG^{m} (49)
1-butanol	S	S		P	TG^{i} (48)	TG^{f} (47)	OG^{i} (34−36)		OG^{m} (43)
1-octanol	S	S		P	TG^{g} (46)	TG^{f}(47)	OG^{d} (28)	OG^{k} (31)	OG^{m} (34)
benzyl alcohol	S	S		P	TG^{g} (55)	TG^{k} (48)	TG^{b} (51)	TG^{k} (45)	TG^{m} (40−43)
nitrobenzene	S	P		P	TG^{j} (33−37)	TG^{l} (35)	TG^{j} (23−25)	TG^{k} (28)	TG^{m} (30−39)
toluene	S	S		P	S		S		P
DMSO	P	TG^{b} (48−50)	OG^{e} (90)	TG^{b,f} (41−45)	TG^{f,g} (82)	TG^{k} (83−90)	Jelly		TG^{m} (28−35)
CCl_4	S	S		P	P		S		P

[a] P, precipitate; S, solution; TG, turbid gel; OG, opaque gel. [b] Stable for >10 months. [c] Syneresis after 1 month. [d] Stable for >6 months. [e] Blue. [f] Pale blue. [g] Stable for >22 months. [h] Syneresis after 9 months. [i] Stable for 1 year. [j] Stable for <1 month. [k] Pale pink. [l] No color change. [m] Stable for >4 months.

CH_3). ^{13}C NMR ($CDCl_3$): δ 172.76, 77.49, 77.34, 65.26, 65.20, 39.50, 36.88, 31.94, 29.72, 29.67, 29.66, 29.64, 29.59, 29.51, 29.38, 29.34, 29.26, 29.21, 29.13, 28.95, 28.89, 28.79, 28.39, 28.33, 26.98, 25.83, 22.72, 19.24, 14.17. Anal. Calcd for $C_{35}H_{63}NO$: C, 81.80; H, 12.36; N, 2.73. Found: C, 82.21; H, 12.47; N, 2.72.

10,12-Pentacosadiynoyl Octadecylamide. Compound **5** was prepared from **1** (500 mg, 1.33 mmol) and *n*-octadecylamine (360 mg, 1.33 mmol). The product (480 mg, 58%) was recrystallized repeatedly from 1:1 ethyl acetate/hexane until 97% pure by HPLC; mp 92.3−92.8 °C. IR (neat): 3349, 3299 (NH), 2915, 2849 (CH), 2177, 2140 ($C{\equiv}C$), 1637 ($C{=}O$) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.42 (br s, 1H, NH), 3.20−3.27 (q, 2H, $J = 6.6$ Hz, NCH_2), 2.12−2.26 (m, 6H, $C{\equiv}CCH_2$ and $O{=}CCH_2$), 1.25−1.65 (m, 64H, CH_3CH_2), 0.86−0.90 (m, 6H, CH_3). ^{13}C NMR ($CDCl_3$) δ: 172.76, 77.54, 77.39, 65.28, 65.21, 39.54, 36.93, 31.98, 29.76, 29.54, 29.41, 29.28, 29.23, 29.16, 28.98, 28.93, 28.82, 28.42, 28.35, 27.00, 25.85, 22.77, 19.28, 14.21. Anal. Calcd for $C_{43}H_{79}NO$: C, 82.49; H, 12.72; N, 2.24. Found: C, 82.41; H, 13.05; N, 2.25.

n-Octadecyl 10,12-Pentacosadiynoate. Compound **6** was prepared from **1** (500 mg, 1.33 mmol) and *n*-octadecyl alcohol (360 mg, 1.33 mmol). The crude product was purified by silica gel column chromatography using toluene as the eluent to obtain 280 mg (34%), mp 49.2−49.9 °C (99.9% by HPLC using a mixture (1:1) of hexan/ethyl acetate as eluent). IR (neat): 2915, 2849 (CH), 2175, 2141 ($C{\equiv}C$), 1724 ($C{=}O$) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 4.05 (t, 2H, $J = 6.8$ Hz, OCH_2), 2.24−2.30 (m, 6H, $C{\equiv}CCH_2$ and $O{=}CCH_2$), 1.26−1.62 (m, 70 H, CH_3CH_2), 0.85−0.92 (m, 6H, CH_3). ^{13}C NMR ($CDCl_3$): δ 173.73, 77.51, 77.35, 65.30, 62.22, 64.41, 34.41, 31.98, 29.76, 29.55, 29.43, 29.33, 29.16, 28.97, 28.93, 28.82, 28.71, 28.42, 28.37, 26.01, 25.04, 22.77, 19.27, 14.21. Anal. Calcd for $C_{43}H_{78}O_2$: C, 82.36; H, 12.54. Found: C, 82.30; H, 13.01.

N-(10,12-Pentacosadiynoyl) L*-Alanine Octadecyl Ester.* Compound **7** was prepared from **1** (330 mg, 0.88 mmol) and L-alanine octadecyl ester (300 mg, 0.88 mmol).[33] The crude product was recrystallized from 1:4 methylene chloride/hexane to yield 430 mg (70%), mp 81.6−82.5 °C (99% by HPLC using a 1:1 mixture of hexane/ethyl acetate as eluent). IR (neat): 3312 (NH), 2956, 2917, 2848 (CH), 2178, 2141 ($C{\equiv}C$), 1737, 1646 ($C{=}O$) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.03−6.05 (d, 1H, $J = 7.5$ Hz, NH), 4.54−4.64 (m, 1H, $HCC{=}O$), 4.08−4.13 (m, 2H, OCH2), 2.17−2.58 (m, 6H, $C{\equiv}CCH_2$ and $O{=}CCH_2$), 1.26−1.69 (m, 72 H, methylene), 0.86−0.90 (m, 6H, CH_3). ^{13}C NMR ($CDCl_3$): δ 173.14, 172.30, 77.51, 77.37, 65.61, 65.26, 65.20, 48.11, 47.80, 36.59, 31.97, 30.99, 30.23, 29.75, 29.55, 29.40, 29.20, 28.96, 28.81, 28.55, 28.39, 28.35, 27.98, 25.85, 25.58, 22.75, 19.26, 18.73. Anal. Calcd for $C_{46}H_{83}NO_3$: C, 79.14; H, 11.98; N, 2.01. Found: C, 79.39; H, 12.13; N, 1.99.

Preparation of Gels and Gelation Temperatures. Weighed amounts of a liquid and the LMOG were placed into glass tubes (5-mm i.d.) that were flame-sealed in most cases (to avoid evaporation of liquid). The sealed tubes were heated 2× in a water bath (until all solid material had dissolved) and cooled rapidly under tap water to ensure homogeneity. Gelation temperatures (T_g) were determined by the inverse flow method.[34] A gel sample 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 increased slowly and 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. Gel samples were prepared and T_g values were measured in very dim light to avoid polymerization of the gelators.

Polymerization of 1 and Its Derivatives. Polymerization of **1** and **3**−**7** gels in borosilicate tubes was initiated by exposing them to radiation from a 450-W Hanovia medium-pressure mercury lamp at 0 °C and room temperature. Polymerization of LMOGs in several gels was monitored qualitatively by the development of color, which in most cases

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(33) L-Alanine octadecyl ester was prepared by modification of a procedure reported for L-alanine decyl ester (Nakamura, N.; Okada, M.; Okada, Y.; Suita, K.; *Mol. Cryst. Liq. Cryst.* **1985**, *116*, 181). A mixture of alanine (890 mg, 10 mmol), 1-octadecanol (2.75 g, 10 mmol), and 4-toluenesulfonic acid monohydrate (2.85 g, 15 mmol) in dry toluene (100 mL) was refluxed for 16 h using a Dean−Stark apparatus to remove water. The resulting solution was then neutralized by washing with 10% aqueous sodium bicarbonate solution (3×) and then with water (3×). The organic phase was separated, dried with anhydrous magnesium sulfate, and concentrated. Purification of the crude, low-melting product by flash chromatography on a silica gel (100−240 mesh) column using ethyl acetate as eluent and recrystallization from hexanes give 2.39 g (70%) of L-alanine octadecyl ester as a white solid (99% by GC), mp 30.4−31.1 °C. IR (neat): 3376 (NH), 2916, 2849 (CH), 1734 ($C{=}O$) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 4.07−4.13 (m, 2H, OCH_2), 3.49−3.56 (q, 1H, $J = 7$ Hz, $HCC{=}O$), 1.50−1.68 (m, 2H, $OCH_2{-}CH_2$), 1.53 (br s, 2 H, NH_2), 1.26−1.34 (m, 33H, aliphatic), 0.86−0.90 (m, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 176.36, 64.89, 50.13, 49.93, 31.90, 30.93, 30.71, 30.23, 29.67, 29.54, 29.49, 29.34, 29.21, 28.59, 25.86, 22.68, 20.78, 20.65.

(34) Takahashi, A.; Sakai, M.; Kato, T. *Polym. J.* **1980**, *12*, 335.

Table 2. Gelation Abilities, Appearances,^{a} and T_g Values (°C; in parentheses) of 5 in Different Liquids as a Function of Concentration

wt % **5**	silicone oil^b	nitrobenzene	ethanol	1-octanol	benzyl alcohol
0.5	jelly (8−15)	jelly^c(<0)	jelly^c(<0)	jelly^c(<0)	jelly^c(<0)
1	TG (38−40)	jelly^c(<0)	OG^c(55−60)	jelly^c(<0)	TG^d(40)
2	TG (69)	TG^d(33−37)	OG^b(55−62)	TG^b(47)	TG^b(53)
3	TG (70)	TG^d(41−46)	OG^b(63−65)	TG^b(49−50)	TG^b(54)
4	TG (71)	TG^d(41−46)	OG^b (63)	TG^b(50−52)	TG^b(55−57)

^{a} TG, turbid gel; OG, opaque gel. ^{b} Stable for >22 months. ^{c} Stable for 2 weeks. ^{d} Stable for <1 month.

was blue.[23d] Irradiation times and appearances after irradiation are summarized in Table 1 of the Supporting Information. Irradiated gels formed from **3** and **6** changed irreversibly to purple near 40 °C and then to red above 45 °C, whereas the other irradiated gels showed reversible color changes upon heating (from blue/pink to red) and cooling.

Results and Discussion

Gelation Studies. Gelation abilities of 2 wt % **1** and **3**−**7** were examined in a variety of organic liquids (Table 1).[35] Except for the 2 wt % **3** gel in DMSO, T_g values and periods of stability of gels of **3**, **5**, and **6** before and after irradiation are very similar. This surprising result, that the oligomerized gelator structures are no more (and no less) stable than their umpolymerized analogues, may be related to our observations from X-ray diffraction that the fibrils retain their morphology upon irradiation (vide infra). The degree of oligomerization has not been established, and our assertions for or against oligomerization rest with the coloration[27a] of the initially uncolored gels. The link between the packing arrangements in the neat powders and the gels of the diynes by X-ray diffraction (vide infra) and the correlation between color changes of each diyne in its powder and gel phases provide compelling evidence that oligomerization is occurring within the gelator fibrils. Some may occur additionally within the small component of dissolved gelator.

At temperatures above 70 °C, the irradiated gels of **3**, **6**, and **7** in all liquids gradually underwent macroscopic phase separation; irradiated gels from **4** and **5** regelled when cooled from >70 °C. Compound **1** formed a gel stable at room temperature only in silicone oil. The corresponding amides are much better LMOGs due to their ability to act as both proton donors and acceptors.[36] In addition, shorter amides, such as **3**, are poorer gelators in terms of the range of liquids gelled and their T_g values than the amides with longer chains; stronger London dispersion forces better stabilize the aggregates. Compound **5**, with the longest alkyl chain, is the most efficient *n*-alkylamide gelator. Most of its gels (sealed in glass tubes and stored at ambient temperatures) have been stable for >22 months. The corresponding ester **6** gels fewer liquids with lower T_g values and periods of stability. Although the chiral amidoester **7** gels more than half of the liquids listed in Table 1, its T_g values are significantly lower than those of **5**. The importance of H-bonding and hydrophobic interactions to gelation ability has been examined by comparing the efficiency of **3**−**5** as LMOGs with those of the structurally related esters, *n*-octadecyl 10,12-pentacosadiynoate (**6**) and methyl 10,12-pentacosadiynoate (**8**). Neither ester can form intermolecular H-bonds as a neat compound, and the stabilization of their assemblies is mainly due to London dispersion forces. Whereas the octadecyl ester **6** gels 4 of the 12 liquids listed in Table 1, the methyl ester **8** was soluble in all liquids listed. For that reason, it is not included in the table and its properties were not investigated further.[37] These results indicate that both hydrogen bonding (involving the amide hydrogen and carbonyl groups) and hydrophobic interactions of long alkyl chains play important roles in the formation and stabilization of these organogels.

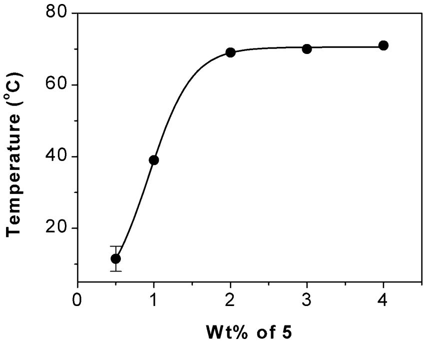

Figure 1. T_g versus concentration for gels of **5** in silicone oil.

Concentration-dependent gelation studies of **5**, the most efficient LMOG, have been conducted in several liquids (Table 2). The dependence of T_g on the concentration of **5** in silicone oil is shown in Figure 1. T_g increases rapidly with concentration to ca. 2.0 wt % and then is virtually independent of concentration. In the lower concentration range, fibril interactions and other associations related to the gelator network are not complete.[6]

Polymerization of 1 and 3−7 Gels. The dependence of photopolymerization efficiency of diacetylenic compounds on molecular packing is well-known. For example, low-density Langmuir−Blodgett films of **1** can be polymerized readily by UV radiation, whereas high-density films require ionizing radiation such as X-rays or electron beams.[38] Efficient 1,4-topochemical polymerization of diacetylenes occurs only when the diyne moieties of neighboring molecules lie within rather strict, emperically determined geometric boundaries.[39,40] In addition, some flexibility around the diacetylenic

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(35) Several studies have been conducted in silicone oil because of its inertness and very low volatility. In some experiments, such as those involving X-ray diffraction and POM, evaporation of the liquid component of gels can complicate interpretation of data and lead to unwanted morphological changes.

(36) Challis, B. C.; Challis, J. A. in *Comprehensive Organic Chemistry*; *The Synthesis and Reactions of Organic Compounds*; Barton, D. H. R.; Ollis, W. D., Eds.; Pergamon Press: New York, 1979; Vol. 2, p 957.

(37) Compound **8** is known to form a red polymer upon irradiation.[23j]

(38) (a) Ogawa, K. *J. Phys. Chem.* **1989**, *93*, 5305. (b) Ogawa, K. *J. Phys. Chem.* **1991**, *95*, 7109.

(39) Enkelmann, V. In *Advances in Polymer Science*; Cantow, H.-J., Ed.; Springer-Verlag: New York, 1984; Vol. 63, p 91; and references cited therein.

(40) Kim, T.; Ye, Q.; Sun, L.; Chan, K. C.; Crooks, R. M. *Langmuir* **1996**, *12*, 6065.

moiety is necessary for efficient polymerization[41] because the interatomic distances before and after reaction differ.

On the basis of our qualitative determinations of polymerization efficiencies of **1** and **3**−**7** from the intensities of coloration (Table 1 of Supporting Information), their diacetylenic units are similarly oriented and vicinal in the gel assemblies. Although polymerization of the diyne units is exothermic, the rates are relatively slow and heat dissipation should be sufficiently rapid to prevent local melting of vicinal unpolymerized network segments. In support of that contention, irradiation of the gels in silicone oil at room temperature and at 0−4 °C for the same period produced approximately equivalent color changes and degrees of polymerization, as indicated additionally by IR spectroscopy. Variations in color are attributed to changes in the conformations of the polymerized chains, some of which are irreversible.[27]

Irradiation of **6** gels in silicone oil led to phase separation as the polymerization proceeded. Silicone oil gels of propylamide **3** and octadecylester **6**, decylamide **4** in DMSO, and the chiral amidoester **7** in several liquids were polymerized much more rapidly than the other gels. Considering that efficient polymerization requires the diacetylenic units to be separated by <4 Å prior to irradiation (rather than moving to this distance afterward),[42] we infer from their ease of polymerization that packing arrangements of fibrils of **3**, **6**, and **7** in their gels place their diacetylenic units within this critical distance, but the fibrils of **4** and **5** in silicone oil gels do not. However, flexibility of the molecular chains of these LMOGs or changes in their local packing near "defect sites," where polymerization may be initiated, can bring the diacetylenic units within the critical distance for polymerization.

In every case, the polymers were insoluble in the liquid used for gelation. Macroscopic phase separation of the polymer has been observed in the silicone oil gels of **3** (at the ca. 10-μm distance range as indicated by POM) and **6** (precipitated visually from the liquid). Except for **6** in silicone oil and **7** in nitrobenzene, polymerized gels of other LMOGs retained their gel phase after being irradiated, heated to ca. 70 °C, and cooled to room temperature. Upon heating, the irradiated gels from **1** and **3** turned from blue to red and remained so after cooling (e.g., Figure 2), and that from **6** changed irreversibly from pink to red. Irradiated silicone gels of **4**, **5**, and **7** that were blue became red when heated to ca. 70 °C and then to violet with time after being cooled to room temperature. The properties of the gels before and after polymerization have been compared as well by spectroscopic methods, POM, and X-ray diffraction (vide infra).

Absorption Spectroscopy Studies. Prior to irradiation, the absorption spectra of gels consisting of 2 wt % **1** and **3**−**7** in silicone oil have only tail absorptions above 350 nm. However, broad absorption bands centered at >400 nm from excitonic transitions[43] are clearly present after irradiations, and several of the irradiated gels develop shoulder peaks also (Figures 3 and 4 and Supporting Information Figures 1−3). Heating the gels after irradiation leads to hypsochromic shifts of the exciton bands due to different resonance contributions or changes of polydiacetylene conformations.[27] Table 3 summarizes the absorption maxima of the new peaks from irradiated gels in silicone oil before and after heating. Based on their reported spectra and a blue/

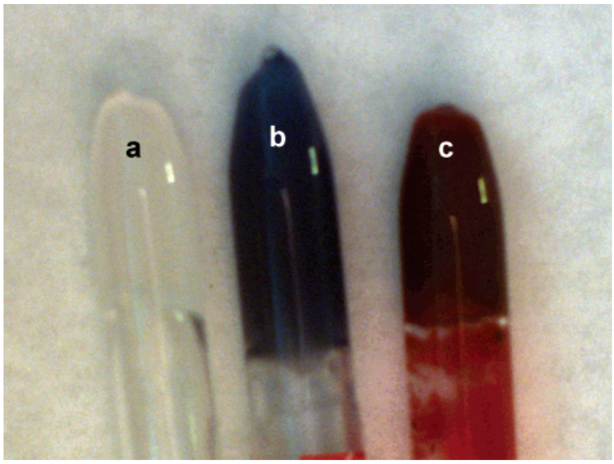

Figure 2. Silicone oil gel of 2 wt % **3** (a) before irradiation, (b) after irradiation for 10 min, and (c) after heating the irradiated gel at ca. 70 °C for ca. 3 min.

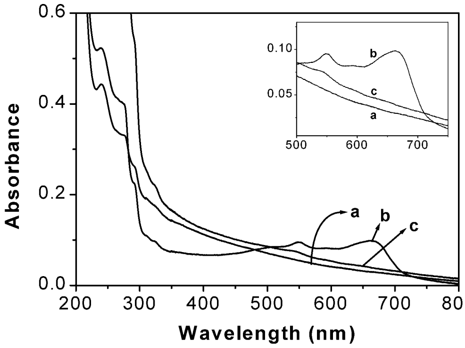

Figure 3. Absorption spectra of a 2 wt % **1** in a silicone oil gel (a) before irradiation, (b) after irradiation for 60 min, and (c) after heating the irradiated gel to ca. 70 °C for ca. 3 min. The region showing the exciton band is expanded in the inset.

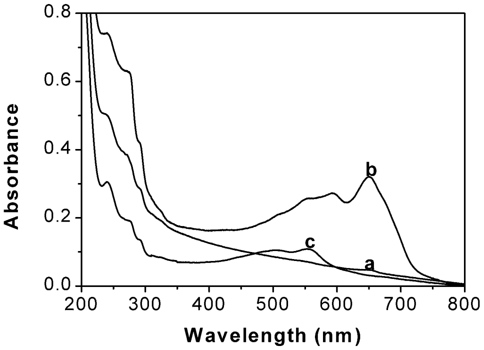

Figure 4. Absorption spectra of a 2 wt % **3** in silicone oil gel (a) before irradiation, (b) after irradiation for 10 min, and (c) after heating the irradiated gel to ca. 70 °C for ca. 3 min.

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[41] Barentsen, H. M.; van Dijk, M.; Kimkes, P.; Zuilhof, H.; Sudhölter, E. J. R. *Macromoleules* **1999**, *32*, 1753.

[42] (a) Baughman, R. H. *J. Polym. Sci. Polym. Phys.* **1974**, *12*, 1511. (b) Baughman, R. H.; Chance, R. R. *Ann. N. Y. Acad. Sci.* **1978**, *313*, 705. (c) Baughman, R. H.; Yee, K. C. *J. Polym. Sci., Macromol. Rev.* **1978**, *13*, 219.

[43] (a) Reimer, B.; Bässler, H. *Phys. Stat. Sol.* (*a*) **1975**, *32*, 435. (b) Lochner, K.; Reimer, B.; Bässler, H. *Phys. Stat. Sol.* (*b*) **1976**, *76*, 533. (c) Chance, R. R.; Baughman, R. H. *J. Chem. Phys.* **1976**, *64*, 3889. (d) Takura, Y.; Mitani, T.; Koda, T. *Chem. Phys. Lett.* **1980**, *75*, 324.

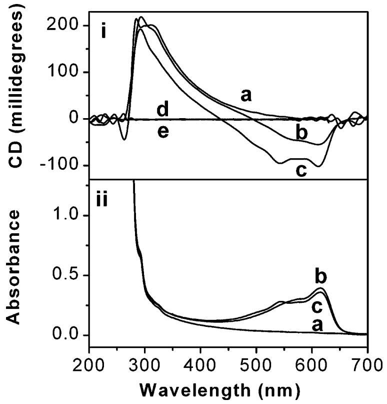

Figure 5. CD (i) and absorption (ii) spectra of a 1 wt % **7** in a silicone oil gel (a) before irradiation, (b) after irradiation for 1 min, and (c) after heating the irradiated gel to ca. 70 °C for ca. 2 min. CD spectra of a solution of 1 wt % **7** in chloroform (d) and of neat silicone oil (e) are also included in (i). Note that the CD data in (i) below ca. 300 nm are not correct because of the very high optical densities at these wavelengths.

Table 3. Absorption Maxima of 2 wt % Silicone Oil Gels (Irradiated at Room Temperature) of 1 and 3−7 Before and After Heating to Ca. 70 °C for Ca. 3 min

LMOG	irradiation time (min)	$\lambda_{\max}$ (nm) (before heating)	$\lambda_{\max}$ (nm) (after heating)
1	60	663, 549	547
3	10	650, 593, 552, 511	554, 505
4	60	673	550, 505
5	60	640	627
6	10	575, 534, 502	540, 481
7	30	613, 571	615, 542

pink color, gels of **3** and **7** in all of the liquids, **4** in DMSO, and **6** in silicone oil (Table 1 of Supporting Information) polymerize efficiently when irradiated for <10 min. The other gelator aggregates must polymerize less efficiently because they require longer irradiation periods to obtain similar spectra and coloration.

CD Spectral Studies. CD spectra (Figure 5[44]) of 1 wt % **7**, the chiral LMOG, in a silicone oil gel include a strong first positive Cotton effect at 312 nm ($\Delta\epsilon$, +33.3 L mol^{-1} cm^{-1}). The data below ca. 300 nm are not useful because of the very high optical densities in this spectral region. Upon irradiation of the gel for 1 min, a less intense, first negative Cotton effect was observed at 611 nm ($\Delta\epsilon$, −9.1 L mol^{-1} cm^{-1}), and another was observed at 563 nm ($\Delta\epsilon$, −7.3 L mol^{-1} cm^{-1}) in the region of the excitonic transition. The intensities of the first negative Cotton effect increased when the irradiated gel was heated to ca. 70 °C for 2 min (at 612 nm ($\Delta\epsilon$, −16.7 L mol^{-1} cm^{-1}) and at 541 nm ($\Delta\epsilon$, −15.5 L mol^{-1} cm^{-1})) whereas the intensity of the positive second Cotton effect was nearly unchanged. The CD spectrum of a solution of 1 wt % **7** in chloroform (d in Figure 5i) does not possess a Cotton effect. Hence, the observed CD signals from the gels are due to the helical arrangement of the molecules of **7** in their fibrils.[45,46] The first negative Cotton effect was enhanced 2-fold after heating the polymerized gel (c in Figure 5i). This may be due to additional polymerization caused by heating, an increase in the helicity of the polymer aggregates caused by annealing (specifically from conformational changes of the polydiyne parts[27a]), or a combination of the two factors.

IR Spectral Studies. IR spectra of both neat powder samples and their gels show characteristic peaks of the diyne and carbonyl moieties. Data for **1**, **3**, and **6** and their 2 wt % gels in silicone oil before and after irradiation are collected in Table 4. Before irradiation, neat **1** showed strong absorption bands at 2918 and 2847 cm^{-1} from asymmetric and symmetric CH_2 stretching vibrations,[47] respectively, and two weak bands at 2178 and 2139 cm^{-1} are characteristic of $-C{\equiv}C-$ stretching.[47] The strong peak at 723 cm^{-1} present in neat **1** and other LMOGs before and after irradiation is assigned to $(CH_2)_n$ rocking motions.[48] In addition, a $C-C{\equiv}$ stretch at 930 cm^{-1} [49] and a carbonyl peak at 1690 cm^{-1} remained in the spectra of **1** before and after irradiation (Supporting Information Figure 5).

In its 2 wt % gel in silicone oil, carbonyl peaks of **1** are found at 1692 (strong) and 1768 cm^{-1} (weak),[50] indicating slightly stronger H-bonding interactions in the neat solid than in the gel aggregates (Supporting Information Figure 5). For the most part, there is very little difference between the spectra before and after the gel is irradiated and heated to ca. 70 °C; afterward, the relative intensity of the carbonyl peak at 1694 cm^{-1} is increased somewhat. Moreover, photooxidation (via hydroperoxide formation) does not appear to be important because gels irradiated under vacuum and in air gave the indistinguishable IR spectra.

The NH and carbonyl stretching frequencies of **3**−**5**, as neat powders or in gels, were virtually the same before and after irradiation (or after irradiation and heating) (Figures 6−9 of Supporting Information). For example, the NH stretching of **3** in its neat solid phase appeared at 3294 cm^{-1} before and after irradiation and at 3295 cm^{-1} after heating the irradiated powder. In its 2 wt % silicone oil gel, the NH stretching is at 3296 (before) and 3297 cm^{-1} (after) irradiation and at 3297 cm^{-1} after heating the irradiated gel (Figure 6). The carbonyl stretching frequency of neat **3** at 1639 cm^{-1} moves to 1637 cm^{-1} after irradiation and heating. In the 2 wt % silicone oil gel, carbonyl peaks are detected at 1640 (stronger) and 1769 cm^{-1} before and after irradiation and at 1638 and 1769 cm^{-1} after subsequent heating.[50]

Polarized Optical Microscopy. POM images of silicone oil gels of **1** and **3**−**7** before and after irradiation

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(44) No contribution from linear dichroism was detected in these spectra. There was no change in absorptivity when the sample cell was rotated by 90° (Figure 4 of Supporting Information). All spectra in Figure 5 were recorded with the cell in the same orientation with respect to the incident light beam.

(45) (a) Selinger, J. V.; Spector, M. S.; Schnur, J. M. *J. Phys. Chem. B* **2001**, *105*, 7157. (b) Schnur, J. M.; Ratna, B. R.; Selinger, J. V.; Singh, A.; Jyothi, G.; Easwaran, K. R. K. *Science* **1994**, *264*, 945. (c) Spector, M. S.; Easwaran, K. R. K.; Jyothi, G.; Selinger, J. V.; Singh, A.; Schnur, J. M. *Proc. Natl. Acad. Sci. U.S.A.* **1996**, *93*, 12943.

(46) An interesting report of circular dichroism in a polymerized Langmuir−Blodgett film of *achiral* **1** has appeared recently, and the polymers appear to be in fibril form. (a) Huang, X.; Liu, M. *Chem. Commun.* **2003**, 66.

(47) *Spectrometric Identification of Organic Compounds*; Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. Eds.; John Wiley & Sons: New York, 1991; Chapter 3.

(48) Martin, J. M.; Johnston, R. W. B.; O'Neal, M. J. *Spectrochim. Acta* **1958**, *12*, 12.

(49) Nyquist, R. A.; Potts, W. J. *Spectrochim. Acta* **1960**, *16*, 419.

(50) IR spectra of several of these LMOGs in silicone oil gels have a peak at >1760 cm^{-1}, an energy uncharacteristic of an acyclic amide or ester carbonyl group. It suggests that at least some of the molecules are in a highly stressed environment.

Table 4. Characteristic IR Frequencies (cm^{-1}) of Neat 3 and 5 and Their 2 wt % Gels in Silicone Oil Before and After Irradiation (10 min for 3 and 60 min for 5) and After Irradiation and Heating to Ca. 70 °C for Ca. 3min

group	powder before hν	powder after hν	powder after hν + Δ	gel before hν	gel after hν	gel after hν + Δ
			Compound **3**			
ν_{N-H}	3294	3294	3295	3296	3297	3296
$\nu_{C=O}$	1639	1637	1637	1640, 1769	1640, 1769	1638, 1769
			Compound **5**			
ν_{N-H}	3349, 3299	3349, 3298	3295	3351, 3292	3351, 3294	3292
$\nu_{C=O}$	1637	1636	1633	1637, 1770	1637, 1770	1630, 1775

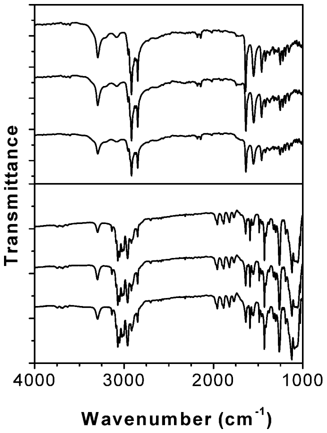

Figure 6. Vertically offset IR spectra of (i) neat **3** and (ii) 2 wt % **3** in a silicone oil gel (a) before irradiation, (b) after irradiation for 10 min, and (c) after irradiation and heating to ca. 70 °C for ca. 3 min.

are presented in Figures 7 and 8 and Supporting Information Figures 10−13. No differences are discernible in the appearances of aggregates irradiated at lower or higher temperatures. Consistent with their lower T_g values (jellies at room temperature), silicone oil gels of **4** and **6** (2 wt %) before irradiation have shorter fibrils than those of the other gelators. Although individual strands are difficult to discern within bundles at the magnifications employed, their lengths are in the 10−100 μm range. The density of aggregates appears to increase after irradiation of **1** (Figure 7) and **4** (Supporting Information Figure 10), and phase separation with microcrystallite formation is evident after irradiation of the gels with **3** (Figure 8) and **6** (Supporting Information Figure 12).

X-ray Diffraction (XRD) Studies. Neat powdered samples of **3**, **6**, and **7** and their silicone oil gels underwent polymerization during X-ray measurements as evidenced by the appearance of a blue color. Other neat LMOGs and their gels did not become colored appreciably during X-ray measurements. We assume that the morphologies of the samples of **3**, **6**, and **7** were unchanged during the X-ray exposures.[42] The diffraction peaks of the 2 wt % LMOG assemblies of **1** and **3**−**7** in silicone oil before and after irradiation were obtained by subtracting the “amorphous scatter” of the liquid components from the total gel diffractograms.[51] They were compared with diffraction patterns of the neat powders (Figure 9 and Supporting Information Figures 14−18). The POM of each of the gels before irradiation for which the diffraction pattern matches that of the neat solid provides no evidence for nonfibrillar LMOG crystallites; if they are present, they must be less than ca. 10 μm in size. From this and the presence of fibrillar assemblies, we are confident that the diffraction patterns are from the gelator networks.

Despite the weakness of some peaks from gels, most coincide with peaks of the neat powders; the molecular packing arrangements of the major components of the gel assemblies and the bulk crystals are the same.[3,51] Unfortunately, we have been unable to prepare single crystals of these LMOGs suitable for X-ray analyses; they would allow the molecular packing in the gel strands to be determined.[3]

Diffractograms of all of the LMOGs as neat powders and in gels before and after irradiation possess a low-angle peak (and, in some cases, higher order diffractions of it) that is indicative of lamellar organizations within the aggregates. The layer thicknesses (d) have been calculated from the low-angle peaks using Bragg’s law. Table 5 summarizes the d values and the calculated extended molecular lengths[52] of the LMOGs. The d values of the neat solid and gel assembly of each LMOG are the same even when the high-angle peaks demonstrate that they are different morphs (e.g., Figure 9); the organizations within layers differ. In addition, the d values of the neat solid before and after irradiation are the same even when the high-angle peaks demonstrate a morphological change; the organizations within layers differ, but not the layer thicknesses. The diffractograms of the silicone oil gel of **6** (Figure 18 of Supporting Information) did not show peaks from the aggregates before irradiation, but they were apparent after polymerization. As evidenced from the POM in Figure 12 of Supporting Information, irradiation of the gel is accompanied by macroscopic phase separation.

The d values of all of the LMOGs except **1** and **3** are shorter than the calculated extended molecular lengths, l. Although **1** and **3** may be interdigitated and extended in layers, their ability to undergo facile photopolymerization requires that neighboring molecules be aligned so that their diyne units are within ca. 4 Å; an interdigitated packing arrangement of fully extended molecules with the long molecular axes perpendicular to the layer planes would require $d > l$. Because (i) there is a low angle peak in the X-ray diffractograms of the neat powders and silicone oil gels of **4**−**7**, and (ii) most diacetylenes with long alkyl chains are known to adopt a lamellar arrangement in their aggregates,[18g,53] we assume that **4**−**7** are also layered in their neat solid and

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(51) Ostuni, E.; Kamaras, P.; Weiss, R. G. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1324.

(52) Calculated by Hyperchem (version 5.1) molecular modeling system at the PM3 level, adding the van der Waals radii of the terminal atoms. (a) *Lange's Handbook of Chemistry*; 13th ed.; Dean, A. J., Ed.; McGraw-Hill: New York, 1985.

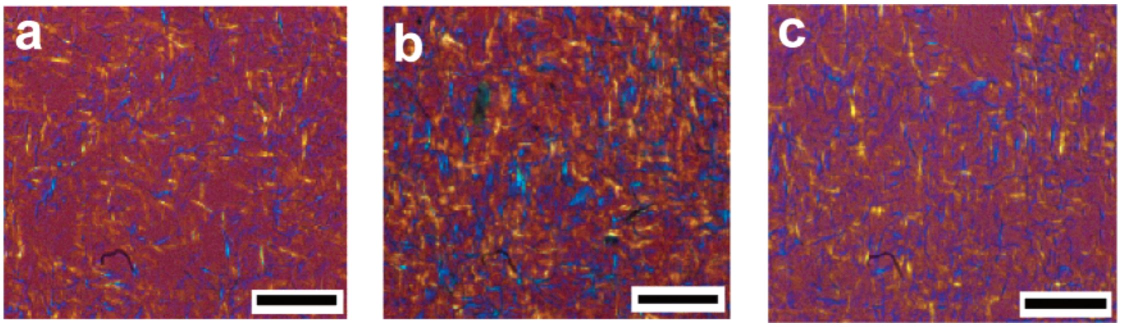

Figure 7. Polarizing optical micrographs (room temperature) of 2 wt % **1** in a silicone oil gel (a) before and after irradiation at (b) 0 °C and (c) room temperature. Black space bars are 100 μm. The images were taken with a full-wave plate.

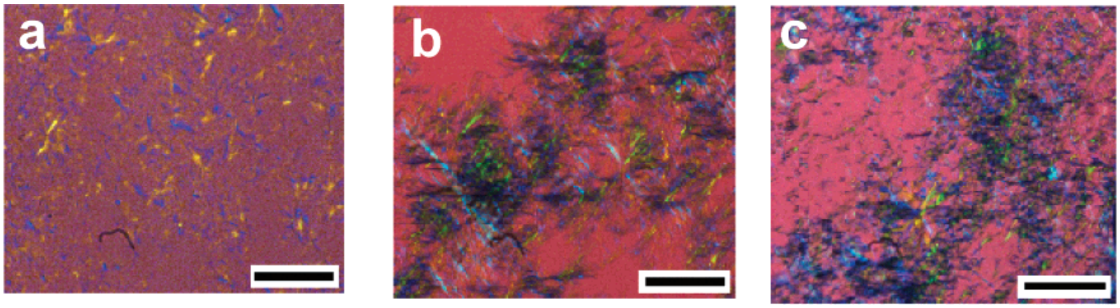

Figure 8. Polarizing optical micrographs (room temperature) of 2 wt % **3** in a silicone oil gel before (a) and after irradiation at 0 °C (b) and room temperature (c). Black space bars are 100 μm. The images were taken with a full-wave plate.

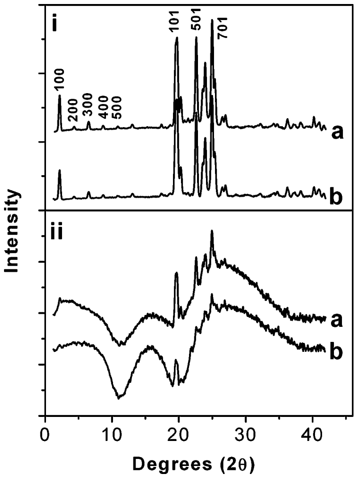

Figure 9. X-ray diffraction patterns (room temperature) of **5** (i) as a neat powder and (ii) in a 2 wt % silicone oil gel (a) before and (b) after irradiation for 60 min. The diffractogram of silicone oil has been subtracted from that of the gels in (ii). The indices of diffraction peaks of the unirradiated powder (line a in (i)) are also indicated.

gel phases. However, because $l > d$ in these phases, **4**−**7** must be either in bent (i.e., less than fully extended) conformations, or, more likely, in extended conformations with their long molecular axes tilted with respect to the layer planes. Regardless, the efficient photopolymerization of **3**, **7**, and **6** in silicone oil gels requires that their diyne groups on neighboring molecules also be aligned next to each other. On the basis of the short irradiation periods necessary for their gelator aggregates to become blue, **3** and **7** undergo much more efficient photopolymerization than do **4** and **5**. FT-IR studies suggest that the NH group of **5** is in at least two different environments but that of **3** is in only one (Table 4). Despite these differences, indicating different packing arrangements, the lamellar thicknesses of **3**−**5** and **7** follow the same progression. The subtle packing differences must be intralayer and cannot involve significant changes in tilt angles if the molecules are in extended conformations.

Table 5. Lamellar Thicknesses (*d*) of 1 and 3−7 from Low-Angle XRD Peaks of the Neat Powders and Calculated Extended Molecular Lengths (*l*, Å)

		lamellar spacing, *d*	
LMOG	extended molecular length, l^{52}	before irradiation	after irradiation (irradiation time, min)
1	34.7	47.6	47.5 (60)
3	38.6	59.0	59.0 (10)
4	47.4	33.2	33.2 (60)
5	57.4	41.1	40.8 (60)
6	57.3	40.9	40.6 (10)
7	60.5	44.2	44.3 (10)

Conclusions

We have explored several structural features that determine whether linear molecules with a diyne unit along a long alkyl chain and an amide, ester, or carboxylic acid unit can act as LMOGs, as well as whether those gels can then be polymerized. There is a minimum alkyl chain length for the amides and esters below which the gelating abilities become very inefficient. Comparison of the gelation properties of amide and ester derivatives of **1** reveals that stabilization of the gelator aggregates is strongly dependent on intermolecular H-bonding.[7,54] Within the series of amides investigated, gelating efficiency increases with the length of the alkyl chain appended to the diyne moiety as a result of greater London dispersion forces. Thus, **5**

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(53) (a) Sarkar, A.; Okada, S.; Matsuzawa, H.; Matsuda, H.; Nakanishi, H. *J. Mater. Chem.* **2000**, *10*, 819. (b) Wang, W. *J. Polym. Res.* **2000**, *7*, 1. (c) Lindsell, W. E.; Preston, P. N.; Seddon, J. M.; Rosair, G. M.; Woodman, T. A. J. *Chem. Mater.* **2000**, *12*, 1572. (d) Wang, G.; Hollingsworth, R. I. *Langmuir* **1999**, *15*, 3062.

forms gels in a variety of organic liquids with greater temporal and thermal stabilities than the shorter amides. Formation of aggregates is supported mainly by London (dispersive) interactions in the case of the long-chained ester **6**, and it is less efficient than the corresponding amide. London interactions among molecules of **8**, the methyl analogue of **6**, are weakened to the extent that it gels none of the liquids examined.

The morphologies of the aggregates in their neat solid phase as well as in silicone oil gels are the same as indicated by X-ray diffraction studies. However, the packing arrangement of **3** differs from those of the homologous amides **4** and **5**. Tilting within layers and/or conformational bending are proposed to explain the disparity between the extended molecular lengths of **4** and **5** (as well as **6** and **7**) and the thicknesses of the lamellae in which they are packed. In addition, **3** and **7** in their neat solid and gel phase can be polymerized more efficiently than **4**−**6** (based on the color changes produced upon irradiation for equivalent periods). This observation indicates that the diyne units are closer and better disposed for intermolecular reactions in aggregates of **3** and **7** than in those of **4**−**6**. Exceptions to this generalization include 2 wt % gels of **4** in DMSO and **6** in silicone oil that polymerize as efficiently as the corresponding gels of **3** and **7**. Clearly, the liquid molecules can direct the packing of aggregates during gelation to some extent, even if they are not incorporated within the aggregates.

Although intermolecular H-bonding is one of the important interactions responsible for the nature and stability of the amide gelators **3**−**5** and **7**, IR studies indicate that H-bonding is more extensive in the neat solids than in some of the gel networks and that it is reduced further upon photopolymerization. Moreover, at least some of the amide groups in gel aggregates experience an unfavorable “stressed” environment.

Polymerized diynes in the gel phases are insoluble in the host liquid when heated to temperatures that exceed those where the monomer gels are converted to sols. In most cases, the polymers separate microscopically from the liquid components of their gels, but the macro-gel structure is maintained. X-ray diffraction studies of the neat powder samples and their gels indicate that the lamellar packing is retained after polymerization, and POM images show intact gelator networks as well as phase-separated polymer aggregates. Some of the polymerized gels that were heated became jellies after several days, whereas the unirradiated gels were stable under the same heating and incubation conditions.

The presence of excitonic transitions in the visible wavelength range after polymerization of these gels allows us to study the nature of their aggregates by UV−vis absorption spectroscopy. The dyne gelator with a chiral group **7** provided gels with helical aggregates. Although the color of an irradiated 2 wt % **7** in silicone oil gel changed from blue to red upon heating to ca. 70 °C, its negative CD Cotton effect was maintained.

These results demonstrate that it is possible to convert these thermally reversible, self-assembling systems into irreversibly formed ones due to polymerizations of the constituent gelator molecules. They describe an approach to the synthesis of microheterogeneous polymerized networks from relatively simple molecules. We envision several applications for such frameworks that require porous, thermally stable materials, including those related to electrical conductivity, chromism, nonlinear optical generation, fluorescence, and liquid crystallinity.[20−26] In addition, it may be possible to replace the original liquids with others that are not gelled by the monomers. Experiments to test these hypotheses will be performed in the future.

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Supporting Information Available: Table summarizing the irradiation times and appearance of **1** and **3**−**7** gels, CD spectra of 1 wt % **7** in silicone oil gel, UV and IR spectra and X-ray diffraction patterns of several neat LMOGs and their 2 wt % gels in silicone oil, and POM images of 2 wt % silicone oil gels. This material is available free of charge via the Internet at http://pubs.acs.org.

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(54) (a) Suzuki, M.; Yumoto, M.; Kimura, M.; Shirai, H.; Hanabusa, K. *Chem. Eur. J.* **2003**, *9*, 348. (b) Mizoshita, N.; Suzuki, Y.; Kishimoto, K.; Hanabusa, K.; Kato, T. *J. Mater. Chem.* **2002**, *12*, 2197. (c) Makarević, J.; Jokić, M.; Frkanec, L.; Katalenic, D.; Žinić, M. *Chem. Commun.* **2002**, 2238. (d) Suzuki, M. Yumoto, M.; Kimura, M.; Shirai, H.; Hanabusa, K. *Chem. Commun.* **2002**, 884.