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New Dicholesteryl-Based Gelators: Chirality and Spacer Length Effect

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Eight new diacid amides of dicholesteryl L(D)-alaninates were designed and prepared. The compounds with spacers containing three, four, five, or six carbon atoms and L-alanine residues are denoted as **1a**, **2a**, **3a**, and **4a**, respectively, and those containing D-alanine residues are denoted as **1b**, **2b**, **3b**, and **4b**, respectively. A gelation test revealed that a subtle change in the length of the spacer and an inverse in the chirality of the amino acid residue can produce a dramatic change in the gelation behavior of the compounds and the microstructures of the gels, as revealed by SEM, XRD, and CD measurements. Importantly, for the compounds **1** and **2**, those containing D-alanine residues (**1b**, **2b**) are more efficient gelators than their analogues with opposite chirality (**1a**, **2a**). For the compounds of longer spacers (**3**, **4**), however, those containing L-alanine residues (**3a**, **4a**) are superior to the corresponding ones with D-alanine residues (**3b**, **4b**). Very interestingly, of the 139 gel systems studied, at least 11 of them gel spontaneously at room temperature. Studies of the rheological properties of the example systems of these gels demonstrated that change in the spacer lengths of the gelators has a great effect upon the mechanical properties of the corresponding gels, and the studies also revealed the thixotropic properties of the gels. Furthermore, it was observed that **4a** forms water-in-oil gel emulsions with some organic solvents by simple agitating the systems at room temperature.

Introduction

Organogels, in which solvents are gelled by low molecular mass organic gelators (LMOGs), have attracted much interest,¹ not only because of their unique features to create various superstructures with respect to self-assembly phenomena but because of their potentials for creating new soft materials, which may find uses in oil recovery, controlled release, bioactivity maintenance, recovery of proteins, nanomaterials preparation, and separation, etc.² It is because of these reasons that many LMOGs have been reported during the last 10–20 years.^{1,3} Nonetheless, the vast majority of new gelator families are still being discovered by serendipity and not by de novo design.⁴ To date, it is also impossible to predict which solvent will be gelled by a particular LMOG, due to the dearth of knowledge of the molecular packing within the network structures of the LMOGs in organogels. Consequently, a great deal of effort has been expended to develop new types of LMOGs and to understand the links between the properties and structures of LMOGs and their organogels.⁵ Various organogels can be obtained with a

wide range of molecules as LMOGs, of which steroid derivatives form a versatile and well-studied class.⁶ For instance, George and Weiss^{4a,7} reported a series of cholesterol-based LMOGs, which are denoted as ALS gelators and display effective and somewhat predictable gelation abilities.

Recently, dimeric cholesterol-based derivatives, which are denoted as A(LS)₂ gelators, were reported as a new class of organogelator architectures and offer new potentialities for the construction of novel cholesterol-based organogelators. The central units of the A(LS)₂ gelators, as for the main functional characteristics, have been chromophores,⁸ ligands,⁹ and polymerizable units.¹⁰ All these units have been successfully incorporated into gel superstructures, thereby leading to stable

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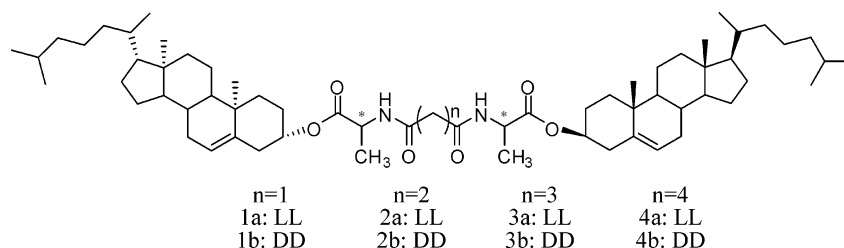
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Scheme 1. Molecular Structures of the Diacid Amides of Dicholesteryl L(D)-Alaninates



organogels with unique functionalities and aggregation modes. For example, Shinkai and co-workers^{9d,10b,c,11} prepared a number of dicholesterol derivatives bearing various functional linkers as versatile gelators and obtained inorganic materials possessing unique structures by using the corresponding gels as templates.

The impact of chirality on assembled systems can be profound. It has been reported that chirality plays critical roles in assembling processes taking place on surfaces and interfaces, in liquid-crystalline phase, and in the formation of supramolecular polymers and gels.¹² Furthermore, the chirality within an individual molecule or a “building block” can be transcribed to nano- or mesoscale fibrous assemblies. It has become a widely accepted concept that the ability to form gels is often associated with the presence of stereogenic centers in the molecular structures of LMOGs.¹³ To our knowledge, however, systematic studies on the effects of chirality of a spacer and the length of it upon the gelation behavior of dicholesterol derivatives have not been reported.

As part of our ongoing research in the design of novel supramolecular gels of gelators with amino acid and cholesteryl as key components,¹⁴ eight new diacid amides of dicholesteryl L(D)-alaninates have been designed and prepared, and their gelling behaviors in various organic solvents and the rheological properties of some gels have been investigated. The details are presented in this report.

Results and Discussion

Design and Synthesis of the Gelators. The compounds designed as potential gelators are composed of three parts, two cholesteryl units and one spacer unit, which contains two L(D)-alanine residues connected via amide bonds to a central aliphatic linker. The amino acid residues are intentionally introduced in order to bring chirality into the spacer and to create sites for hydrogen bonding. As demonstrated already, cholesterol has a strong tendency to aggregate in various organic solvents through van der Waals interaction between the molecules containing it. The alkyl spacer unit is a promising structure to adjust the distance between the two cholesterol units and thereby the foregoing interactions between the gelator in a gel phase. Integration of the three structures may create a mutual balance to modulate the

packing arrangement of the molecules and eventually obtain a particular supramolecular structure and function. To investigate the effects of the amino acid chirality and the length of the spacer connecting the two cholesteryl units upon the gelation behavior of the compounds in various organic solvents, eight new diacid amides of dicholesteryl L(D)-alaninates were designed and prepared by varying the amino acid chirality and the length of the spacer (cf. Scheme 1).

Gelation Behavior of the Compounds. The gelation behavior of compounds **1a–4a** and **1b–4b** were tested in 33 solvents at a concentration of 2.5% (w/v), and the results are listed in Table 1. With reference to the data shown in Table 1, it can be seen that, generally speaking, most of the cholesterol derivatives prepared can act as versatile gelators of various organic solvents.

The following is shown by further reference to the data: (1) For compounds **1a** ($n = 1$) to **4a** ($n = 4$), the number of solvents gelled by them increases along with increasing the length of the spacer; specifically, **1a**, **2a**, **3a**, and **4a** gel 7, 22, 24, and 26 of the 33 solvents, respectively. (2) For the compounds with a shorter spacer, **1b** and **2b**, those that contain D-alanine moieties are more efficient gelators than the corresponding compounds **1a** and **2a**. On the contrary, for the compounds with a longer spacer, **3a** and **4a**, those containing L-alanine moieties are more efficient gelators than the corresponding compounds **3b** and **4b**. (3) For the compounds studied, **2b** is the most powerful one. It gels 28 of the 33 solvents tested, and furthermore, the solvents gelled by it range from polar solvents like ethanol to apolar solvents like carbon tetrachloride. These findings demonstrate clearly that the chirality of the amino acid moieties and the length of the spacer connecting the two cholesteryl units have a profound effect upon the gelling performance of the compounds studied. This is not difficult to understand, because both the chirality and the length of the spacer must affect the assembling behavior of the gelators, and thereby result in different supramolecular structures in the solvents. Similar effect has been found by other groups^{12,13} in the studies of the gelation behavior of other LMOGs.

It is rather surprising to find that some of the gels listed in Table 1 could form straightforwardly. For example, dissolving **4a** in triethylamine, butyl acetate, *n*-heptane, *n*-octane, *n*-nonane, *n*-decane, or commercial oils (e.g., kerosene, diesel oil, or petrol) at room temperature and then keeping the solution without agitation will result spontaneously in a gel. The kinetics of the gel formation processes are different from each other. Under the experimental conditions, for most of the systems containing alkyl organic solvents, the gels formed within 10 min after dissolving the gelator in the solvents. For other systems, however, the gels formed 20 min later. A similar phenomenon was also observed for other systems, including **1b**/*n*-octane, **1b**/*n*-nonane, **2a**/*n*-nonane, and **2b**/*n*-octane, **1b**/petroleum ether (bp 90–120 °C).

Very interestingly, **4a** has been shown to form water-in-oil type gel emulsions with a high internal-phase ratio in some alkyl organic solvents as well as in commercial fuels by simple agitation of the mixtures (cf. Figure S1). To date, as we know, this is the first report that dicholesterol derivatives form gel emulsions. As

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Table 1. Gelation Performances of Some Diacid Amides of Dicholesteryl L(D)-Alaninates in Various Organic Solvents^a

solvents	1a	1b	2a	2b	3a	3b	4a	4b
methanol	I	I	I	I	I	I	I	I
ethanol	P	G	P	G	G	P	TG	I
1-propanol	P	G	P	G	G	PG	G	PG
1-butanol	P	TG	G	P	TG	PG	G	G
1-pentanol	P	TG	S	G	G	P	S	P
1-hexanol	P	S	S	PG	G	P	G	P
1-heptanol	P	S	P	G	G	P	PG	P
1-octanol	P	S	PG	G	G	P	S	P
1-nonanol	P	S	PG	G	G	P	S	P
1-decanol	P	S	S	PG	G	PG	S	P
cyclohexane	G	G	G	G	PG	G	G	I
<i>n</i> -pentane	I	I	PG	I	PG	I	PG	I
<i>n</i> -hexane	P	G	P	G	P	G	G	I
<i>n</i> -heptane	G	G	G	G	PG	G	G*	I
<i>n</i> -octane	P	G*	G	G*	G	P	G*	I
<i>n</i> -nonane	P	G*	G*	G	G	P	G*	I
<i>n</i> -decane	G	G	G	G	G	G	G*	I
benzene	S	S	G	TG	S	S	PG	G
toluene	S	S	TG	G	S	S	TG	G
ethyl acetate	P	TG	G	G	G	PG	G	I
butyl acetate	P	S	G	G	G	TuS	G*	I
pentyl acetate	P	S	G	G	G	TuS	G	G
acetone	P	G	G	G	G	P	G	I
ether	G	P	G	G	I	G	G	I
petroleum ether ^b	G	G*	G	G	PG	G	G	I
triethylamine	P	P	G	TG	TG	G	G*	I
CCl ₄	S	S	TG	G	S	S	TG	I
pyridine	S	S	S	G	TG	S	G	PG
DMSO	TuS	TuS	G	G	G	TuS	G	I
DMF	P	P	G	G	G	G	G	I
formic acid	G	P	G	P	P	P	I	P
acetic acid	PG	G	S	P	G	P	G	P
propyl acid	S	S	S	PG	S	S	S	P

^a Concentration of gelator = 2.5%, w/v; G = turbid gel; PG = partial gel; TG = transparent gel; P = precipitate; I = insoluble; TuS = turbid solution; G* = gels forming at room temperature. ^b bp 90–120 °C

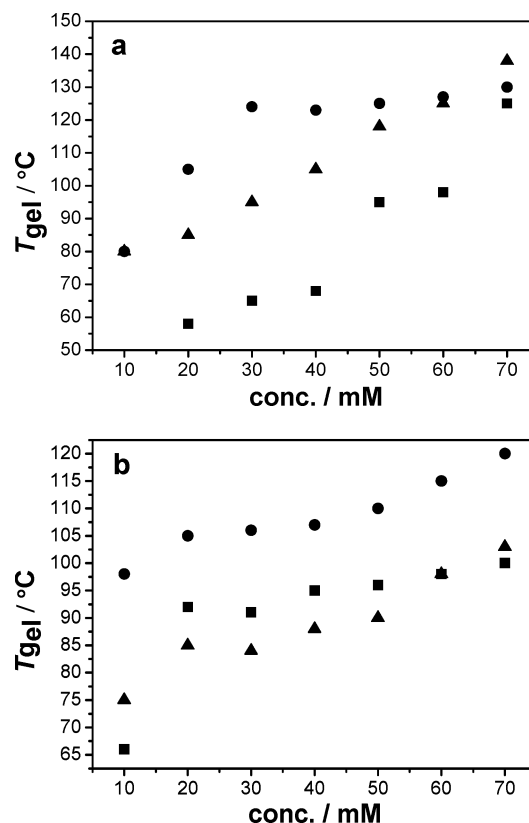
Table 2. Critical Gelation Concentration (cgc) of Gels of Different Gelators in *n*-Decane

gelator	1a	1b	2a	2b	3a	3b	4a
cgc (% w/v)	1.67	0.20	0.19	0.19	0.50	0.45	0.16

expected, these gel emulsions are not sensitive to the presence of salts, an important property for the potential applications of the systems. Furthermore, the emulsions are very stable, and no significant changes can be found after 6 months of storage in a closed container.

The gelling ability of a given gelator is not only relevant to the number of solvents gelled by it but also the minimum amount of it needed to gel a given volume of solvent (critical gelation concentration, cgc). Table 2 lists the cgc values of the gelators **1a–4a** and **1b–3b** in *n*-decane. Examination of the data shown in the table reveals that the cgc values of the systems, except for **1a**/*n*-decane, are less than or equal to 0.5% (w/v), quite low values if compared with those of other gelators containing a cholesteryl unit, indicating again that the compounds prepared in the present study are efficient gelators. More interestingly, the gels listed in Table 2 showed exceptional stability over time, almost no significant change after half a year of storage in a closed container. Thus, the gels with *n*-decane as solvent were studied in detail to have a better understand of the effects of chirality and spacer length upon the gelation behaviors of the gelators and the properties of the gels.

Gel Stability Studies. The “thermostability” of an organogel can be expressed by its specific solution-to-gel or gel-to-solution phase transition temperature (T_{gel}). Figure 1a,b shows the plots

**Figure 1.** Gel-to-sol transition temperature (T_{gel}) as a function of gelator concentration in *n*-decane: (a) **2a**, ■; **3a**, ●; **4a**, ▲; (b) **1b**, ■; **2b**, ●; **3b**, ▲.

of the specific temperatures of the gel systems against the concentrations of the gelators. Reference to the plots shown in the figure reveals that the stability of each gel is very dependent upon the concentration of the gelator. For the systems of **2a**, **4a**, **2b**, and **3b** in *n*-decane, the T_{gel} of each of them increases linearly along with increasing the concentration of the gelator in the system. For the systems of **3a** and **1b** in *n*-decane, however, the value increases rapidly with increasing the concentration of the gelators at a low concentration regime, specifically, concentrations below 30 and 20 mM for **3a** and **1b**, respectively. Beyond the concentrations, the T_{gel} almost reached its maximum, indicating that a stable and complete network structure formed in the gel at this stage. A similar result was reported by Ihara and Weiss.¹⁵

Upon further examination of the data shown the figures, it can be seen that the thermostability of the gel systems containing **2b** are almost always superior to those containing **2a**. But for the systems containing **3a** and **3b**, the thermostability of the systems of **3a** are better than those of **3b**, indicating again that both the chirality of the amino acid residues and the length of the spacers, even though there is only one methylene subunit difference between compounds **2** and **3**, play crucial roles for the properties of the gels. Furthermore, for the gel system of **2b**/*n*-decane, the gel forming at a low concentration of the gelator, 10 mM (1%, w/v), is translucent and is of a high T_{gel} value (98 °C), consistent with the finding that this gel is extraordinarily stable over time. With careful examination of the data for **2a**/*n*-decane shown in Figure 1a, it can be noted that the T_{gel} of this system increases slowly along with increasing the concentration of the gelator at concentrations below 40 mM, but beyond this concentration, the slope increased dramatically. This two-stage dependence of the

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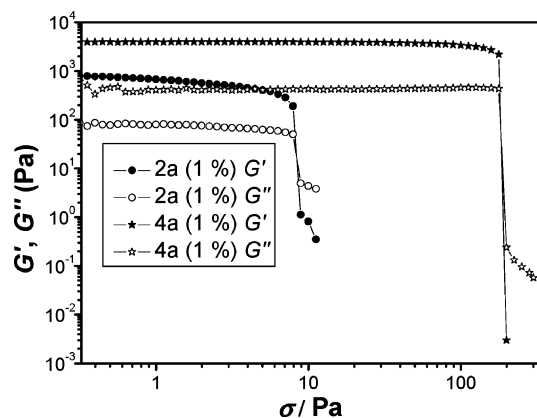


Figure 2. Determination of the linear regime. Measurement of the evolution of G' and G'' as a function of the applied shear stress. The samples are gels of **4a** and **2a** in *n*-decane.

T_{gel} values on the concentration of the gelator may be attributed to the formation of junction zones having low heats of interaction between the gelator molecules.¹⁶

Rheological Studies. As above-mentioned, one of the promising properties exhibited by some of the gels reported in Table 1 is their spontaneous formation at room temperature. This finding is interesting, since it can be taken as an indication of a possible non-temperature-dependent thixotropic property, which is important for the potential applications of the gel systems. Therefore, the rheological properties of selected examples of the gel systems were examined.

To look at the effect of spacer length upon the mechanical properties of the gels forming at room temperature, **2a** and **4a** in *n*-nonane (1.0%, w/v) were chosen as example gels, and their storage modulus G' , associated with the energy storage, and loss modulus G'' , associated with the loss of energy, were measured as functions of shear stress at room temperature. The results are shown in Figure 2. With reference to the figure, it is seen that at low stress values, the G' parameter for any of the gel systems studied is 1 order greater than its corresponding G'' , which shows the dominant elastic character of the materials.¹⁷ Furthermore, both G' and G'' remain roughly constant below a critical stress value of around 8 Pa for the system of **2a**, known as the yield stress value. Similarly, the critical stress value for the system of **4a** is about 199 Pa. Above the stress values, sharp decreases of both G' and G'' are observed for the two systems, which can be attributed to a partial breakup of the gel that begins to flow.

Frequency sweep is an important method to detect the tolerance performance of a material to external forces.¹⁸ Accordingly, the test was conducted for the materials above-mentioned. The results are shown in Figure 3. Clearly, the G' values of the two gels exhibit weak dependence on frequency, specifically, from 400 Pa for **2a** and 7000 Pa for **4a** at $0.0628 \text{ rad s}^{-1}$ to 700 Pa for **2a** at 328 rad s^{-1} and 12 600 Pa for **4a** at 628 rad s^{-1} , a typical viscoelastic behavior, suggesting that the two gels have good tolerance to external forces. Comparison of the G' value of the gels indicates that the storage modulus of the gel of **4a** is obviously larger than that of **2a**, indicating that the former is elastically stronger than the latter. Furthermore, unlike **4a**, the G' values of **2a** become erratic in the high-frequency regime (e.g., $f > 328 \text{ rad s}^{-1}$). The differences of the two gels revealed by frequency

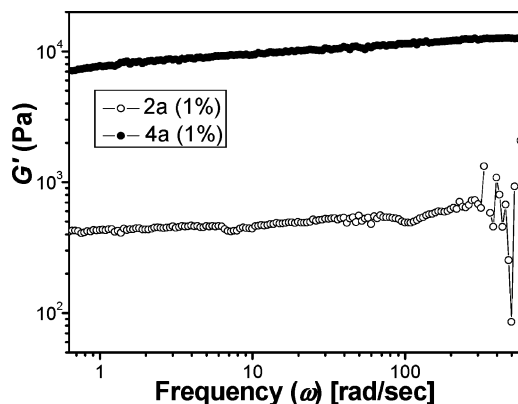


Figure 3. Evolution of G' as a function of the frequency. The applied shear stress is equal to 0.5 Pa. The samples are gels of **4a** and **2a** in *n*-decane.

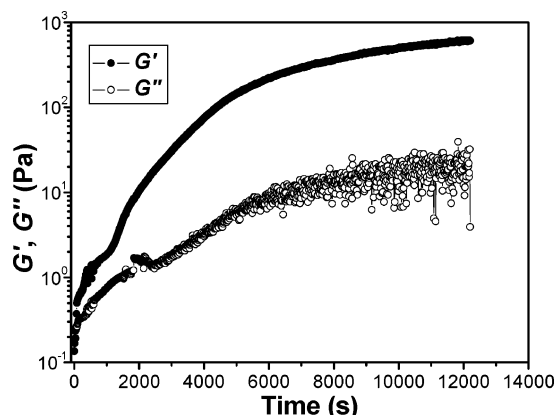


Figure 4. Evolution of G' and G'' as a function of the time after an initial shear stress of 9 Pa for 3 min stopped at t equals zero. The applied stress is 0.5 Pa, and the frequency of the measurement is 1 Hz. The sample is a gel of **4a** [0.5% (w/v)] in *n*-decane.

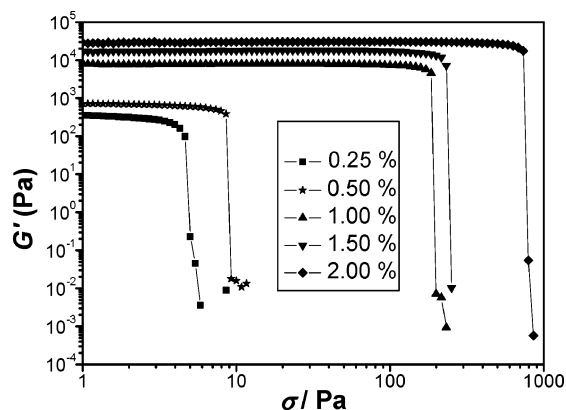


Figure 5. Determination of the linear regime. Measurement of the evolution of G' as the applied shear stress at different concentrations of **4a** in *n*-decane.

sweep measurements demonstrate, as expected, that the spacer lengths of the gelators have a significant effect upon the mechanical properties of the resulting gels.

It is reasonable to take spontaneous formation of a gel at room temperature as an indication of its thixotropic property. Accordingly, the shear stress stimulus responsive properties of the gels forming at room temperature were examined by choosing **4a** in *n*-decane as an example system. The examination was conducted at three different concentrations (0.50, 1.0, and 1.5%, w/v). A typical result is depicted in Figure 4. Reference to the figure reveals that at t equals zero, which corresponds to the

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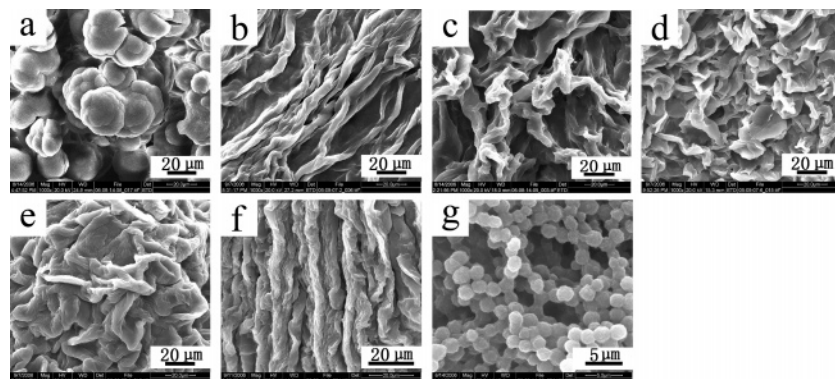


Figure 6. SEM images of the gel networks of the gelators of different spacer length and/or inherent chirality in *n*-decane: (a) **1a**, (b) **2a**, (c) **3a**, (d) **4a**, (e) **1b**, (f) **2b**, and (g) **3b**.

Table 3. FTIR Data for the Gelators in CDCl₃ (solution) and in *n*-Decane (xerogel)

		λ_{\max} (cm ⁻¹)			
		NH		C=O	
		stretch	bend	amide	ester
1a	gel	3301	1526	1653	1729
	solution	3315	1537	1666	1737
1b	gel	3301	1526	1649	1733
	solution	3300	1531	1667	1737
2a	gel	3311	1538	1646	1736
	solution	3302	1535	1643	1737
2b	gel	3310	1543	1644	1739
	solution	3297	1541	1642	1733
3a	gel	3324	1533	1645	1728
	solution	3340	1540	1663	1727
3b	gel	3312	1542	1644	1739
	solution	3321	1542	1654	1729

moment of release of the initial shear stress, the sample is more viscous than elastic, as evidenced by $G' < G''$, suggesting that the gel network was disrupted by the initial shear stress. However, the sample gradually recovers its elastic property after removal of the external stress, as shown by the fact that the value of G' is larger than that of G'' (cf. Figure 4), a typical thixotropic property of supramolecular gels.¹⁹

Similar results were observed in other gel systems of different gelator concentrations (cf. Figures S2 and S3, Supporting Information). However, the maximum G' values recovered and the specific recovery times are dependent upon the concentration of the gelator in the systems. Careful comparison of the results shown in the figures reveals that the gel recovery is getting faster and the maximum values of G' and G'' reached by the gel systems are getting greater upon increasing the gelator concentration. It is to be noted, however, that only ~50% of the elasticity of the initial gel can be recovered at equilibrium for the gel systems of higher gelator concentrations. But for the 0.5% (w/v) system, ~80% of the elasticity can be recovered. These results show clearly that the concentration of the gelator in the gel system also plays crucial roles for the mechanical properties of the gels.

To further elucidate the importance of gelator concentration to the rheological properties of a supramolecular gel, the G' values of **4a** in *n*-decane at different concentrations are shown in Figure 5 as functions of shear stress amplitude. From the figure, it can be seen that the value of G' increases from 350 to 29 000 Pa along with increasing the gelator concentration from 0.25 to 2.0% (w/v), and correspondingly, the yield stress changes

from 4.29 to 755.50 Pa, indicating again that both the stability of the gel network and the elastic property of the gel well depend upon the concentration of the gelator in the solvent. Specifically, for gelator **4a**, its concentration shows a profound effect upon the yield stress and thixotropic property of its gels.

Scanning Electron Microscopy (SEM) Studies. To have a visual insight into the morphologies of the aggregates, the xerogels prepared by freeze-drying of each of the gels of **1a**, **2a**, **3a**, **4a**, **1b**, **2b**, and **3b** in *n*-decane (3%, w/v) were studied by scanning electron microscopy (SEM). Figure 6 shows some typical SEM images of the xerogels. With reference to the images, it is seen that the lengths of the spacers of the gelators affect the aggregation mode of the gelators significantly (from a to d and e to g). As expected, the different inherent chirality of the gelator molecules resulted in very different microstructures of the xerogels, as evidenced by the differences between the SEM images of **1a**/*n*-decane and **1b**/*n*-decane, **2a**/*n*-decane and **2b**/*n*-decane, as well as **3a**/*n*-decane and **3b**/*n*-decane, respectively.

Further examination of the SEM images reveals that the morphologies of the xerogels are characterized by thick fibrous (b and f), entangled network structures (c and e), and stacked cauliflower-like aggregates of the gelator (d), which are the commonly found structures of organogels. On the other hand, the xerogel of **1a** in *n*-decane adopts cotton-like network structures. Very surprisingly, the structure of the xerogel of **3b** in *n*-decane is a network aggregate of the microspheres, of which the diameter is about 2 μ m. The sharp difference between the morphologies of the xerogels is an indication of the different gelling mechanisms followed by the gel systems concerned. These results show again that a small change in the structures of the gelators can result in a dramatic change in the aggregation mode.

FTIR Spectroscopy Studies. FTIR measurements can provide useful information for confirming formation of hydrogen bonds. Accordingly, the FTIR spectra of the xerogels of **1a**–**4a** and **1b**–**3b** in *n*-decane were recorded. As controls, the FTIR spectra of solution samples, the gelators in CDCl₃, were also recorded. Figure 7 shows an example FTIR spectrum of **4a** in CDCl₃ (a) and that of the xerogel of **4a** in *n*-decane (b). From the spectrum of the control, it can be observed that the two typical bands of **4a**, corresponding to the stretching and bending vibrations of NH, appeared at 3309 and 1539 cm⁻¹, respectively. Upon gelation, the bands shifted to 3302 and 1545 cm⁻¹, respectively, an evidence for the participation of the NH group in the formation of hydrogen bonds, which should be one of the driving forces for the formation of the gel networks.²⁰ Similar spectral shifts were also found for other gel systems (cf. Table 3). It is a little bit surprising that the direction of the spectral shifts of the systems containing **2a** and **2b** are different from other gel systems (cf. Table 3),

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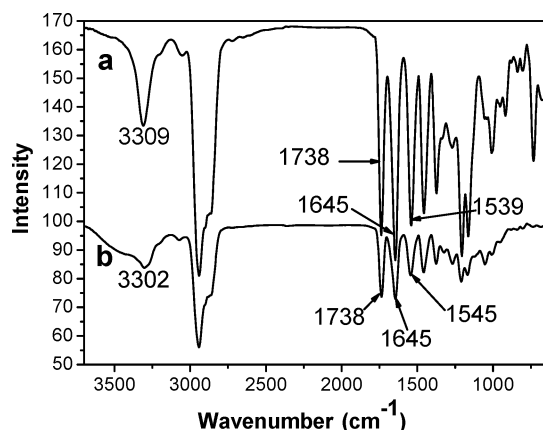


Figure 7. FTIR spectra of **4a** in CDCl_3 [solution (a)] and **4a** in n -decane (xerogel) (b)].

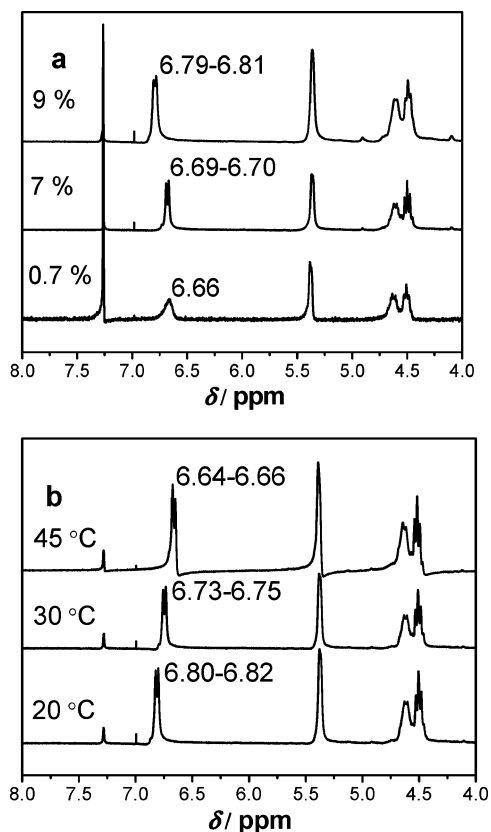


Figure 8. Partial ^1H NMR spectra of **2b** in CDCl_3 : (a) concentration (w/v) dependence at $25\text{ }^\circ\text{C}$ and (b) temperature dependence at a concentration of 9% (w/v).

suggesting that a different aggregation mode might be adopted by the two systems.^{3a}

^1H NMR Spectroscopy Studies. To obtain further information on the formation mechanism of the gel networks, the aggregation behavior of the gelators in solution was studied in detail by employing a ^1H NMR technique. CDCl_3 was chosen as solvent, since the gelators to be studied cannot gel it within a wide concentration range (below 9%, w/v). ^1H NMR measurements of **2a**, **2b**, and **4a** in CDCl_3 demonstrated that the position of the NH proton, of which the δ value is around 6.5 ppm, is quite sensitive to the increase in the concentration of **2a**, **2b**, or **4a**, as evidenced by a clear downfield shift of the spectral position of the NH proton (cf. Figure 8a and Figures S4 and S5 of the Supporting Information). Specifically, the shifts of the amide NH are 0.09, 0.15, and 0.09 ppm for compounds **2a**, **2b**, and **4a**,

Table 4. X-ray Characterization of Xerogels of **2a** and **2b** in n -Decane

gelator	peak	hk	θ (deg)	d (nm)
2a	1	11	2.28	3.87
	2	20	2.86	3.09
	3	40	5.64	1.57
2b	1	10	2.50	3.53
	2	11	4.20	2.10
	3	20	5.16	1.71

respectively, when the concentrations of the compounds increased from 0.7% (w/v) to 9% (w/v). This observation can be taken as more evidence for the participation of the amide NH proton in the hydrogen-bond formation between the gelator molecules, as revealed by FTIR spectroscopy studies.²¹

Hydrogen-bond formation is also supported by the result from temperature-dependent ^1H NMR measurements. Figure 8b depicts the temperature dependence of the ^1H NMR spectrum of **2b** in CDCl_3 [9% (w/v)]. The figure shows that the amide NH signals shift significantly toward higher field, evidence of disruption of the hydrogen bonds in which the NH proton was involved.²²

XRD Studies. The structures of the xerogels were investigated using a XRD technique. The gels of **2a** or **2b** in n -decane were used as example gels, and the data obtained from the studies are listed in Table 4 and shown in Figure S6. Obviously, the dry gels exhibit different packing arrangements, depending on the chiralities of the amino acid residues. The xerogel of **2a** in the solvent showed three reflections, corresponding to d spacings of 3.89, 3.09, and 1.57 nm, respectively. These reflections are indexed in sequence as (110), (200), and (400) of a rectangular columnar lattice, while the xerogel of **2b** had a hexagonal columnar lattice structure. As the spacings are much smaller than the smallest sizes of the microstructures of the gel networks (cf. Figure 6), it is supposed that the XRD data came from the elemental fibers of the aggregates of the gelators. The fibrous feature of the primary structures is supported by the results that the aggregates adopt a helix-like structure (cf. CD spectroscopy studies). In fact, a similar assumption has been adopted by other groups²³ for the explanation of aggregates with different morphologies, including ribbons, spherulite-like particles, threads, and flakes.

On the bases of the results obtained from XRD analysis and FTIR measurements, as well as the discussions made above, possible formation processes of the gel networks of **2a** and **2b** were proposed and are schematically shown in Figure 9. It can be seen that the model is characterized by the presence of hydrogen bonds between the spacers and the aggregation of the cholesteryl units of the gelators. It is worth mentioning that the structure of the slice of each elemental fiber corresponding to a specific gelator is characterized by different lattice parameters, and the molecule numbers in the two slices are different. It is the slices that could pile up into fibers via van der Waals interaction. Furthermore, the structures of the fibers are not closed, and they could combine with each other via similar van der Waals and hydrogen-bonding interactions, leading to larger fibers and eventually the gel networks.

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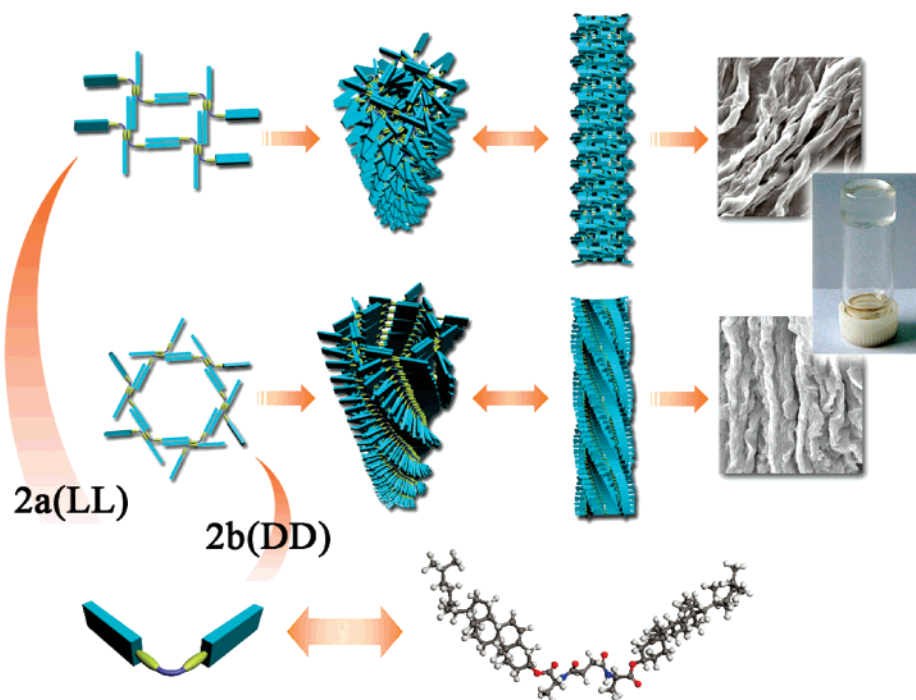


Figure 9. Schematic representation of the formation mechanisms of the aggregates of **2a** and **2b** in *n*-decane.

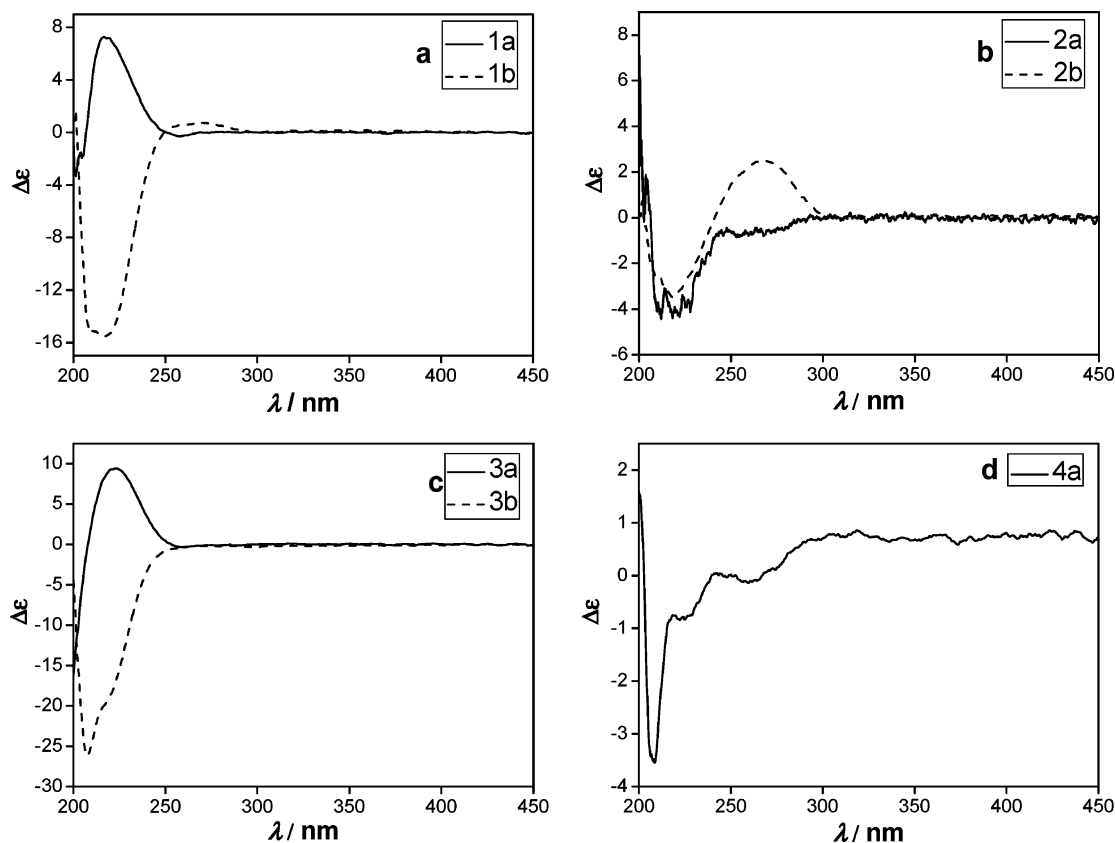


Figure 10. CD spectra of the gels of the gelators in *n*-decane (1.5%, w/v) at room temperature: (a) **1a** and **1b**, (b) **2a** and **2b**, (c) **3a** and **3b**, and (d) **4a**.

CD Spectroscopy Studies. It is well-known that circular dichroism (CD) appears when the chromophoric moieties of chiral molecules are organized in an appropriate orientation. Therefore, CD spectroscopy measurements were performed in order to investigate the expression of chirality and the order in the self-assemblies of gelators in a gel phase. For the present study, the investigation was performed at a concentration of 1.5% (w/v)

using *n*-decane as aprotic solvent. Circular dichroism bands were observed for the gels of **1a–4a** and **1b–3b** in *n*-decane, with a λ_{\max} value at about 215 nm, ascribable to the π - π^* transition of the amide bond (cf. Figure 10). Importantly, the intensity of the CD signal for **2a**/*n*-decane decreased gradually and eventually disappeared upon increasing the temperature from 25 to 90 °C, indicating that the CD signal observed in the gel state originated

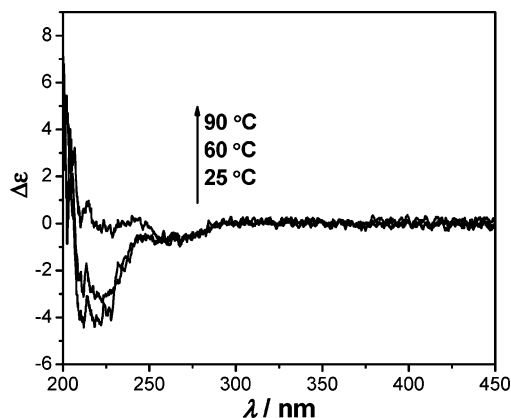


Figure 11. Temperature dependence of the CD spectra of the gel of **2a** in *n*-decane (1.5%, w/v).

from the chirality of the network structures, rather than from the inherent chirality of the gelators (cf. Figure 11).²⁴ The effect of the length of the spacers connecting the two cholesteryl units in the gelator molecules via the two amino acid residues on the chirality of the physical networks is also shown in Figure 10. Upon further examination of the CD spectra, it can be observed that the signs of the CD bands are different from each other. Specifically, the CD signals of the gels containing **1a** or **3a** are positive, whereas those containing **2a** or **4a** are negative, indicating that the chirality of the assemblies in the two kinds of gels are opposite, even though the chirality of the molecules of the gelators **1a–4a** are the same.²⁵ It is clear that the length of the spacer has a remarkable effect upon the aggregation mode of the gelators, which is in accordance with the results from SEM observation. It is not surprising that, on the other hand, the CD signals of the gels containing **1b** or **3b** are negative, opposite to those of the corresponding systems with **1a** or **3a** as a gelator. Clearly, this difference can be attributed to the difference in the chirality of the amino acid residues in the gelators.

It is quite surprising that, in contrast to those of **1b** and **3b**, the CD spectrum for the gel of **2b**/*n*-decane is characterized by an exciton-coupling band, of which the first sign is positive, indicating that the dipole moment of the gelator tends to orient in the clockwise direction.^{11a} It is to be noted, however, that the macroscopic helicity of an aggregate formed by self-assembly of individual molecules is not necessarily related to the microscopic helicity in a Cotton effect.²⁶ This might be used to explain why the clockwise direction in the aggregate cannot be found evidently in the SEM images.

CD spectroscopy studies demonstrate that both the length of the spacer connecting the two cholesteryl units in a gelator molecule and the chirality of the amino acid residues in the gelator have pronounced effects upon the aggregation mode.

Conclusion

In summary, it has been demonstrated that the gelation behavior of the diacid amides of dicholesteryl L(D)-alaninates in various organic solvents can be adjusted to some extent by either varying

the amino acid chirality and the length of the spacer connecting the two cholesteryl moieties. The compounds containing D-alanine residues and relatively shorter spacers gel more solvents than their analogues with opposite chirality. For the compounds of longer spacers, however, an opposite result was obtained. As for the thermostability, characterized by the value of T_{gel} , of a gel studied, the effect of chirality and spacer length is also obvious, but there is no simple relationship between the chirality, the lengths of the spacers, and the related T_{gel} . Within the gel systems studied, at least 11 of them, including **1b**/petroleum ether, **1b**/*n*-octane, **1b**/*n*-nonane, **2a**/*n*-nonane, **2b**/*n*-octane, **4a**/triethylamine, **4a**/butyl acetate, **4a**/*n*-heptane, **4a**/*n*-octane, **4a**/*n*-nonane, and **4a**/*n*-decane gel spontaneously at room temperature. As expected, these gels are thixotropic, as revealed by rheological studies, and the mechanical properties of the gels could be adjusted either by altering the spacer length or by changing the gelator concentration. SEM, XRD, and CD spectroscopy studies revealed that the chirality and the spacer length affect the aggregation mode, the morphology, and the chirality of the network structures of the gels. In addition to the well-known van der Waals interaction between cholesteryl moieties of the gelators, concentration and temperature-dependent ¹H NMR and FTIR measurements demonstrated that intermolecular hydrogen bonding between the amide NH and the carbonyl groups in the molecules of gelators is another important driving force for the formation of the gels.

Experimental Section

Gelation Test. A weighted amount of potential gelator and a measured volume of selected pure organic solvent were placed into a sealed glass tube (10 mm i.d.), and the system was heated in an oil or water bath until all solid materials were dissolved. The solution was cooled to room temperature in the air, and finally, the test tube was turned upside down to observe if the solution inside could still flow. A positive test is obtained if the flow test is negative. It is to be noted that some of the gels obtained are turbid (G), but some are transparent (TG). In some cases, solution and gel may coexist within a system and they are referred to as “partial gels” (PG). Systems in which only solution remained until the end of the tests are referred to as solutions (S). Systems that are clear solutions when they are hot but precipitation or crystallization occurs when they are cooled down to room temperature are denoted by P (precipitation) and R (recrystallization), respectively. Insoluble systems, in which the potential gelator could not be dissolved even at the boiling point of the solvent, were also found, and they are labeled as insoluble (I). In a few cases, the turbid solutions (TuS) were also observed.

Gel-to-Sol Transition Temperature (T_{gel}) Measurement. Temperatures of gel-to-sol transition (T_{gel}) were determined by using a conventional “falling ball” method.²⁷ In the test, a small glass ball (diameter ~ 3 mm) was carefully placed on the top of the gel to be tested, which was produced in a test tube (Φ 10 mm). The tube was slowly heated (0.5 °C/min⁻¹) in a thermostated water or oil bath until the ball fell to the bottom of the tube. The temperature corresponding to the end of the falling process was recorded and taken as the T_{gel} of the system.

SEM Measurement. SEM pictures of the xerogel were taken on a Quanta 200 scanning electron microscopy spectrometer (Philips-FEI). The accelerating voltage was 15 kV, and the emission was 10 mA. The xerogel was prepared by freezing the gel in liquid nitrogen and then evaporated by a vacuum pump for 12–24 h. Prior to examination, the xerogel was attached to a copper holder by using conductive adhesive tape, and then it was coated with a thin layer of gold.

Rheological Measurements. Rheological measurements were performed using a stress-controlled rheometer (TA instrument AR-G2) equipped with aluminum-coated parallel-plate geometry (40

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mm diameter, 0.500 mm gap between the two plates). A solvent-trapping device was placed above the plate to avoid evaporation. All measurements were conducted at ambient temperature (25 °C).

The first step of an experiment consists of determining the so-called linear regime of the gel. This was done by measuring the storage modulus G' , associated with the energy storage, and the loss modulus G'' , associated with the loss of energy, as a function of the stress amplitude. The linear regime is such that both dynamic moduli are independent of the stress amplitude and reflect the properties of the unperturbed network. In that regime, G' and G'' are measured as functions of the oscillatory shear stress.

In the second step of the experiment, the modulus as a function of frequency was measured from 0.01 to 100 Hz at a constant shear stress of 0.5 Pa in the linear regime.

The third step of the experiment is oscillatory experiments at a constant frequency. A constant oscillatory shear stress that is enough to destroy gel structure (i.e., beyond the linear regime) is applied to the sample for 3 min. After that, a very small constant oscillatory shear stress (1 Hz, 0.5 Pa) in the linear regime is applied in the same procedure. In this case, the storage modulus G' and the loss modulus G'' are recorded as a function of time.

FTIR Measurement. The solution and the gel sample were measured on a Bruker EQUINX55 spectrometer in an attenuated total reflection (ATR) way with ZnSe as sample slot. The samples were placed on a glass or a mica slice as a gel film, frozen in liquid nitrogen, and finally dried in vacuum conditions for 12–24 h.

^1H NMR Measurement. ^1H NMR data of samples were collected on Bruker AVANCF 300 MHz spectrometer.

XRD Measurement. X-ray diffraction (XRD) data of samples were collected on a D/Max-2550/PC with Cu K α X-ray radiation generated under a voltage of 40 kV and a current of 40 mA. The scan rate was 0.5°/min. The xerogel was prepared by freezing the gel in liquid nitrogen and then evaporated by a vacuum pump for 12–24 h.

CD Measurement. CD spectra were measured using a JASCO J-810 spectropolarimeter. The gel samples were prepared in closed vials and then transferred to an optical cell (0.1 mm optical path length) for the measurement. The CD spectrum of the **2a**/*n*-decane [1.5% (w/v)] gel at different temperatures was recorded from low temperature to high temperature. The temperature of the gel system was increased in steps of 5 °C/min, allowing ample equilibration time after each increase to a maximum of 90 °C.

Preparation of **1a and **1b**.** Cholesteryl L(D)-alaninate primary amine was synthesized according to a previous report.¹⁴ Malonic acid (0.208 g, 2 mmol) was dissolved in 20 mL of tetrahydrofuran (THF) and then 40 mL of THF solution containing 1.83 g (4 mmol) of cholesteryl L-alaninate primary amine and 0.824 g (4 mmol) of DCC were added dropwise to the above solution with stirring. The reaction mixture was stirred at 50 °C for 10 h. After the reaction, the mixture was filtered and the filtrate was evaporated to dryness, and the resulting solid was washed with hot methanol three times and dried in vacuum to give the desired product in 30% yield as a white or yellowish powder. The procedures used for the preparation of **1b** are similar to that for **1a**. Satisfactory results were obtained. For **1a**: ^1H NMR ($\text{CDCl}_3/\text{Me}_4\text{Si}$, 300 MHz) δ (ppm) 7.24 (s, CONH, 2H), 5.38 (s, alkenyl, 2H), 4.63–4.66 (m, $\text{CH}(\text{CH}_3)\text{COO}$, 2H), 4.50–4.57 (m, oxycyclohexyl, 2H), 3.24 (s, COCH_2CO , 2H), 0.68–2.47 (m, methyl, cholesteryl protons, 92H). Anal. Calcd for $\text{C}_{63}\text{H}_{102}\text{O}_6\text{N}_2$: C, 76.94, H, 10.45, N, 2.85. Found: C, 76.65, H, 10.08, N, 2.74. For **1b**: ^1H NMR ($\text{CDCl}_3/\text{Me}_4\text{Si}$, 300 MHz) δ (ppm) 7.26 (s, CONH, 2H), 5.38 (s, Hz, alkenyl, 2H), 4.63–4.65 (m, $\text{CH}(\text{CH}_3)\text{COO}$, 2H), 4.50–4.59 (m, oxycyclohexyl, 2H), 3.24 (s, COCH_2CO , 2H), 0.68–2.35 (m, methyl, cholesteryl protons, 92H). Anal. Calcd for $\text{C}_{63}\text{H}_{102}\text{O}_6\text{N}_2$: C, 76.94, H, 10.45, N, 2.85. Found: C, 76.71, H, 10.08, N, 2.74.

Preparation of **2a–4a and **2b–4b**.** Cholesteryl L-alaninate primary amine (1.83 g, 4 mmol) and succinic acid (0.24 g, 2 mmol) were dissolved in 50 mL of tetrahydrofuran, and the mixture was stirred at 0 °C. To the system, 0.824 g (4 mmol) of dicyclohexylcarbodiimide (DCC) and 0.048 g (0.4 mmol) of *N,N*-dimethylaminopyridine (DMAP) were added, and the mixture was stirred at 0 °C for 4 h. After the reaction, the mixture was filtered, the filtrate was evaporated to dryness, and the resulting solid was washed with hot methanol three times and dried in vacuum to give a desired product in 30% yield as a white powder. The procedures used for the preparation of **3a**, **4a**, **2b**, **3b**, and **4b** are similar to that for **2a**. Satisfactory results were obtained.

For **2a**: ^1H NMR ($\text{CDCl}_3/\text{Me}_4\text{Si}$, 300 MHz) δ (ppm) 6.60–6.63 (d, J = 7.0 Hz, CONH, 2H), 5.37 (s, alkenyl, 2H), 4.61–4.64 (m, CHCOO , 2H), 4.49–4.56 (m, oxycyclohexyl, 2H), 2.47–2.55 (m, CH_2 , 4H), 0.68–2.29 (m, methyl, cholesteryl protons, 92H). Anal. Calcd for $\text{C}_{64}\text{H}_{104}\text{O}_6\text{N}_2$: C, 77.06, H, 10.51, N, 2.81. Found: C, 76.93, H, 10.12, N, 2.51.

For **2b**: ^1H NMR ($\text{CDCl}_3/\text{Me}_4\text{Si}$, 300 MHz) δ (ppm) 6.59–6.61 (d, J = 7.2 Hz, CONH, 2H), 5.38 (s, 2H, alkenyl), 4.62–4.68 (m, CHCOO , 2H), 4.49–4.61 (m, oxycyclohexyl, 2H), 2.35–2.57 (m, CH_2 , 4H), 0.68–2.32 (m, methyl, cholesteryl protons, 92H). Anal. Calcd for $\text{C}_{64}\text{H}_{104}\text{O}_6\text{N}_2$: C, 77.06, H, 10.51, N, 2.81. Found: C, 77.19, H, 10.56, N, 2.46.

For **3a**: ^1H NMR ($\text{CDCl}_3/\text{Me}_4\text{Si}$, 300 MHz) δ (ppm) 7.88–7.91 (d, J = 8.2 Hz, CONH, 2H), 5.36 (s, alkenyl, 2H), 4.64–4.66 (m, $\text{CH}(\text{CH}_3)\text{COO}$, 2H), 4.59–4.61 (m, oxycyclohexyl, 2H), 2.30–2.33 (m, CH_2 , 6H), 0.68–2.00 (m, methyl, cholesteryl protons, 92H). Anal. Calcd for $\text{C}_{65}\text{H}_{106}\text{O}_6\text{N}_2$: C, 77.18, H, 10.56, N, 2.77. Found: C, 77.39, H, 10.53, N, 2.68.

For **3b**: ^1H NMR ($\text{CDCl}_3/\text{Me}_4\text{Si}$, 300 MHz) δ (ppm) 7.83–7.86 (d, J = 8.0 Hz, CONH, 2H), 5.41 (s, alkenyl, 2H), 4.62 (m, $\text{CH}(\text{CH}_3)\text{COO}$, 2H), 4.57–4.60 (m, oxycyclohexyl, 2H), 2.03–2.40 (m, CH_2 , 6H), 0.65–2.00 (m, methyl, cholesteryl protons, 92H). Anal. Calcd for $\text{C}_{65}\text{H}_{106}\text{O}_6\text{N}_2$: C, 77.18, H, 10.56, N, 2.77. Found: C, 77.10, H, 10.52, N, 2.54.

For **4a**: ^1H NMR ($\text{CDCl}_3/\text{Me}_4\text{Si}$, 300 MHz) δ (ppm) 6.33–6.36 (d, J = 7.3 Hz, CONH, 2H), 5.37 (s, alkenyl, 2H), 4.62–4.66 (m, $\text{CH}(\text{CH}_3)\text{COO}$, 2H), 4.53–4.60 (m, oxycyclohexyl, 2H), 2.25–2.29 (m, COCH_2 , CH_2CO , 4H), 0.68–1.86 (m, CH_2CH_2 , methyl, cholesteryl protons, 96H). Anal. Calcd for $\text{C}_{66}\text{H}_{108}\text{O}_6\text{N}_2$: C, 77.29, H, 10.61, N, 2.73. Found: C, 77.15, H, 10.67, N, 2.77.

For **4b**: ^1H NMR ($\text{CDCl}_3/\text{Me}_4\text{Si}$, 300 MHz) δ (ppm) 6.30–6.33 (d, J = 6.9 Hz, CONH, 2H), 5.38 (s, alkenyl, 2H), 4.60–4.66 (m, $\text{CH}(\text{CH}_3)\text{COO}$, 2H), 4.53–4.58 (m, oxycyclohexyl, 2H), 2.25–2.33 (m, COCH_2 , CH_2CO , 4H), 0.68–1.84 (m, CH_2CH_2 , methyl, cholesteryl protons, 96H). Anal. Calcd for $\text{C}_{63}\text{H}_{102}\text{O}_6\text{N}_2$: C, 77.29, H, 10.61, N, 2.73. Found: C, 77.19, H, 10.51, N, 2.57.

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Supporting Information Available: Photographs of the gel emulsion of **4a** in the mixture of *n*-heptane and water, figures of the evolution of G' and G'' for the gels of **4a**/*n*-decane at different concentrations (1.0% and 1.5%, w/v) as a function of time, partial ^1H NMR spectra of **2a** and **4a** in CDCl_3 at different concentrations at 25 °C, and XRD patterns of the xerogels of **2a** and **2b** in *n*-decane. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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